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STUDIES ON MECHANICAL ALLOYING OF Ni - 20 Cr - 2 TbO₂



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SYNOPSIS

Oxide Dispersion Strengthened (ODS) alloys contain a small volume fraction of very fine oxide particles, typically of 100 - 1000Å° mean particle size, in a metal or alloy matrix. ODS alloys are noted for their superior mechanical properties at temperatures approaching the melting point at which strengthening by precipitate particles becomes relatively weak. Most of the methods developed to produce ODS alloys suffer from a common limitation of the severe difficulty of incorporating into the matrix highly reactive solutes like chromium, titanium and aluminium which are particularly needed in superalloys to confer solid solution strengthening and precipitation hardening. A novel method, called mechanical alloying, developed in recent years overcomes this limitation, as it is capable of combining the incorporation of an oxide dispersion with the incorporation of reactive solutes. The mechanical alloying technique essentially consists of dry-blending the constituent powders of the oxide, matrix metal and solutes in a high energy comminutor mill such as an attritor.

The overall objective of this dissertation is to provide some insight into the mechanical alloying process from a theoretical as well as practical standpoint. A typical ODS superalloy, namely, Ni-20Cr-2ThO₂ is chosen for the subject of investigations; the alloy should have all the chromium in solid solution and thorium particles of a mean size of about 300Å° should be uniformly dispersed in the alloy matrix. A laboratory model of an attritor has been specially designed and fabricated to carry out the mechanical alloying experiments.

Successful mechanical alloying is primarily dependent on the mechanical energy input given to the attritor which in turn is a complex function of several variables involved in the attritor milling operation. A detailed study has therefore been undertaken to examine the effect of the milling parameters on the degree of mechanical alloying of chromium in nickel. The milling parameters investigated include, among others, the following: the attritor speed (RPM), ratio of the weight of the grinding balls to the weight of the powder charge, diameter of the grinding balls, impeller geometry and starting particle sizes of nickel and chromium. Employing Electron Probe Microanalysis (EPMA), the 'effectiveness of alloying' has been quantified in terms of the average chromium content picked up in the milled, composite particles and the degree of inhomogeneity of distribution of chromium within them.

Studies on the influence of milling parameters on the efficacy of mechanical alloying yielded the following results. The rate of alloying, in general, increases with increasing attritor speed, balls-to-powder weight ratio and ball diameter. The results also suggest the existence of certain threshold values for these three parameters below which effectiveness of alloying would be so poor that extremely long milling times would be required. Furthermore, an examination of the experimental data has enabled optimization of the milling parameters. Thus, for the attritor design used, the optimum speed works out to be about 350RPM, optimum balls-to-powder weight ratio is 35/1 and the optimum ball diameter is 8mm. A triangular shape geometry for the impellers of the attritor appears to be much more effective than either round or flat shape. The experiments on the effect of initial particle sizes show that the particle size of chromium has more predomi-

nant effect on the degree of alloying than of nickel; the finer the chromium particle size, the more effective and faster is the alloying.

It is also noticed from transmission electron microscopic observations that the distribution of thoria becomes optimum when the milling parameters are optimised with respect to alloying of chromium in nickel. A magnetic coercivity index has been found to be useful in monitoring qualitatively the degree of mechanical alloying. A 'peak-crossed drop' in coercivity is found to be invariably associated with samples which have undergone satisfactory alloying. The peak in coercivity is attributed mainly to the attainment of a relatively high degree of cold work in the milled particles.

The question of whether or not mechanical alloying is true alloying has been examined in some detail. Using the results of x-ray diffraction, EPMA and Scanning Auger Microprobe Analysis, it has been possible to conclude that mechanical alloying can lead to the formation of a true, homogeneous solid solution of chromium in nickel.

An 'energy balance' model is proposed in the present work to relate mechanical alloying with attritor milling parameters. Here the heat energy required to cause alloying of the solute is balanced against a kinetic energy expression involving the three principal milling parameters (attritor speed, ball-to-powder weight ratio and ball diameter). Based on the results of some milling experiments with

and without thorium, an enhanced diffusivity mechanism is proposed to explain the relatively low temperature diffusion of chromium in nickel observed in the mechanical alloying process. The enhanced diffusivity is considered to be arising from the localised dynamic recrystallization of the cold worked matrix due to the local rise in temperature during collisions between the balls. The heat energy requirement for mechanical alloying is thus deemed to be the heat energy necessary to raise the local, mean temperature during attritor milling to the level of the recrystallization temperature of the cold worked matrix metal.

Chapter I introduces the reader to the various aspects covered in this thesis. Chapter II is a concise review of the properties of oxide dispersion strengthened alloys. The different methods of preparation of ODS alloys are described in Chapter III wherein special attention is paid to the technique of mechanical alloying. This chapter concludes with a note on the scope of the present work. The experimental details on the attritor design and the various techniques employed to monitor the mechanical alloying process are included in Chapter IV. Results on the optimisation of attritor milling parameters are presented in Chapter V. Chapter VI is devoted to a discussion on whether or not mechanical alloying is true alloying. A model for mechanical alloying is presented and discussed in Chapter VII. Chapter VIII summarises the work and lists the conclusions.

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LIST OF SYMBOLS

F	= obstacle strength
ϕ	= included angle between the bowed segments of a pinned dislocation
Γ	= line tension of the dislocation
τ	= applied shear stress
b	= burgers vector of dislocation
λ	= effective interparticle spacing
G	= shear modulus of the matrix
τ_y	= flow stress
τ_m	= matrix flowstress
τ_p	= athermal, particle bypassing stress
λ_s	= mean planar, centre-to-centre particle spacing
r_s	= mean planar particle radius
τ_{se}	= shear strength contribution from stored energy of deformation
$\bar{n}$	= average number of dislocation loops per particle
γ	= plastic shear strain
τ_h	= strain-induced increment to the flow stress

- f = volume fraction of the dispersoids
 τ_c = the critical stress for particle shear
 τ_e = flow stress for $\frac{L}{l} = 1$
 $\frac{L}{l}$ = Grain Aspect Ratio (GAR), L being grain length and l grain width
 k = GAR coefficient
 $\dot{\gamma}_s$ = steady state creep strain rate
 A = pre-exponential frequency factor
 Q_c = creep activation energy
 Q_{real} = true activation energy for creep
 $Q_{apparent}$ = apparent activation energy for creep
 R = universal gas constant
 n = stress exponent
 T = absolute temperature (Kelvin)
 T_m = melting point (Kelvin)
 T_R = recrystallization temperature of cold worked matrix (Kelvin)
 T_A = ambient temperature (Kelvin)
 T_j = water temperature at inlet

- T_2 = water temperature at outlet
 τ_b = back stress
 Q = activation energy for diffusion
 D = diffusion coefficient at temperature T
 D_0 = pre-exponential frequency factor
 HE_v = heat energy density, or the minimum heat required for mechanical alloying in unit volume of the attritor
 P'_b = weight of the powder participating in attritor per unit volume of the attritor
 C_p = specific heat capacity of the powder
 C_{pA} = specific heat capacity of the attritor as a whole
 C_{pw} = specific heat capacity of water
 t = time in minutes
 W = balls-to-powder weight ratio
 ρ_b = density of ball material
 P_{contact} = local contact pressure
 A_{contact} = area in contact
 P_{average} = average kinematic pressure of the ball medium
 A_{average} = average area over which the P_{average} is transmitted

- D' = ball diameter
- d = average length of contact
- KE_c = average kinetic energy density intensified by contact pressure
- N = shaft RPM
- L = length of impeller
- R' = number of impeller revolutions (shaft RPM x milling time in minutes)
- δ = packing factor of balls of a uniform diameter



CHAPTER 1

INTRODUCTION

CHAPTER I



INTRODUCTION

Oxide dispersion strengthened (ODS) materials are known to possess remarkable engineering properties that include high yield strength, outstanding creep resistance and excellent oxidation resistance. These materials generally contain a small volume fraction (about 0.01 to 0.03) of hard, second phase particles of a stable oxide in an otherwise homogeneous matrix. The particles, which are usually in the range of $100-1000\text{\AA}$ diameter with typical interparticle spacing in the range of $500-5000\text{\AA}$, are incoherent with the matrix and remain stable upto very high homologous temperatures. Even at the small volume fractions of the dispersoid, the increase in tensile and creep strength is impressive and persists upto temperatures close to the melting point of the material where strengthening by other mechanisms becomes weak. This class of materials is not new: as early as 1910, Coolidge (1) used thoria dispersed tungsten for filaments. Jeffries (2) also studied how thoriated tungsten could stand long hours of high temperature exposure without sagging.

Engineering applications of dispersion hardened materials preceded an understanding of the mechanisms responsible for their unique properties. Ever since the advancement of the concept of dislocations in solids, there have been numerous

attempts to relate the deformation behaviour of these materials with varied forms of dislocation-dispersoid interactions. Several theoretical models and a wealth of experimental data are available in literature explaining the deformation and oxidation behaviour of dispersion hardened materials. Some models have been overtaken by newer experimental data; yet a quantitative understanding of deformation and oxidation mechanisms is still incomplete. Thoria in nickel (3), alumina in aluminium (4), silica in copper (5), and thoria in nickel-chromium alloy (6) are some of the extensively investigated examples of ODS alloys. Chapter II presents a brief review of the important engineering properties of ODS alloys and the several theoretical models explaining these properties.

Most of the engineering properties depend critically on a uniform distribution of the second phase particles in the matrix. This is not as easily achievable in ODS systems as in precipitation hardened systems wherein the second phase is grown in situ from a supersaturated matrix. A variety of powder metallurgy techniques including some chemical methods have been developed to produce ODS alloy powders, and these are concisely surveyed in Chapter III. Most of these techniques however are not universally applicable; alloys have to be tailored to suit the technique. This limitation is especially felt if reactive solutes are to be the alloy constituents. Additions of reactive solutes to the matrix phase are needed in advanced technology ODS superalloys for precipitation hardening (e.g., titanium and aluminium) or even for increased ductility (e.g., zirconium and boron).

A novel powder metallurgy method of introducing oxide particles and reactive solutes uniformly in a metal matrix was first pioneered by Benjamin (7). He introduced chromium, titanium and aluminium as well as zirconium and boron into a nickel matrix along with yttria by dry-milling all the constituents together in a high energy ball mill called 'attritor'. In this technique, which he named 'mechanical alloying', he was able to achieve uniform interdispersion of all the alloying constituents and the oxide particles as well. The phenomenon of mechanical alloying and attritor processing raise some questions and this dissertation is primarily an attempt to provide answers to them in qualitative and quantitative terms.

For following mechanical alloying, Ni-20Cr-2ThO_2^* is chosen as a model alloy in the present investigations. This alloy, which has been extensively investigated by Wilcox and his co-workers, represents a simple combination of a reactive solute and an oxide dispersoid. To analyse the degree of alloying, several experimental techniques (described in Chapter IV.) have been used in this work, which mainly include magnetic coercivity measurements and electron probe microanalysis. These tools have provided a clear picture of the degree of alloying as influenced by a variety of attritor milling parameters. The milling parameters could be varied over a range of values in a specially built attritor described in Chapter IV.

* Chromium is 20 w/o, thorium is 2 v/o and rest nickel in this composition. Hereafter all percentages of oxide dispersoid refer to volume percentages in this work.

The results of the experiments on the effect of milling parameters on mechanical alloying constitute Chapter V.

A relevant question is whether mechanical alloying is true alloying of the solutes. The problem has been examined in this thesis in Chapter VI using X-ray diffraction and Scanning Auger Microprobe analysis. Alloying of any kind must involve diffusion of the species and so it is desirable to know what kind of diffusion mechanism may be operating that enables mechanical alloying to take place in an attritor. Chapter VII of this thesis discusses a possible diffusion mechanism in the light of some experimental results.

Chapter VII takes this study further leading to an 'energy balance' model that relates mechanical alloying to process parameters such as attritor speed, weight proportion of the grinding balls, and ball diameter. With some limitations, the model is capable of predicting the main process parameters of attritor milling. The results of the work are summarised in Chapter VIII wherein the main conclusions are also indicated along with suggestions for further work in the area.

CHAPTER II

PROPERTIES OF ODS ALLOYS

PROPERTIES OF ODS ALLOYS

CHAPTER II

PROPERTIES OF OXIDE DISPERSION STRENGTHENED ALLOYS

2.1. INTRODUCTION

ODS alloys are useful at temperatures where coherent particles precipitated from an alloyed matrix coarsen and even dissolve. Thermally stable metallic oxide particles are commonly preferred as the dispersoids in ODS materials to ensure that degradation in properties does not occur as a result of growth or decomposition of the particles during high temperature service. The choice of the oxide is governed by some of the following main considerations:

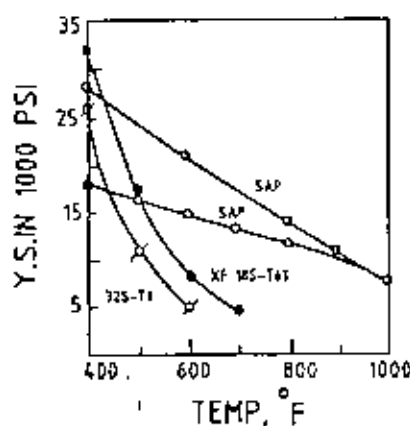
- i) the oxide must have a large negative heat of formation, and preferably have no allotropic modifications up to service temperatures.
- ii) it must have negligible solubility in the matrix,
- iii) it must have negligible reaction with the reactive solute elements in the matrix.

A 1977 review (8) has compiled numerous case histories of dispersion strengthening of as many as 21 metals with different oxides, describing the resulting properties and characteristics. The development in the fifties of SAP (Sintered Aluminium Powder) alloys (9), which have Al_2O_3 dispersion in the range

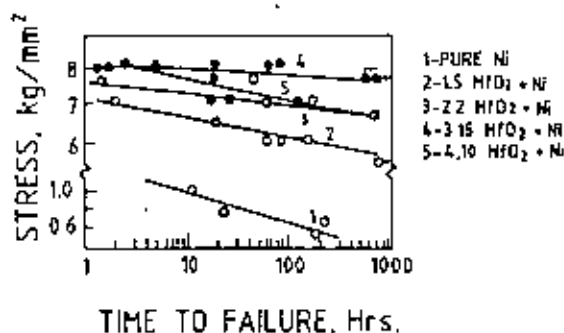
of 5 to 15 volume % in an aluminium matrix, stirred greater interest in dispersion strengthened materials for engineering applications. Because of its enhanced heat-resistant properties, SAP was a candidate material for nuclear reactor claddings and automotive engine piston components (10). Ni-20Cr-2ThO₂ composition (designated TDNiC, also called TDNiCr) in sheet form was developed (6) in the early seventies as a successor to TD Nickel (Ni-2ThO₂) (3) for potential applications in gas turbine combustors/vanes. Even prior to this, some properties of Ni-20Cr-2ThO₂ were investigated by Gregory and Goetzel (11). Copper dispersion hardened with about 1 Vol.% Al₂O₃ which could retain the electrical conductivity at a useful level of about 85% IACS* became commercially available (12) for electrical contacts and similar applications. The typical magnitudes of improvement in yield strength, creep strength and oxidation resistance respectively of some Al-Al₂O₃ alloys (10), Ni-HfO₂ alloys (8), and a Ni-Cr-Y₂O₃ alloy (13) are illustrated in Fig.1.

In modern times, the demands for advanced gas turbine materials capable of withstanding higher turbine entry temperatures in high performance aircraft engines have focussed the attention of metallurgists to produce complex ODS superalloys that combine solid solution strengthening, precipitation hardening and oxide dispersion strengthening. An example of such an ODS superalloy is

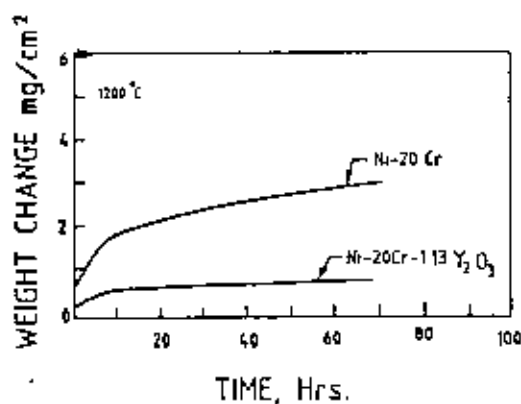
*International Annealed Copper Standard, taken as 100%.



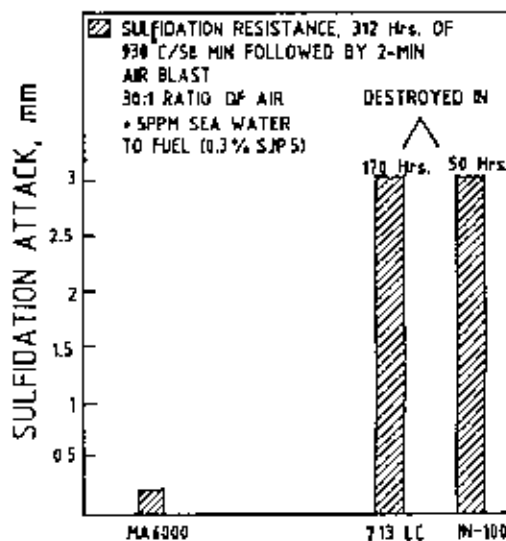
a) YIELD STRENGTH AT ELEVATED TEMPERATURE OF SAP ALLOY COMPARED TO COMMERCIAL ALUMINUM ALLOY (XF10S-T41 & 32S-T4) [Ref. 10]



b) CREEP STRESS VERSUS RUPTURE LIFE OF NICKEL AND Ni-HfO₂ ALLOYS [Ref. 8]



c) ISOTHERMAL OXIDATION KINETICS OF AN ODS ALLOY COMPARED TO A NON-ODS ALLOY [Ref. 13]



d) HOT CORROSION RESISTANCE TEST ON AN ADVANCED ODS SUPERALLOY (MA6000), 713 LC SUPERALLOY AND IN-100 SUPERALLOY. [Ref. 15]

FIG 1 SOME PROPERTIES OF ODS ALLOYS

IN-853 with the nominal composition $\text{Ni-19.7Cr-0.9Al-2.3Ti-0.07Zr-0.007B-2.25Y}_2\text{O}_3$ and its improved creep strength over a wide range of temperatures stretching from about $0.4T_m$ to about $0.8T_m$ (T_m being the melting temperature of the alloy) can be seen in Fig.2(14). The ODS superalloys possess the additional advantage of enhanced hot corrosion resistance, as illustrated in Fig.1d for a recently developed version designated as MA6000 (15) with the nominal composition $\text{Ni-15Cr-4W-2Mo-4.5Al-2.5Ti-2Ta-0.01B-0.15Zr-1.1Y}_2\text{O}_3$ in comparison with an advanced, non-ODS nickel base superalloy.

Although increasing the dispersoid content increases the mechanical strength, the tendency to brittleness and severe difficulties in fabrication to useful shapes set an upper limit to the volume fraction loading of the oxide in the matrix (16). With the availability of oxides as fine as $50\text{-}300\text{\AA}$ in mean particle size, even moderate volume fractions of the order of 0.01 to 0.03 are as effective in strengthening as higher volume fractions of coarser particles, since it is the interparticle spacing rather than the dispersoid size that is of predominant importance for strengthening.

The strengthening that the oxide dispersion provides is essentially a result of the increased resistance to dislocation motion. This chapter briefly delineates the important aspects of the underlying dislocation mechanisms that have been identified by various workers to account for the ambient and elevated temperature deformation behaviour including yielding, work-hardening, ductility and

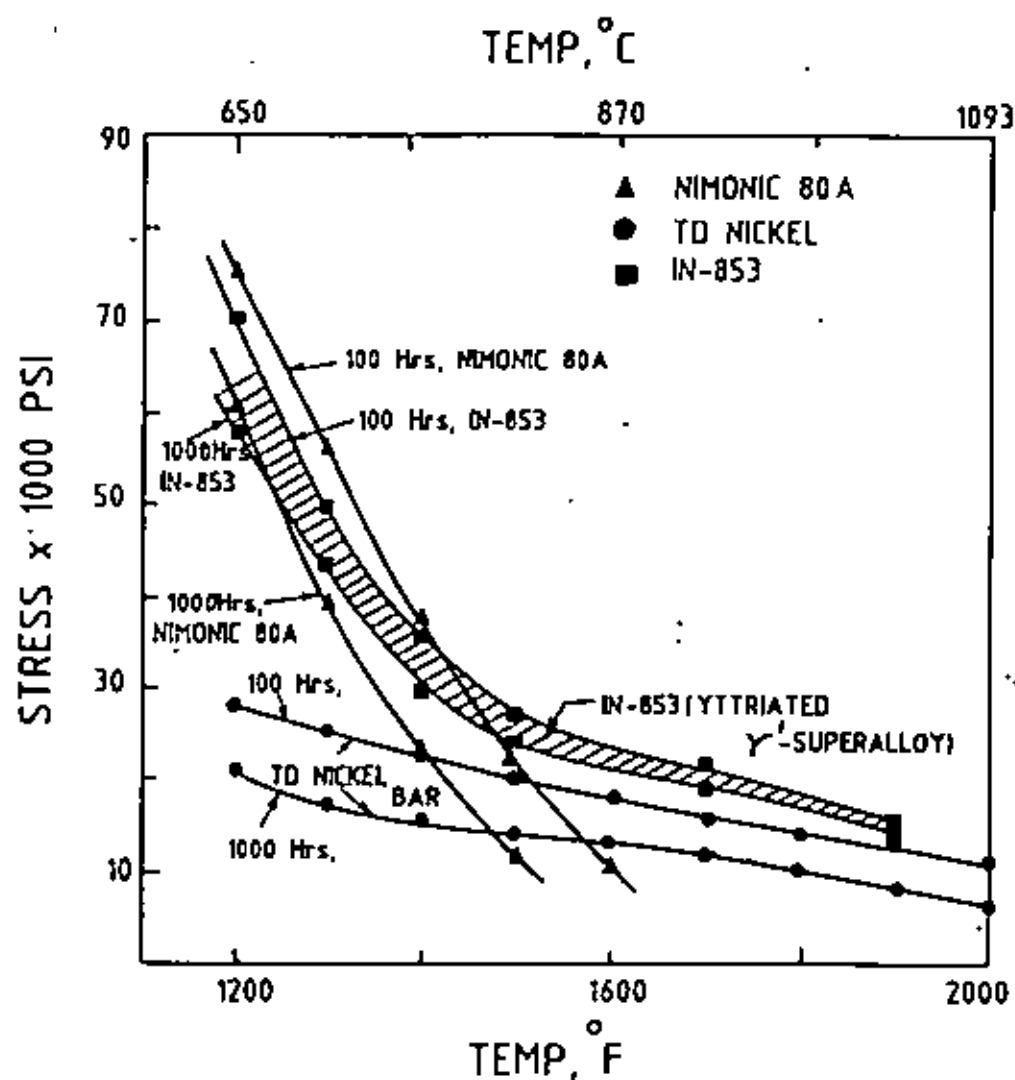


Fig. 2. 100 Hrs AND 1000 Hrs CREEP RUPTURE STRESS BEHAVIOUR OF IN-853 SUPERALLOY COMBINING OXIDE DISPERSION STRENGTHENING AND PRECIPITATION HARDENING (Ref: 14)

creep. The peculiar features of recrystallization of ODS materials and their effects on mechanical properties are discussed which is followed by a note on the ductility behaviour of ODS alloys. A brief survey of the reported models for improved oxidation resistance is also included.

2.2 DEFORMATION AT AMBIENT TEMPERATURES

Yielding in particle-hardened alloys occurs when the applied stress reaches the stress required to cause measurable plastic deformation by the movement of dislocations through the array of particles in the matrix. In the generalised model for such alloys (17), the dislocation motion is hindered by the obstacles and the breakaway of the dislocation from the obstacles is said to be rate-controlling for flow: when the included angle between the bowed segments of a pinned dislocation as shown in Fig.3 reaches a critical value, the dislocation breaks away from the obstacle. At the critical point of equilibrium, the obstacle strength F , is balanced by the opposing resultant of the dislocation line tension forces given by the relation:

$$F = 2 \Gamma \cos \frac{\phi}{2} \quad (\text{eqn. 1})$$

Where Γ is the line tension of the dislocation. It can be shown that the applied stress τ , needed for the dislocation to break away is related to F as:

$$F = \tau b \lambda \quad (\text{eqn. 2})$$

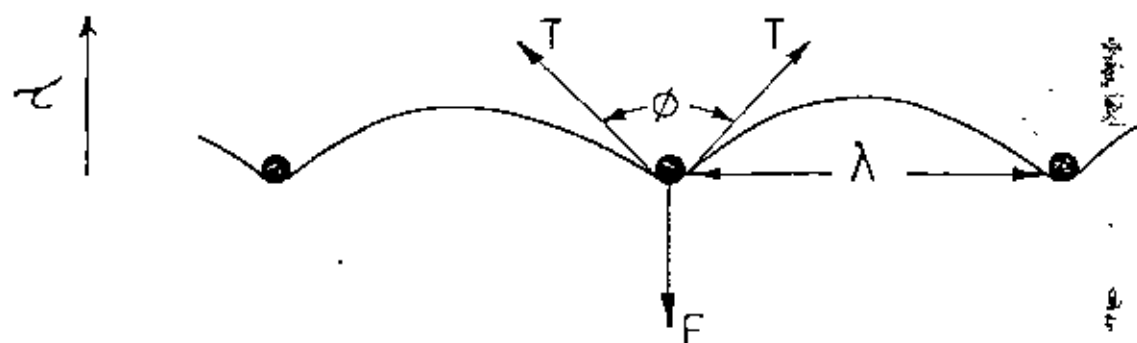


Fig 3. DISLOCATION, HELD UP AT OBSTACLES, BOWS TO AN ANGLE ϕ AS SHOWN, UNDER THE ACTION OF APPLIED STRESS

$$\text{and} \quad \tau = \frac{Gb}{\lambda} \cos \frac{\phi}{2} \quad (\text{eqn. 3})$$

where b is the burgers vector of the dislocation, λ is the effective inter-particle spacing and G is the shear modulus of the matrix.

For all values of $\phi > 0$, the particles can be sheared by the glide dislocation with a force equal to the obstacle strength: this is typical in solid solutions or precipitation hardened alloys. When $\phi = 0$, the particles behave as impenetrable obstacles and this situation exemplifies dispersion hardening. The vital term in Eqn.2 is λ which is a measure of the strength of the obstacle: smaller the λ , stronger is the obstacle. While the above analysis assumes a regular array of particles, Foreman and Makin (18) derived, on the basis of computer simulation, a more precise expression for the flow stress for a random array of particles having the whole range of obstacle strengths ($0 \leq \phi \leq \pi$).

Kocks (19) showed that the macroscopic effect of a random array of particles is to lower the flow stress by a factor of 0.84 with respect to a regular array of similar obstacles. When particles tend to form clusters, the mechanical properties are further lowered. When particles are cut, the flow stress can comprise of contributions from several mechanisms like coherency hardening (such as AlCu_2 precipitates in aluminium alloys), modulus hardening (soft particle strengthening such as copper in iron), order hardening (such as γ' in superalloys). Such mechanisms are absent in dispersion hardened alloys in which dislocation looping governs the flow stress. A consequence of this is that for the same volume fraction of particles, the strength of the material increases with increasing particle diameter upto a critical diameter (curve A in Fig.4), when the particles are

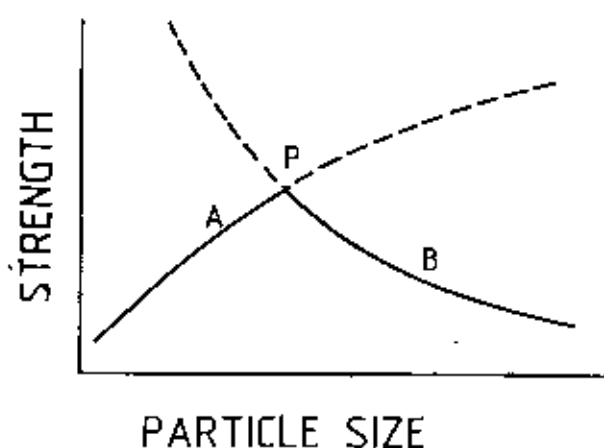


Fig. 4 A SCHEMATIC SHOWING STRENGTH INCREASE WITH PARTICLE SIZE, CURVE A, AS IN PARTICLE CUTTING MECHANISM (PRECIPITATION HARDENING), AND STRENGTH DECREASE, CURVE B, AS IN OROWAN BOWING MECHANISM (DISPERSION HARDENING), (Ref. 20)

deformable. Beyond the critical size, the particles become non-deformable and following the Orowan mechanism (described in Section 2.2.1) the yield strength decreases with increasing particle diameter for the same volume fraction (curve b in Fig.4). For non-deformable particles such as in dispersion hardened alloys the strength is independent of the properties of the particles but is strongly dependent on the dispersion parameters (size and distribution). We will now briefly examine some of the important mechanisms of yielding and work hardening in dispersion hardened alloys.

2.2.1 Direct particle strengthening

When the particles are directly responsible for strengthening, the increase in flow stress is the stress required to make the dislocations overcome the particles by either dislocation bowing or cross-slip. Particle shear by dislocations in dispersion hardened alloys was proposed as the yielding mechanism by Ansell and Lenel (21) and further supported by Ansell (22) but as will be seen shortly, many later investigations proved this mechanism to be inapplicable in dispersion hardening, particularly in ODS alloys.

Orowan Bowing

The dislocation bowing mechanism for yielding proposed by Orowan (23,24) is illustrated in Fig.5. Here the dislocation blocked by the particles bows between them, under increased applied stress, acting against its own line tension, until

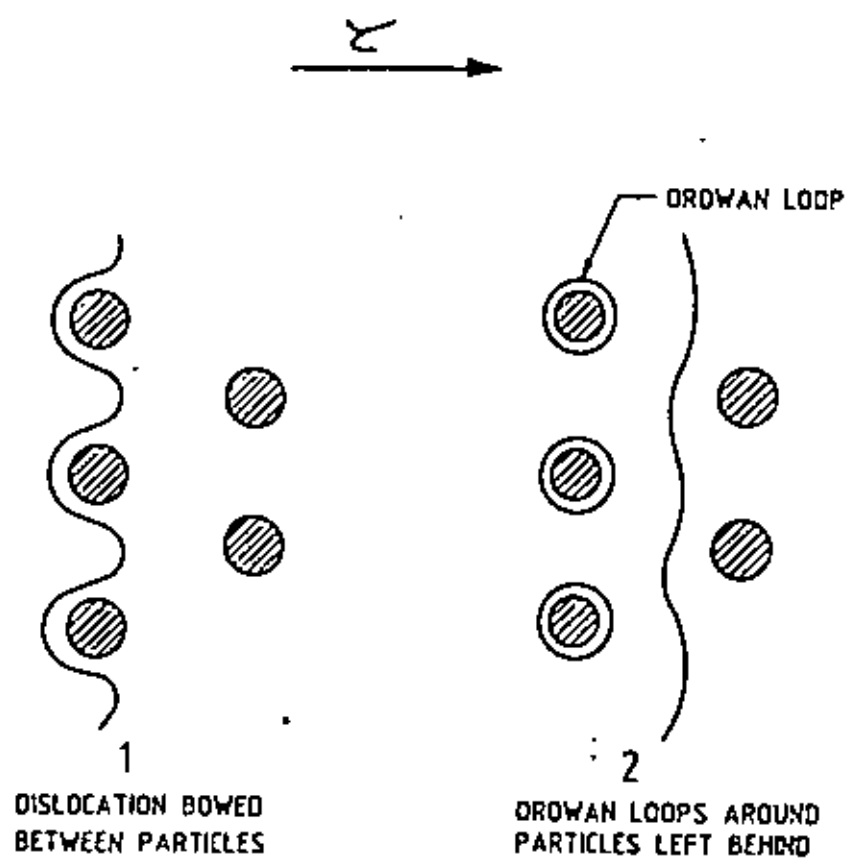
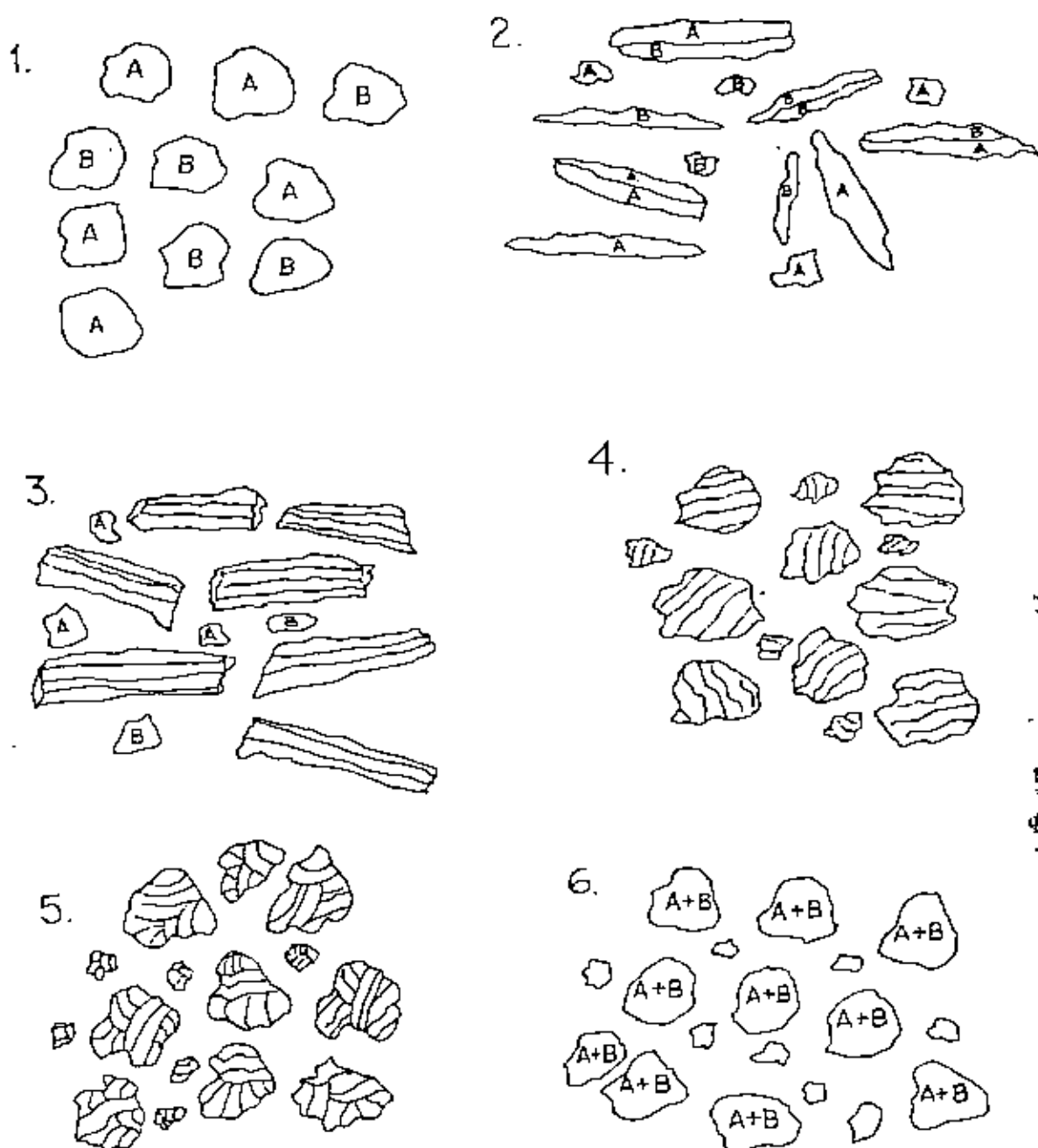


Fig. 5. OROWAN BOWING MECHANISM.



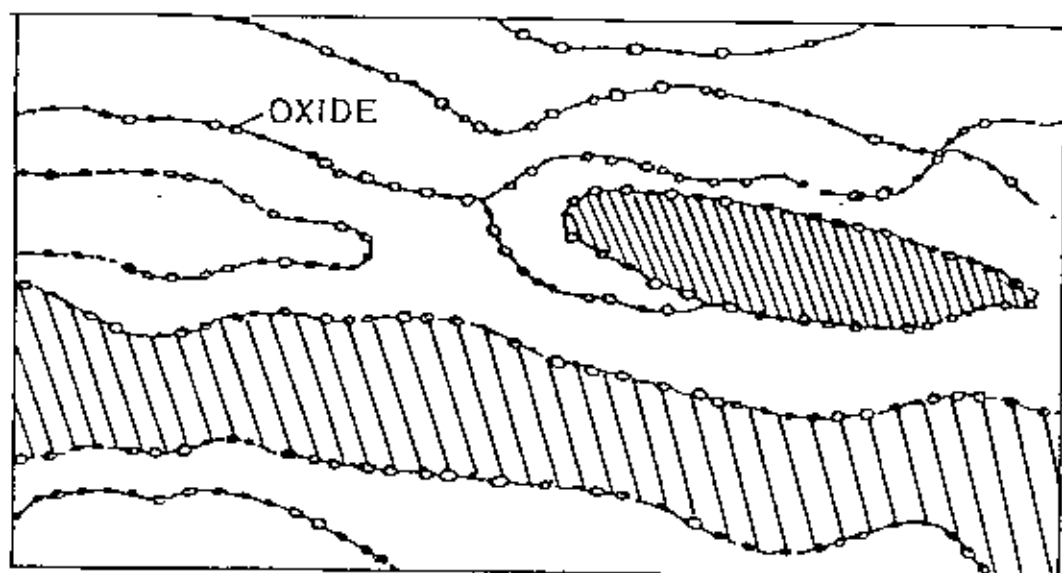
- 1 STARTING MIX OF ELEMENTS A & B
- 2 INITIAL STAGE
- 3 PERIOD OF WELDING PREDOMINANCE
- 4 EQUIAXED PARTICLE FORMATION
- 5 RANDOM WELDING ORIENTATION
- 6 STEADY STATE PROCESSING

FIG 14 THE STAGES OF MECHANICAL ALLOYING

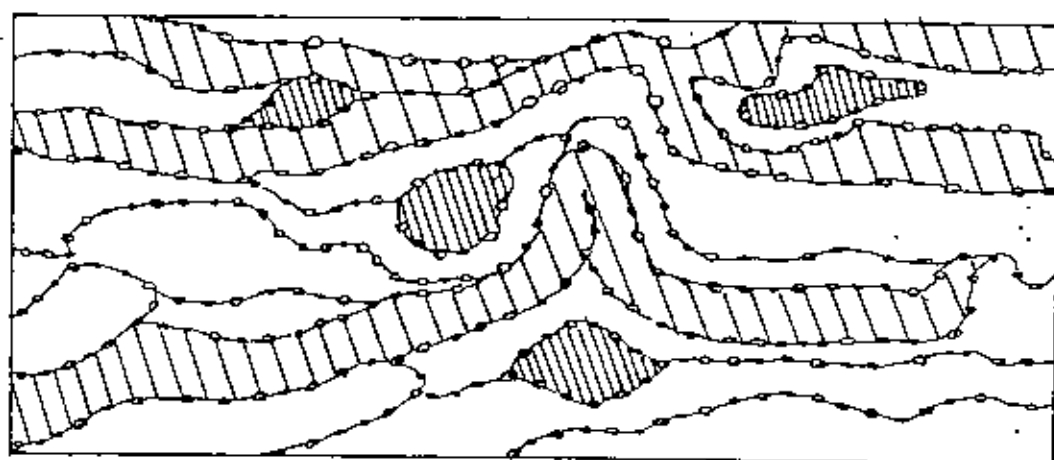
3.8.4 THE FIVE STAGES IN MECHANICAL ALLOYING

Benjamin and Volin (123), by following the progress of mechanical alloying with time in a high speed blender, arrived at the following generalised division of five consecutive stages involved in the mechanism of mechanical alloying, as schematically illustrated in Fig.14. These are as follows:

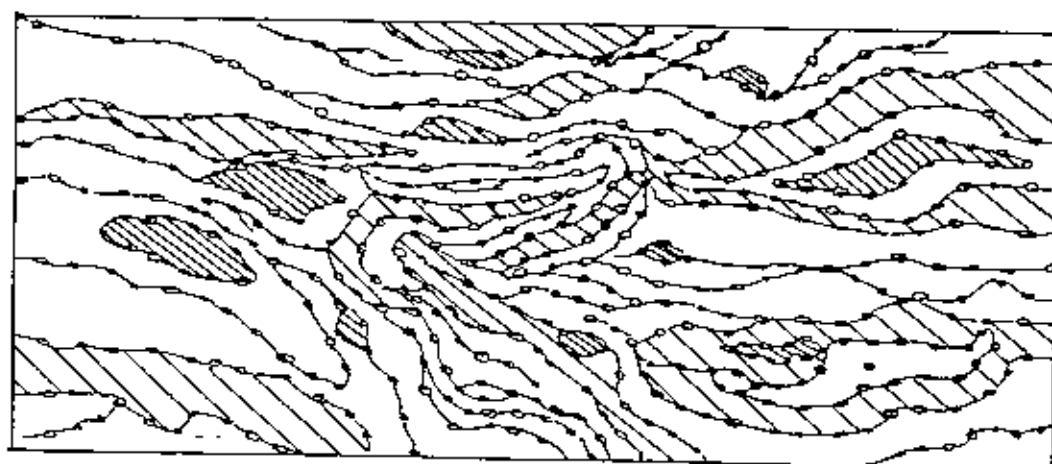
- i) an initial period wherein there is an increase in the number of particles coarser and finer than present in the starting charge. The coarser particles are composite plates formed by the flattening of the different ingredients of the charge; the fine particles are mostly fragments of the more friable ingredients of the starting mix.
- ii) a period of welding sets in afterwards wherein coarser powder fraction increases while finer size fraction remains approximately constant. Coarser particles, here, have multilayered composite structure with lamellae running parallel to the ball surfaces or the long axis of the flakes. These individual, elemental lamellae are much smaller in volume than the initial elemental particles and therefore must be the comminuted fragments of the initial elemental powders.
- iii) This is followed by a period of equiaxed particle formation wherein the amount of coarse plate-like particles sharply decrease and more equiaxed particles are developed. The finer powder fraction now displays parallel lamellae similar to the coarser powder



INITIAL STAGE



INTERMEDIATE STAGE



FINAL STAGE

FIG 13 OXIDE PARTICLES BEING DISTRIBUTED
IN THE COMPOSITE PARTICLES DURING
MECHANICAL ALLOYING (Ref. 119)

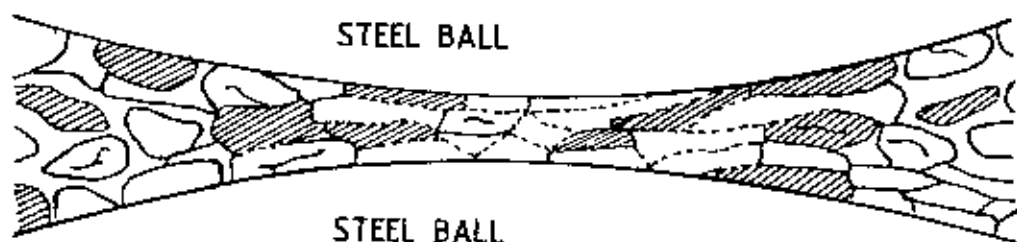
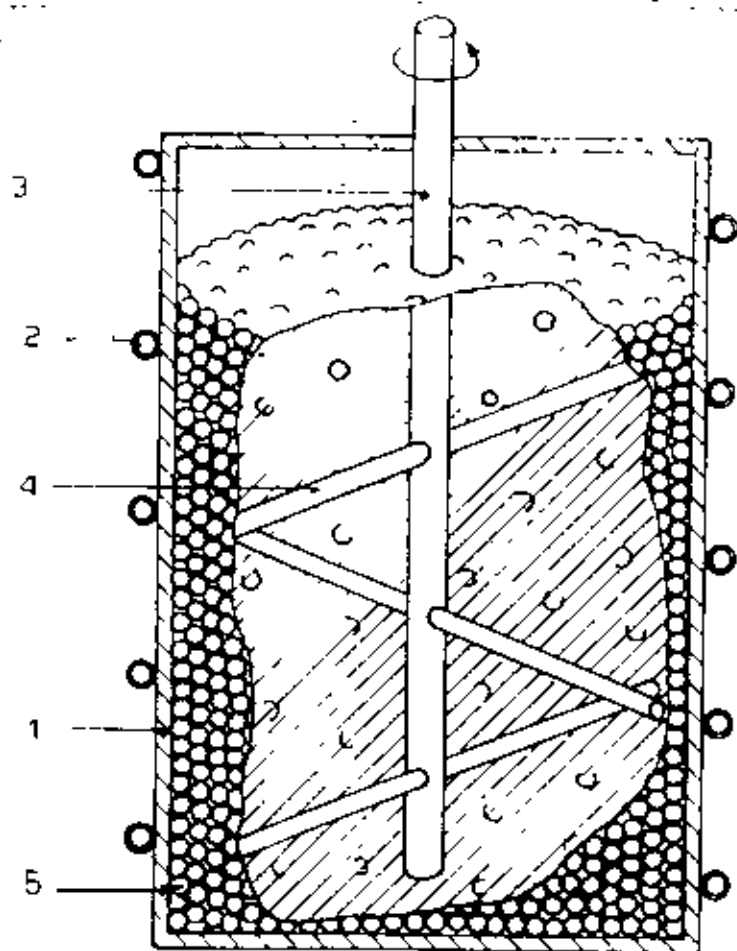


FIG 12 COMPOSITE PARTICLE FORMATION IN POWDER
TRAPPED IN COLLISION BETWEEN BALLS (Ref. 119)

need for high energy grinding mills like attritors for mechanical alloying of ODS alloys with high melting points.

The underlying phenomenon in mechanical alloying (129) is the repetitive process of particle welding and flaking off at the ball surfaces as the powder particles are trapped in the attritive collisions between the balls. During collisions, particles are compressively deformed to an extent that causes rupture of any adsorbed surface contamination and exposes atomically clean metal surfaces. These surfaces are easily cold welded among themselves leading to the formation of composite particles of the constituents (Fig.12). With time, the lamellar thickness within the composite particles is progressively reduced in successive collisions, thus refining composite particles. While some particles are being welded, ~~others which cannot take further deformation are being fractured~~, others which cannot take further deformation are being fractured leading to comminution. A steady state processing is soon attained, characterized by a saturation in hardness and constant particle size distribution which is relatively coarse. The oxide dispersoid which is sub-optical in size, is believed (129) to be initially entrapped along the cold weld interfaces; with milling time, the oxide concentration along the weld seams decreases as the welds move closer together (Fig.13). At a stage where the lamellae within the composite particles are no longer optically resolvable, the oxide particles also would have attained optimum interparticle spacing which is approximately the spacing between the welds. Further milling is not necessary as the mechanical alloying is deemed to be complete at this stage.



- 1 VESSEL
- 2 COOLING COIL
- 3 SHAFT
- 4 IMPELLERS
- 5 GRINDING BALLS

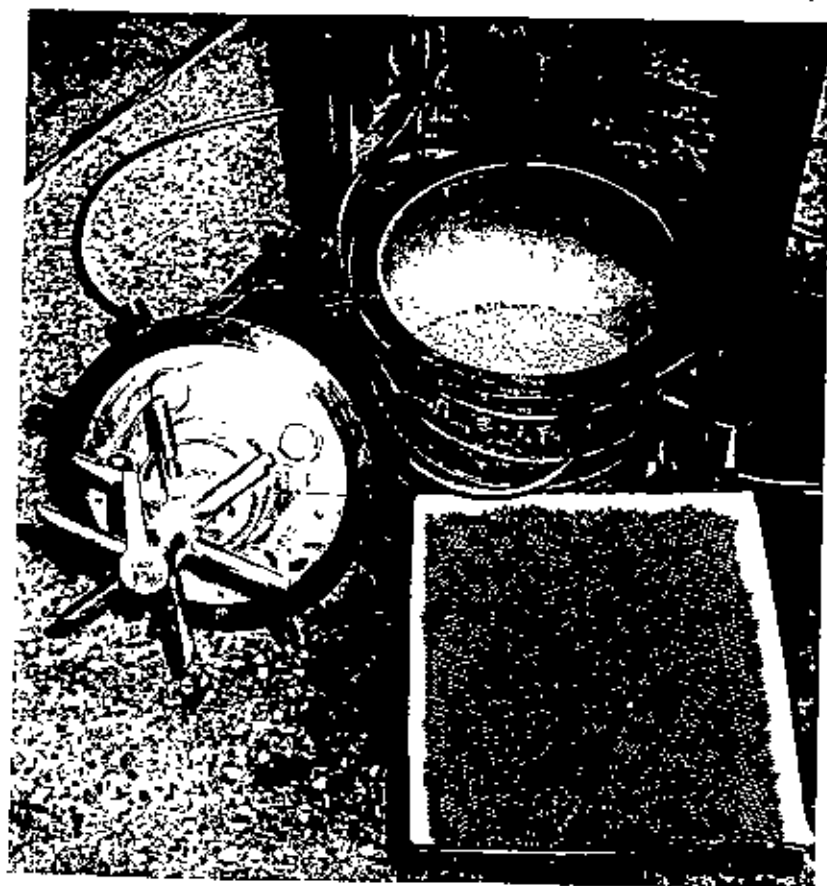


FIG 11 A SCHEMATIC AND ACTUAL VIEW OF ATTRITOR

a schematic and actual view of an attritor, as used for mechanical alloying. It consists of a stationary, vertical, water-cooled vessel with a gastight lid that supports a centrally mounted, motor-driven shaft with impeller arms on it. The shaft is unsupported at its bottom end. The rotation of the impellers agitates the ball charge to a high level of kinetic energy which is utilised in the mechanical alloying of the powder constituents.

3.8.3 PHENOMENOLOGY OF MECHANICAL ALLOYING

The key features of mechanical alloying are the high energy input made possible by the comparatively high speeds of operations of the mill and the absence of surfactants or milling vehicles. These features promote cold welding between the particles which is a crucial aspect in the mechanism of mechanical alloying.

Cold welding, a well known method of joining metals, is capable of producing truly metallurgical bonds (127). Cold welding however is generally a function of the ratio of welding temperature to the melting point. Thus low temperature melting metals like aluminium cold weld easily and do so to such an extent that milling methods of producing Al-Al₂O₃ alloys - be it ball milling or attritor milling - require the presence of surfactants/other organic media to control excessive particle welding (99,128). With higher melting point metals like nickel or iron, cold welding is more difficult, requiring 5 to 20 times energy input over that needed for aluminium or lead (7). Such high energy levels are not obtainable in conventional ball mills and hence the

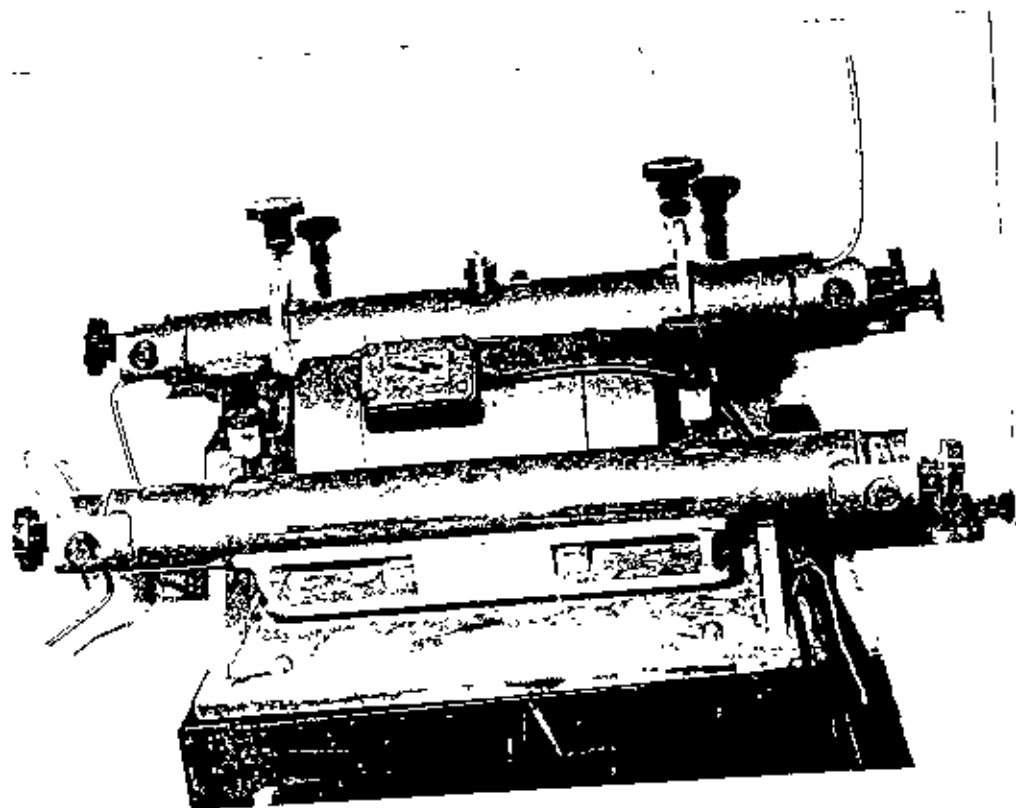


FIG 10 A VIBRATORY BALL MILL

energy grinding mill with a relatively high charge of hard, grinding balls which are kept in a state of intense agitation. The milling is generally done dry without the use of any liquid medium or surface-activating agent, in contrast to ball milling where surfactants and wet-milling vehicles are commonly used. In some cases, inert atmosphere such as argon is also used to prevent the oxidation of alloying elements.

Reactive elements like titanium and aluminium cannot be added directly in elemental form even for the mechanical alloying process, because of the risk of their oxidation in the presence of the sealed-in air in the mill. Recourse is therefore taken to use crushed and powdered master alloys like Ni-Ti-Al (for adding titanium and aluminium) or Ni-Zr (for adding zirconium). In the master alloy form the thermodynamic activity of the reactive elements is reduced by several orders of magnitude thus greatly subduing their oxide-forming tendency.

Mechanical alloying can be performed in a vibratory mill (122) such as the one illustrated in Fig.10, or a high speed shaker mill (123) but an attritor, which is essentially a high energy ball mill, is most commonly employed presumably because of its amenability for large scale, production-oriented use as witnessed by the installation of industrial size attritors for production of mechanically alloyed ODS nickel base superalloys (124). Attritor is originally a comminution/blending equipment, patented by Szegvari (125) and is commonly used in chemical industries like paints and inks. Perry's Chemical Engineering Handbook (126) describes it as a non-rotary stirred ball mill. Fig.11 shows



strengthening mechanisms as demonstrated in terms of its impressive creep properties in Fig.2.

Ever since its first application for producing an ODS superalloy, mechanical alloying has been used and is still being used to produce a variety of ODS alloys based not only on a nickel matrix but others like iron, aluminium, cobalt, titanium, etc. Table 1 (78) lists some of the important ODS alloys produced by mechanical alloying along with the names of their producers. Benjamin (119) also hints at the extraordinary potential of mechanical alloying for the development of new and exotic combinations of metals and materials, other than ODS alloys alone. A recent example of such newer applications is a report (120) of the development of Cu-15Ru composite for electrical contacts wherein hard, fine ruthenium particles embedded in a copper matrix by means of mechanical alloying provide the required heat resistant electrical conductivity while the copper matrix ensures the electrical continuity. The technique overcomes the severe problems of fabricating pure ruthenium. Another example of a different application of mechanical alloying is the possibility of generating extended solid solubility, as observed in a study (121) of mechanical alloying of iron in copper wherein extended solubility of iron upto about 3% was observed against the equilibrium solid solubility of less than 1% Fe at 800°C.

3.8.2 The Process

Mechanical alloying consists of blending elemental and master alloy powder constituents of the matrix with the dispersoid oxide powder in a high

0.8 T_m where creep strengthening due to γ' precipitates ($\text{Ni}_3(\text{Ti,Al})$) in conventional superalloys becomes ineffective. This goal has been realised only partially with TD Nickel which despite its excellent creep strength at temperatures as high as about 1200°C (i.e. around 0.8 T_m) has poor strength at intermediate temperatures (0.3-0.5 T_m) and poor oxidation resistance. This deficiency was overcome to some extent by the development of TDNiCr (3). While TDNiCr had the required oxidation and hot corrosion resistance, the problem still remained as to how to bring in the required intermediate temperature strength which γ' precipitation-hardening can effectively provide. This implies that the matrix of ODS nickel base superalloy must also contain titanium and aluminium. Neither the chemical methods (like that employed in TDNickel preparation) nor the oxidation methods (like that employed for SAP) can handle the addition of reactive elements like titanium and aluminium to the nickel matrix without oxidation of these solutes. Similar difficulties and other limitations as described in Section 3.7 are present in mechanical mixing too. The necessity therefore arose to find a better method for this purpose. Mechanical alloying eventually provided the solution.

Mechanical alloying developed by Benjamin in the early seventies (7,116,117) is an elegant route for producing ODS alloys with reactive solutes, and remains unsurpassed in its versatility. Over the years, the technique has acquired commercial viability with some compositions of ODS superalloys already in the market (118) for engineering applications. The first grade of such a superalloy to be made by mechanical alloying is IN-853 previously referred to in Section 2.1 and its composition ensures the availability of multiple

oxides subsequently by molten alkali or alkaline earth metals may be futile because of the excessive growth of the dispersoid and the necessity to remove the reaction product oxides and carrier agents (usually salts) (7).

3.7 MECHANICAL MIXING

It is possible to obtain dispersion of oxides in metals by simply mixing the oxide and metal powders in a ball mill (112) or a blender (113). For example, mechanical mixing has been tried with some success for obtaining Al_2O_3 dispersion in nickel (114). A basic limitation however is that extremely fine metal powders are required: Cremens (115) shows, from topological considerations that the metal powder size should be in the range of 0.5 to 0.05μ for a uniform dispersion of 0.1 to 0.005μ size oxide. It is also generally recognized that simple mechanical mixing in conventional mixers or blenders does not easily yield the desired uniformity and fineness of dispersion (87). Furthermore, the finer the matrix metal powders, greater is their specific surface area, rendering them highly reactive or pyrophoric and thereby susceptible to contamination. This leads to handling problems and oxidation of reactive solutes if any.

3.8 MECHANICAL ALLOYING

3.8.1 Background

The original development of TD Nickel in the sixties (105) provided an opportunity to push the operating temperatures of superalloys to about

for Ni-ThO₂. Here, nickel and thorium nitrate solutions in methanol were mixed, dried and pulverized. The powders were heated in dry hydrogen or inert atmosphere converting the thorium salt to its irreducible oxide while nickel oxide was reduced to metallic state. The process resulted in fine nickel powder coated with thorium particles.

3.6 ELECTRODEPOSITION AND VAPOUR PLATING

Electro-deposition technique was employed to produce Al₂O₃ dispersed in nickel (110). Submicron size Al₂O₃ particles were maintained in agglomeration-free suspension in an electroplating bath of nickel. Under proper conditions, Al₂O₃ codeposited with nickel resulting in an optimum dispersion of fine Al₂O₃ in nickel. Vapour plating in fluidized bed (111) was tried for dispersions of Al₂O₃ and ThO₂ in gold, in which Au(CO)Cl vapours were decomposed in a heated, fluidized bed of the oxide particles resulting in a coating of gold on the oxide.

All the above chemical methods suffer from one serious limitation or the other. Many are restricted to a few systems, and are elaborate. Most of them produce inherently very fine powders which therefore tend to be reactive or pyrophoric and prone to contamination. The selective reduction principle common to many of these methods cannot be applied to ODS alloys requiring reactive solute elements like titanium and aluminium in the matrix because such elements form extremely stable oxides; any attempt to reduce these

hydrogen reduction of nickel ammonium carbonate aqueous solution in which an aqueous solution of thorium has been incorporated. The reduction is done at about 150°C.

A chemical method of selective reduction of oxide mixture was applied to produce Ni-Cr-ThO₂, Co-Cr-W-ThO₂ etc. as described by Triffleman (107). For example, for Ni-Cr-ThO₂ alloy the starting ingredients in this method are nickel, chromic acid, thorium nitrate solution which are mixed into a homogeneous solution and thermally decomposed to get a mixture of oxides and basic salts. Reduction is carried out in two stages, first with cracked ammonia or natural gas, and then with cracked ammonia or hydrogen and lamp black. The resultant powder is mixed with graphite, pressed and vacuum-sintered to obtain Ni-Cr-ThO₂ with acceptable, low levels of carbon and oxygen. There have also been other methods to have chromium in solid solution in the matrix. For instance, Ni-ThO₂ powder was mixed with chromium powder (108) and homogenised into a solid solution of chromium in nickel by high temperature diffusion in very dry hydrogen atmosphere; it was subsequently contacted with an organic solvent to leave some carbon that serves to reduce Cr₂O₃ formed during mixing.

3.5 IGNITION SURFACE COATING

Fine metal powders can be coated with a thin film of a reactive metal oxide, by ignition surface coating method, described by Murphy and Grant (109)

to facilitate faster diffusion of oxygen and to minimise coarsening of the dispersoid that would occur as internal oxidation progresses from surface to core. Thus ODS superalloys containing reactive γ' forming solutes in the matrix, viz., titanium and aluminium, would be extremely difficult to produce by either of the oxidation methods, because the oxygen potential cannot be raised above the extremely low values required to oxidize the reactive solutes, and the oxidation rate of the desired dispersoid-forming elements would be prohibitively slow.

3.4 SELECTIVE REDUCTION METHODS

These methods essentially consist of coprecipitating an intimate mixture of the salt of the matrix metal and dispersoid metal, then decomposing to a mixture of the oxides, and subsequently reducing the oxide of the matrix metal selectively such that it leaves the dispersoid oxide in an unreduced state because of its greater thermodynamic stability under the applied conditions of reduction. This is the basis of the commercial process for Du Pont Company's Ni-2ThO₂ known as TDNickel (105). In this process, an aqueous solution of nickel nitrate is mixed with a thorium sol and ammonium hydroxide and ammonium carbonate solutions. Thorium particles are thereby coated with nickel hydroxide carbonate. The dried and milled precipitate is then reduced in dry hydrogen at about 600°C to obtain reduced nickel dispersed with fine ThO₂ particles. Similar steps apply to TD Cobalt. Sherritt Gordon Mines Limited developed (106) their version of Ni-3.5 ThO₂ called D5 Nickel by a process of high p

care was taken to avoid the undesirable formation of Cr_2O_3 in the process.

3.3 INTERNAL OXIDATION

Internal oxidation is based on the preferential oxidation of a reactive solute element in a dilute solid solution alloy taken either as powder or wrought shape preferably as a thin strip or wire. It is a prerequisite in this technique that the oxide of the solute must have a greater negative heat of formation than the oxide of the matrix metal, which enables diffusion of oxygen at a controlled partial pressure suitable for oxidising only the solute and not the matrix element. Further, the rate of oxygen diffusion into the matrix must be greater than the outward diffusion rate of the solute. $\text{Cu-Al}_2\text{O}_3$ has been produced in this manner from prealloyed powders (102).

In a variation of this technique, appropriate quantity of the oxide of the matrix metal is mixed with the prealloyed powder, pressed and sintered, during which the oxygen for internal oxidation of the reactive solute in the prealloyed powder is provided by the matrix oxide as it gets reduced to a metallic state. This way Lewis et al (103) produced $\text{Ni-Al}_2\text{O}_3$. A somewhat similar method is described in the patent of Nadkarni and Klar (104) to produce $\text{Cu-Al}_2\text{O}_3$.

The severe limitations of internal oxidation are: (i) the necessity of good solid solubility of the dispersoid metal in matrix metal, and (ii) the necessity of starting with very fine powders or ultra-thin strips or wires.

3.2 SURFACE OXIDATION

The stable oxide film on a reactive metal powder surface forms a dispersion when the powder is compacted and sintered, hot pressed, or hot extruded. The production of SAP (Sintered Aluminium Powder) is a classic example of this technique (95). In this method, the compaction process breaks up the stable oxide film around the particles and allows cold welding to take place between particles, thus trapping the oxide as a dispersion. SAP is reported to have 50-100Å thick, 500-1500Å diameter, disc-shaped Al_2O_3 particles (95), although some workers (96) found Al_2O_3 in SAP as an almost continuous skeletal network. Surface oxidation method was used to produce some other ODS alloys also such as Mg-MgO (97). However attempts to produce Ti-TiO₂ in this manner (98) resulted in a highly embrittled alloy presumably because of the extensive solid solubility of oxygen in titanium.

In a slight variation based on the same principle, flake aluminium powder was ball milled with a surfactant and a milling vehicle to yield a much more uniform dispersion of Al_2O_3 than in SAP (99). Another variation is that a reactive element in solid solution in the flake powder is allowed to undergo preferential oxidation during the course of milling. In this manner, Schilling and Grant (100) wet-milled prealloyed Cu-Al powder in a high energy ball mill (attritor) to produce submicron thick (0.1 - 0.3 μ at edges) flake powder with a surface area large enough to promote room temperature oxidation of the aluminium. Schilling (101) attritor milled in air prealloyed powders of Fe-Cr-Al-Y to obtain flake powders of the alloy that contained Al_2O_3 and Y_2O_3 .

CHAPTER III

METHODS OF PREPARATION

3.1 INTRODUCTION

Powder metallurgy techniques are most commonly employed to produce fine, stable dispersions in metal/alloy matrices. Conventional melting and casting techniques can not be applied to ODS alloys since fine and uniform dispersion of oxide particles cannot be obtained by such methods. Although a very recent concept of 'mix-alloying' (94) is understood to be a possibility for producing ODS alloys from a liquid state, no definite results of any laboratory attempts of it are known. All the available methods can be broadly classified as follows:

Oxidation Methods:	Surface oxidation of powders
	Internal oxidation of powders, thin strips or wires
Chemical Methods:	Selective reduction of chemically produced oxide mixtures
	Ignition surface coating
	Electrodeposition/vapour deposition
Mechanical Methods:	Mechanical mixing of constituents
	Mechanical alloying

These methods are reviewed briefly in this chapter with an emphasis on mechanical alloying.

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CHAPTER III

METHODS OF PREPARATION

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of mechanically alloyed Ni-20Cr containing any of the dispersoids of ThO_2 , Y_2O_3 , La_2O_3 etc. One such result is illustrated in Fig.1c. Under oxidation/corrosion conditions where TDNiCr does degrade, the degradation is attributed to the loss of the protective Cr_2O_3 to CrO_3 gaseous phase above 1100°C (92).

It is generally believed that dispersion of an oxide phase in nickel-chromium alloys has the following major effects on oxidation behaviour (110):

- i) selective oxidation of chromium to form a continuous, protective scale of Cr_2O_3 is promoted;
- ii) scale-forming reaction appears to occur preferentially at oxide-metal interface (anionic oxidation) in contrast to the oxide-oxygen interface (cationic oxidation) at which it occurs in dispersoid-free alloys;
- iii) growth rate of Cr_2O_3 is subdued in comparison with dispersion-free alloys and adhesion of Cr_2O_3 to the substrate is improved.

ODS superalloys are remarkable in yet another aspect, i.e., their superior hot corrosion resistance, an important criterion for applications in the gas turbine hardware such as combustors and turbine vanes. Chromium again is the dominant element responsible for hot corrosion resistance of superalloys and the oxide dispersion enhances it. For example, hot corrosion tests showed (93) that while a non-ODS, high strength nickel base superalloy, IN-100, suffered attack of $\sim 7600\mu$ in crucible test and about 3300μ in rig test, MA 755 E, a yttria dispersed nickel base superalloy, suffered only 300μ attack in crucible test and 76μ attack in rig test. This illustrates the clear superiority of ODS superalloys against hot corrosion.

to less than 50% and the material then responded to partial recrystallization upon annealing at 1200°C. However, Doble & Quigg (74) showed that longitudinal rolling of as-extruded TDNickel bar produced a strong $\{123\} \langle 142 \rangle$ texture that rendered the material highly resistant to recrystallization whereas transverse rolling gave $\{100\} \langle 010 \rangle$ texture which made it recrystallize easily.

They concluded that a highly recrystallization resistant structure has a sharp texture, which tends to equalise the differences in the Schmidt factors between grains thereby eliminating gradients of stored energy which are known to promote nucleation of recrystallization.

2.7 OXIDATION AND CORROSION RESISTANCE

Oxide dispersion in a metal or alloy matrix confers not only strengthening but also increased resistance to environmental attack like oxidation and hot corrosion, which is vital for materials of gas turbine hardware such as combustors, turbine vanes etc. TDNickel (Ni-2ThO₂) developed as a highly creep resistant superalloy was however found to be inadequate in oxidation resistance for gas turbine applications (3). This was remedied by alloying the matrix with chromium, usually upto 20% as in TDNiCr (Ni-20Cr-2ThO₂) (11). The weight gain for TDNiCr after 120 hrs under cyclic oxidation at about 1316°C was reported (87) to be about one-fifth of TDNickel and about one-half of a non-ODS nickel base superalloy. Giggins and Pettit (88), as well as other investigators (89), confirm improved oxidation resistance of Ni-20Cr alloy in the presence of 2 V/O ThO₂, and so also with Y₂O₃ and CeO₂ in Ni-Cr alloys (90). Mitchells (91) reported improved isothermal and cyclic oxidation resistance

annealing below 1506 K of an extruded, yttria dispersed nickel base superalloy did not bring about any grain growth, whereas annealing above 1506 K resulted abruptly in elongated grain growth (81). The coarse, elongated grain structure, with its high grain aspect ratio required for high temperature creep strength of ODS alloys, are often produced by massive grain coarsening treatments. This can be achieved by moving a hot zone, with a steep thermal gradient, along the length of the material. Such moving zone treatment, invented originally by Andrade (82) is the basis for the ZAP (Zone Aligned Polycrystals) technique employed by Allen (83) for directional recrystallization of TDNiCr. Cairns et al (84) and Benjamin et al (85) describe similar techniques in their patents for producing high GAR in mechanically alloyed ODS superalloys.

2.6.4 Texture Effects

Preferred orientation in ODS alloys generally has a marked influence on properties. Killpatrick and Young (86) found that the 1100°C yield and tensile strengths of a TDNiCr sheet were significantly influenced by the orientation with respect to rolling direction. The material exhibited a strong $\{100\} \langle 001 \rangle$ cube texture which is the reason attributed for the observed anisotropy in properties. Fabrication processes employed for producing ODS alloys in useful shapes impart deformation textures whereas the annealing treatments produce certain recrystallization textures. Wilcox et al (38) found that as-extruded TDNickel bar which resists recrystallization had a strong $\langle 100 \rangle$ component and a weak $\langle 111 \rangle$ component of the dual $\langle 100 \rangle \langle 111 \rangle$ fibre texture. By wire drawing to heavy reduction, the $\langle 100 \rangle$ texture component decreased to

phase alloy, between which abnormal grain growth can occur provided there is at least one large grain.

Grain mobility anisotropy

Gilman (78) proposed that the elongated grain structure in ODS alloys is a case of abnormal grain growth induced by an orientation-dependent difference in the grain boundary migration rates. This orientation dependence may be such that a faster, unidirectional growth of a few, large grains is facilitated.

Anisotropy of dispersoid distribution

Gessinger (79) drew upon the doped tungsten model of aligned gas bubbles (75) to explain the elongated grain formation in recrystallized, mechanically alloyed ODS alloys. Cairns et al (80) however suggested that the mechanically alloyed ODS superalloy they investigated could be containing arrays of carbonitride particles, resulting from the carbonitride films on the prior particle boundaries, which would restrain lateral grain growth while permitting unidirectional growth.

2.6.3 Techniques of recrystallization

Generally, recrystallization to elongated grain structure in ODS alloy tends to occur suddenly and only at relatively high temperatures. For instance,

reduction in the same direction; however, 100% recrystallization was obtained after an annealing treatment at only 680°C for 1 hr when the bar was cold rolled 87% in a direction transverse to the bar axis. These results have been explained in terms of the effect of textures to be discussed in Section 2.6.4.

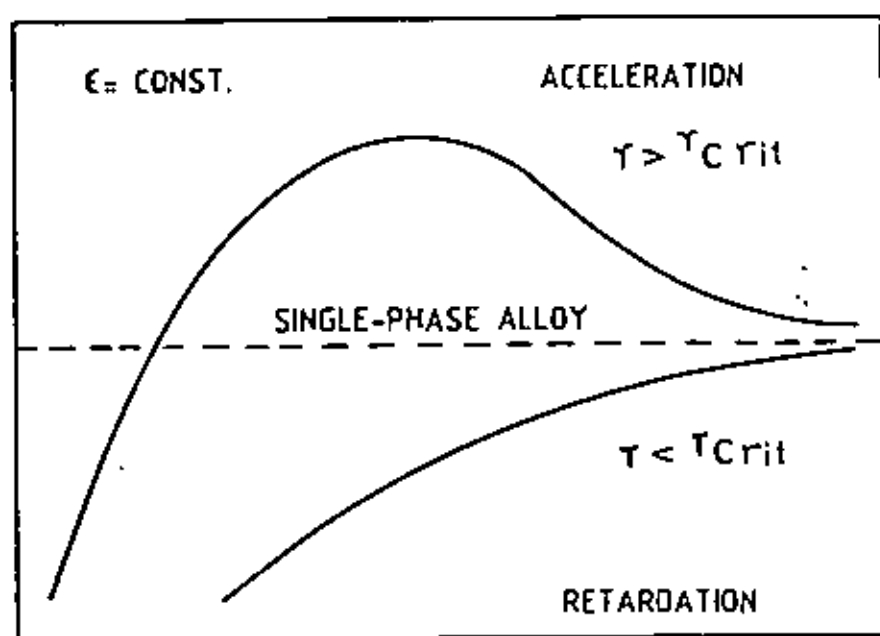
2.6.2 Elongated grain structure in recrystallization

When recrystallization does occur in ODS alloys, it usually results in an elongated grain structure. The highly elongated grain structure of doped tungsten filaments, that is responsible for their non-sag properties, is considered to be a consequence of the restraint to lateral grain growth by stringer-like alignment of potassium bubbles (75). The situation with regard to recrystallization of ODS alloys is not as straightforward because the dispersoid particles are distributed fairly uniformly in the matrix rather than in an aligned fashion. Some important mechanisms proposed for an elongated grain growth in the recrystallization of ODS alloys are briefly described below.

Secondary recrystallization theory

Based on a study of recrystallization in TD Nickel, Petrovic and Ebert (76) proposed that the observed elongated grain structure is in fact a result of secondary recrystallization, preceded by a development of sub-optical ($\sim 1\mu$) grain size which must be the primary recrystallization step. Hillert (77) proposed lower and upper bound limits for the initial grain size in a two

TIME FOR 50 % RECRYSTALLIZATION



INTERPARTICLE SPACING

Fig. 9. SCHEMATIC DEPICTION OF INFLUENCE OF DISPERSED PARTICLES ON RECRYSTALLIZATION DEPENDING ON PARTICLE SIZE, γ (Ref. 7)

a model wherein the second phase particles exert on a migrating boundary a drag force which increases with decreasing particle size and the growth is inhibited at a critical grain diameter at which the driving force for migration of the boundary is balanced by the drag force. In contrast, Doherty and Martin (70) in a study of Al-Cu alloy containing a dispersion of CuAl_2 particles show that both nucleation rate and growth rate of new grains are strongly affected by interparticle spacing. Nucleation of new grains may be retarded or accelerated by particles depending on whether they are relatively fine or coarse. Hornbogen and Köster (71) suggested that very fine particles would retard recrystallization at all interparticle spacings, and relatively coarse particles do so only at smaller interparticle spacings (see Fig.9); the critical size for nucleation enhancement is however directly related to the degree of prior strain in the material.

As indicated by Jones and Hansen (72), the inhibiting effect of a fine dispersion of particles on recrystallization can be linked to the fact that such particles homogenize slip and distribute dislocations more uniformly thus rendering subgrain formation difficult. When subgrains do form, they are stabilized by the particles retarding the nucleation of recrystallization.

The ease of recrystallization in ODS alloys seems to be dependent not only on the amount of deformation but also on the mode of deformation. Doble et al (73,74) found that no recrystallization occurred by annealing at about 1315°C for one hour an as-extruded TDNickel bar that was cold rolled 87% in a direction parallel to the bar axis, or when it was swaged with 95%

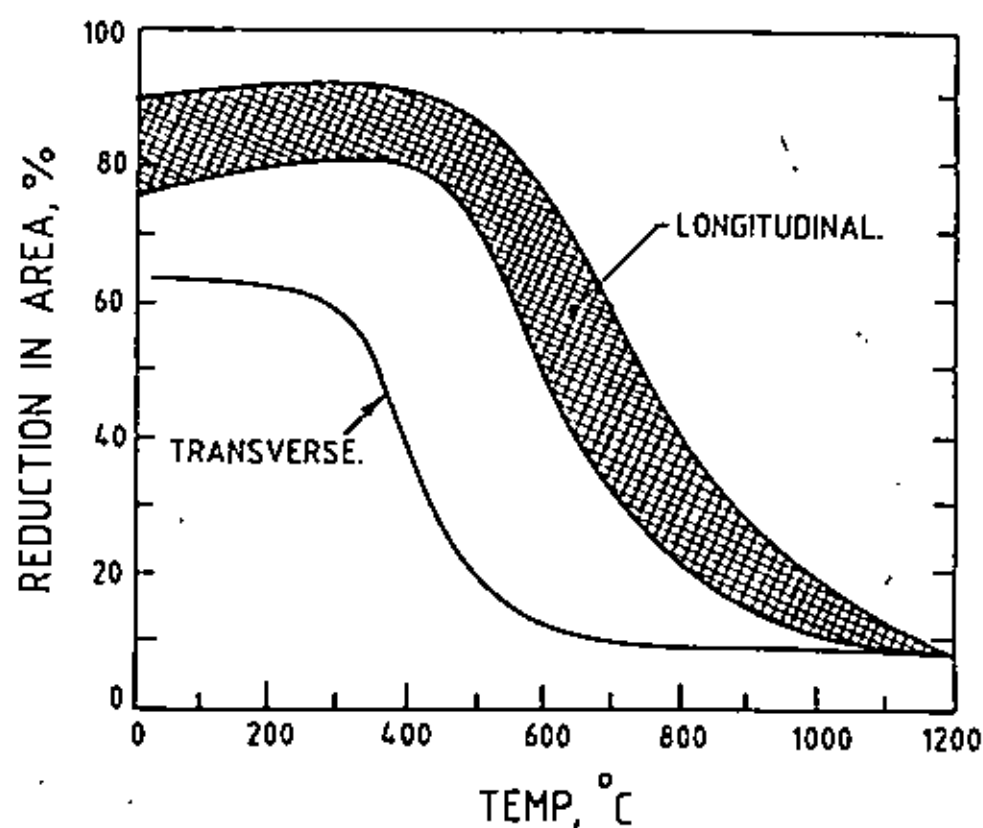


Fig. 8. EFFECT OF TEMPERATURE ON THE TENSILE DUCTILITY OF TD NICKEL BAR. (Ref: 67)

of the matrix, (ii) occurrence of short range order and (iii) a possible lowering of the volume self-diffusivity of the matrix. In a study of different compositions of commercial ODS nickel base superalloys, Olawummi Ajaja et al (67) conclude that the applied stress sensitivity to intermediate temperature ($T \approx 760^\circ\text{C}$), steady state creep rate decreases with increasing solid solution strengthening.

2.5 DUCTILITY AND FRACTURE

The three stages, namely, void nucleation, void growth and void coalescence that constitute total plastic strain leading to fracture in a ductile metal are also applicable to dispersion strengthened materials. These aspects of ductile fracture in two-phase alloys are reviewed by Rosenfield (68).

The marked drop in tensile ductility of TD Nickel at elevated temperatures above $0.3T_m$ (67), as illustrated in Fig.8, is a characteristic feature of many other ODS alloys too. This transition is associated with a change in fracture mode from transgranular to intergranular which is explained by the dominance of grain boundary sliding with increasing temperature leading to grain boundary cavitation.

2.6 RECRYSTALLIZATION AND TEXTURES

2.6.1 Resistance to recrystallization

The unique feature of ODS alloys is their resistance to recrystallization upto a fairly high fraction of their melting point. Zener (69) first proposed

Bhat and Arunachalam (63) attribute the high n and high Q_c values in ODS alloys to an athermal barrier offered by the particles to dislocation motion. They suggest that incorporation of a temperature-dependent back stress in the power law creep equation in the following manner brings out the true values of activation energy and stress exponent:

$$Q_{\text{real}} = Q_{\text{apparent}} + n \frac{RT^2}{G} \frac{dG}{dT} + n \frac{RT^2}{\tau - \tau_b} \frac{d\tau_b}{dT} \quad (\text{eqn. 12})$$

where τ_b is the back stress.

This modification brought down the Q_c and n values of TD Nickel and Inconel MA753 close to normal values of single phase materials.

The back stress may be looked upon as a threshold stress below which creep does not occur. A threshold stress for creep has been observed, for example, by Whittenberger (64,65) in thin TDNiCr sheet and is generally associated with diffusional creep (64). Lund and Nix (59) suggest that the threshold stress could be the Orowan particle bypass stress and show that the creep stress of single crystal TDNiCr can simply be described by the additive rule of the sum of the creep stress of particle-free matrix and the Orowan stress.

Alloying of pure metal matrix in ODS systems to form a matrix of solid solution further decreases the high temperature steady state creep rate. Wilcox and Clauer (66) attribute this to (i) a decrease in the stacking fault energy

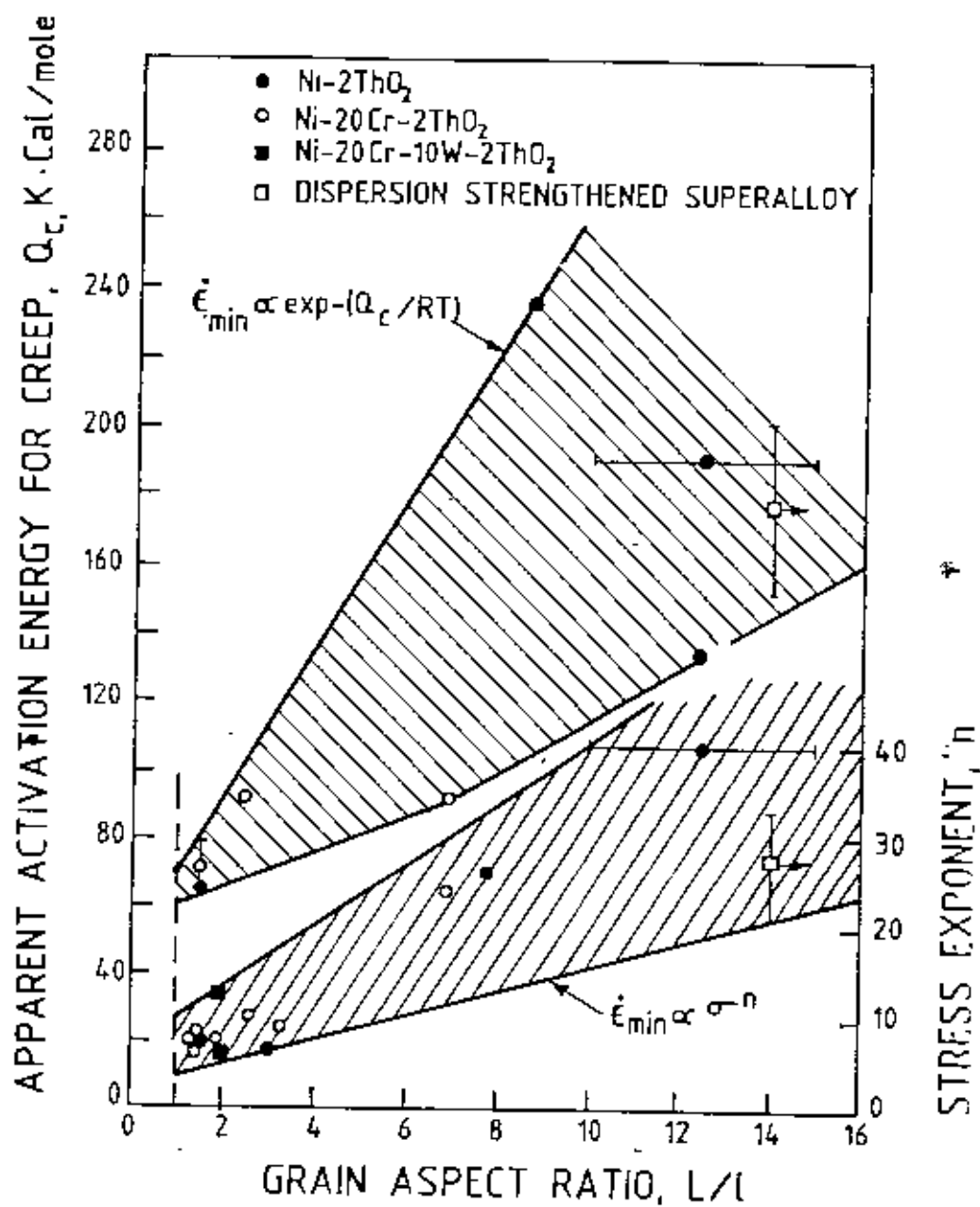


Fig. 7. APPARENT CREEP ACTIVATION ENERGY, Q_c , AND CREEP STRESS EXPONENT, n , OF ODS NICKEL BASE ALLOY AS A FUNCTION OF GRAIN ASPECT RATIO. (Ref: 67)

Q_c and n are variously reported and generally very high. For instance, different workers reported (55,56) creep activation energy values between 150 to 400 Kcal/mole for SAP alloys, whereas Q_c is about 34 Kcal/mole for pure aluminium which is nearly the activation energy for self-diffusion (Q_{SD}) of aluminium. Wilcox and Clauer (34) determined an activation energy of 190 Kcal/mole for TD Nickel against Q_{SD} of about 65 Kcal/mole for pure nickel. In contrast, in another study, Wilcox and Clauer (57) found an activation energy of only 64 Kcal/mole for TD Nickel. Similarly, stress exponents ranging from 6 to 40 were determined for TD Nickel (34,58). Lund and Nix (59) observed the creep stress exponent to vary widely in the range of 9 to 75 for Ni-20Cr-2ThO₂ tested at temperatures ranging from 0.55 - 0.95 T_m .

Wilcox and Clauer (60) analysed these variously reported values of Q_c and n for different ODS nickel alloys. They suggest the generalized trend that $Q_c \approx Q_{SD}$ and $n \approx 6$ to 7 when the grains are equiaxed, but Q_c and n progressively become high as the GAR increases, as illustrated in Fig.7 (67). Lund and Nix (61) suggest that incorporation of temperature variation of shear modulus in the power law creep equation brings down the apparently high Q_c (Q_{app}) close to Q_{SD} , and apply this idea successfully to TD Nickel, bringing down Q_{app} of 190 Kcal to about 60 Kcal/mole. Malu and Tien (62) show that application of this procedure did not work well for the lower temperature creep regime in Inconel MA753, an ODS, iron-base superalloy.

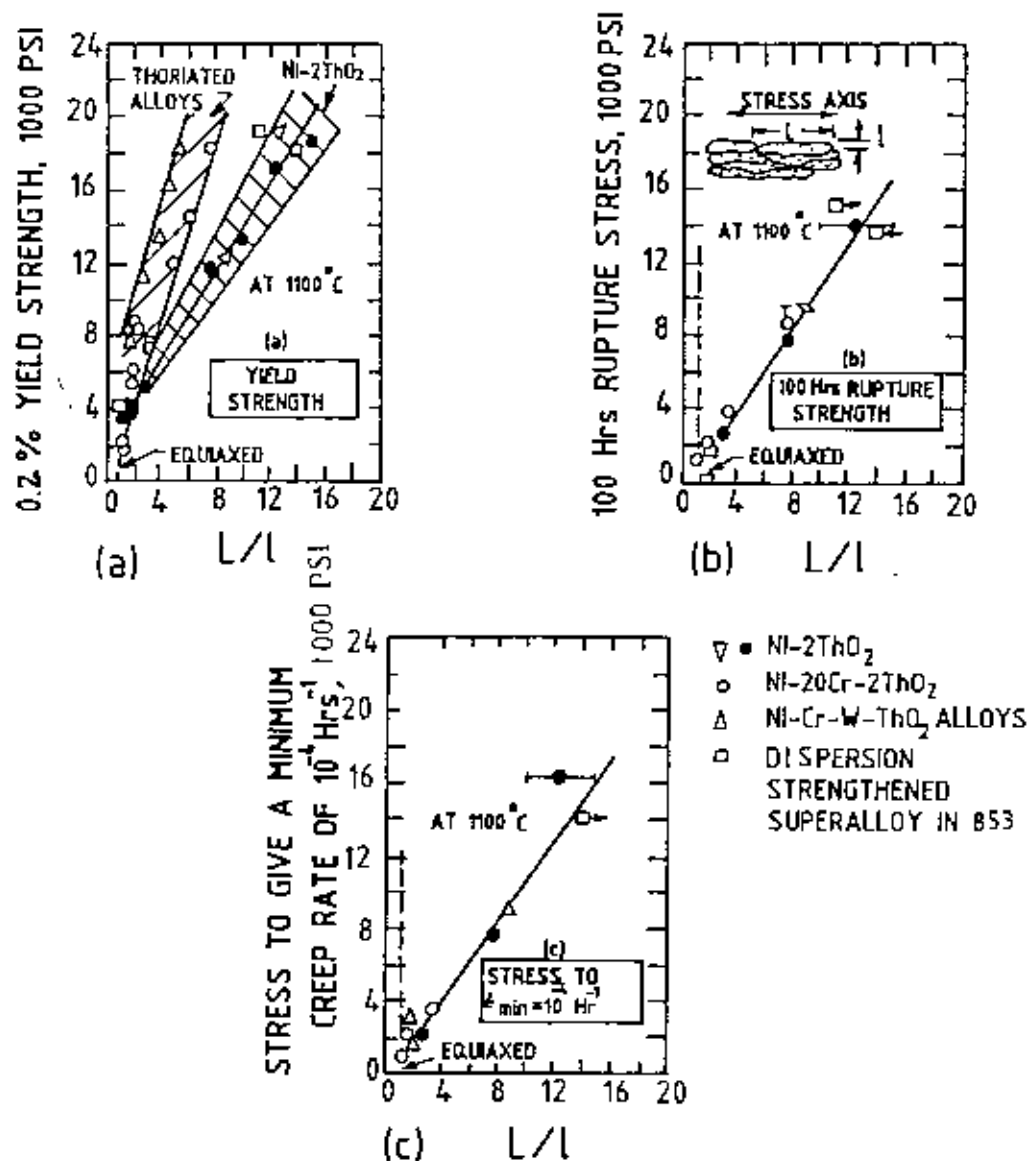


Fig. 6. EFFECT OF INCREASING GRAIN ASPECT RATIO (L/l) ON SOME MECHANICAL PROPERTIES OF ODS-NICKEL BASE SUPERALLOYS. (Ref: 57).

For the marked drop in the work-hardening rate in ODS alloys at high temperatures, Gould, Hirsch and Humphreys (53) proposed that the Orowan loops disappear by climb over the particles through dislocation pipe diffusion of vacancies thus diminishing the chances of formation of both Orowan loops and prismatic loops.

2.4.2 Creep

The generally superior creep strength even at temperatures close to $0.8T_m$ is one of the most important properties of ODS alloys, especially for advanced engineering applications. For example, TD Nickel_x supports a stress of 19 KSI for 1000 hr rupture life against a stress of 1 KSI for the same life in the case of pure nickel. Creep of ODS alloys can be best described by the empirical equation (54):

$$\dot{\gamma}_s = A e^{-\frac{Q_c}{RT}} \left(\frac{\tau}{G}\right)^n \quad (\text{eqn. 11})$$

where A = a pre-exponential factor .

$\dot{\gamma}_s$ = steady state creep strain rate

Q_c = creep activation energy

T = creep temperature (Kelvin)

n = stress exponent

High ' Q_c ' and high 'n' in ODS alloys

Compared to most other single phase metals and alloys, the high temperature creep behaviour of ODS alloys is rather unusual in that the values of

ckel were analysed by Wilcox and Clauer (51), who then rationalised the conflicting results by proposing a modified Hall-Petch relation based on the Grain Aspect Ratio (GAR) in the following form:

$$\tau = \tau_e + K \left(\frac{L}{l} - 1 \right) \quad (\text{eqn. 10})$$

where τ_e = flow stress when $\frac{L}{l} = 1$

K = GAR coefficient

$\frac{L}{l}$ = Grain Aspect Ratio, where L is the grain length and l is the grain width

This relation could explain the different results at the same temperature of 1100°C of Ni-ThO₂, Ni-Cr-ThO₂, Ni-Cr-W-ThO₂ as a difference arising out of their varying GAR, as illustrated in Fig.6 (51). This shows that the variously reported values of 1100°C yield strength as well as 100 hr creep rupture strength linearly increased, within a scatter band, as a function of GAR (Fig.6a & 6b); similar trend is also seen (Fig.6c) to be valid for the stress to give creep strain rate of 10⁻⁴ hr⁻¹. Fraser and Evans (52) attribute the strength of TD Nickel at high temperatures (above 0.5 T_m) to the development of fibrous grain structure and the consequent inhibition of grain boundary sliding which they consider to be the dominant mechanism of yielding at high temperature. Wilcox and Clauer (51) also interpret the effect of high GAR in ODS alloys as one of suppressing boundary sliding at high GAR where most of the boundaries are oriented parallel to the stress axis, resulting, on an average, in a low resolved shear stress on the boundaries and thus minimising the overall amount of sliding.

2.3.3 Third Stage

This stage begins with the transition from uniform plastic strain to localised necking and shows lower work-hardening rate than in the second stage. Brown and Stobbs (48) attribute the third stage to an image stress which is a uniform shear stress in the material that maintains a stress-free external surface. The image stress may be thought of as arising from an external distribution of image particles and is considered (48) to be a linear function of the shear strain. The image stress being small compared to the back stress that is responsible for the initial linear hardening stage, may be the reason for the similarity of the third stage with the matrix behaviour.

2.4 DEFORMATION BEHAVIOUR AT ELEVATED TEMPERATURES

2.4.1 Yield Stress

The unique feature commonly observed in ODS alloys is the retention of a large fraction (almost half) of their ambient temperature yield strength even at temperatures close to melting point. The eventual fall in yield strength in the high temperature range is generally attributed (49,50) to the climb of dislocations around the particles.

The validity of the Hall-petch relation for grain and cell size strengthening in TD Nickel at room temperature (37) could not be extended to high temperatures (around 1100°C) when the results of different workers on TDNi-

$$\tau_h = 3 f^{3/2} \frac{\bar{n} G b}{\tau_s} \quad (\text{eqn. 8})$$

where, f is the volume fraction of the dispersoids. When $\frac{\bar{n} G b}{\tau_s}$ reaches a critical value τ_c , the flow stress increment, τ_h will not increase further. τ_c was assumed to be the critical stress for particle shear and estimated to be about 0.1G.

2.3.2 Second stage

The second stage is characterised by a plastic relaxation of the back stress through punching out of the prismatic dislocation loops at the particle-matrix interface. Ashby (43) gave for the second stage the following parabolic relation:

$$\tau_h = 0.24 \sqrt{\frac{b f \nu}{2 \tau_s}} \quad (\text{eqn. 9})$$

Prismatic loops were observed in worked Cu-SiO₂ by different workers (44,45). Humphreys and Hirsch (46) proposed that the second stage hardening is primarily due to prismatic loops by cross slip, with negligible contribution from the Orowan loops; they found support for this model in experiments on dispersion hardened copper. Cocks (47) argued that reasonable agreement of his experimental results on deformed Cu-SiO₂ was possible only when the theoretical estimates of Ashby's (43) and Humphreys and Hirsch's (46) models were added, which suggests that both the mechanisms could be operating.

These stages are:

- i) an initial linear stage where strength increases linearly with plastic strain as a result of build-up of dislocation loops around particles;
- ii) a second, parabolic stage where prismatic loops formed by cross slip of Orowan loops or punching from particle-matrix interface cause hardening through interaction with glide dislocations resulting in tangles and forests;
- iii) an essentially linear, third stage leading to failure, which is controlled by matrix features.

These three stages have been observed, for instance, in Cu-SiO_2 (40).

Several workers proposed a variety of mechanisms to account for the work hardening behaviour of ODS alloys, which have been reviewed well by Kothari (41). The main mechanisms and models will now be briefly described.

2.3.1 First stage

The model proposed by Fisher, Hart and Pry (42) is often cited and is one of the earliest references on the theory of work hardening of dispersion strengthened alloys. They postulated that the residual Orowan loops around the particle exert a back stress on the dislocation sources necessitating a strain-induced increment to the flow stress and the back stress is given by:

stress, to fully account for the flow stress of cold rolled Ni-Cr-ThO₂. They have also established that the threshold stress below which the strain rate sensitivity of recrystallized Ni-1.14 ThO₂ is zero corresponds to the Orowan stress.

In another study (38) of thermomechanical processing, it was found that the decreasing cell size of dislocation substructure obtained through increasing wire drawing reductions on TD Nickel and TDNiCr bars followed the Hall-Petch type relation for the yield strength of these alloys at room temperature. Rasmussen and Grant (39) attributed the observed strengthening in cold worked ODS alloys to a decrease in the apparent interparticle spacing by Orowan loops surrounding the particles.

2.3 WORK-HARDENING

When an ODS alloy is progressively deformed beyond the yield stress, work hardening occurs which is primarily related to the increasing number of Orowan loops around the particles with increasing deformation. The average number of loops per particle, $\bar{n}$, is given by $\frac{2\gamma_s\gamma}{b}$ where γ is the plastic shear strain. These dislocations, known as the geometrically necessary dislocations, are required to maintain the compatibility of the macroscopically homogeneous deformation of two-phase alloys. As $\bar{n}$ increases with deformation, different relaxation mechanisms occur leading to the well-known, three stages of work hardening.

For example, Raymond and Neumann (35) found that the substructure was retained in a Ni-20Cr-2ThO₂ alloy even after exposures upto 1510K. Particles anchor the dislocations and stabilize the substructure which influences the deformation behaviour. Because particles are not directly responsible here, the strengthening is said to result from indirect particle-dislocation interactions.

Viewed from this background, ODS alloys in the fabricated form are already substructure-strengthened. Depending on the application and the material, they are used in this as-received condition itself or after a recrystallization treatment. Wilcox and Jaffee (29) found that the yield strength of an as-extruded TD Nickel alloy is substantially higher than that of the recrystallized TD Nickel at room as well as elevated temperatures and they attribute this difference to a contribution from the stored energy of deformation:

thus it is stated that (29),

$$\tau = \tau_m + \tau_p + \tau_{se} \quad (\text{eqn. 7})$$

where τ_{se} = shear strength contribution from stored energy of deformation. Preston and Grant (36) also proposed an empirical relationship between yield strength and stored energy of working.

Arunachalam and Lipsitt (37) in a study of stress relaxation measurements in thoriated nickel and nickel-chromium alloys suggest that contribution from substructure strengthening is necessary, besides the matrix flow stress and Orowan

bowing mechanism than with particle shear mechanism of Ansell. So also, Wilcox and Jaffee (29), who studied the yield stress of recrystallized TD Nickel over a wide range of temperatures, found agreement with Orowan bowing model than with particle shear model. Similar disagreement with particle shear mechanism was recorded by Sastry and Vasu (30) in Ni-ZrO₂.

Cross Slip

Ashby (31) as well as some others (32) proposed that the screw components of the particle-bowed dislocations may bypass the particles by cross slip. Cross slip has been suggested to account for low temperature ($T < 0.5T_m$) tensile and creep deformation of Ni-ThO₂ (33,34). In any case, since cross slip is related to the stacking fault energy which generally decreases on alloying, a dispersion hardened matrix that is solid solution strengthened is less likely to show cross slip than a pure metal matrix.

2.2.2 Indirect particle-dislocation interactions

Fabrication of oxide dispersion strengthened alloys usually involves extensive hot/warm working such as extrusion or rolling as well as cold working with intermittent anneals. These processes lead to consolidation of the powder to theoretical densities and also produce some deformation-induced substructures which are stable upto very high temperatures, thereby increasing the resistance to deformation not only at ambient temperatures but also at elevated temperatures.

it forms a semicircle of diameter approximately given by λ . As the dislocation segments on opposite sides of the particle move towards each other and annihilate, a dislocation loop (commonly known as Orowan loop) is left around the particle.

τ_y , the flow stress can then be expressed as a sum of τ_m , the matrix flow stress, and τ_p , the athermal, particle bypassing stress given by $\frac{2\Gamma}{b\lambda}$ (τ_p , unlike τ_m , is not significantly influenced by temperature):

$$\begin{aligned} \tau_y &= \tau_m + \tau_p \\ \text{since } \tau_p &= \frac{1}{2} G b^2 \end{aligned} \quad (\text{eqn. 4})$$

using eqn. 2, we can express eqn. 4 in the well-known form

$$\tau_y = \tau_m + \frac{Gb}{\lambda} \quad (\text{eqn. 5})$$

Kelly and Nicholson (25), and Ashby (26) refined the expression for Orowan stress increment by taking into account the contributions from edge and screw dislocations to the line tension and the dislocation dipole effects. It may be mentioned that Ashby (26) takes λ , the effective interparticle spacing, as

$$\lambda = \lambda_s - 2r_s \quad (\text{eqn. 6})$$

where

r_s = mean planar particle radius

λ_s = mean, planar centre-to-centre particle spacing.

Chaturvedi et al (27) found agreement of flow stress behaviour with Orowan bowing mechanism in a study of Co-Ni-Cr-Ti superalloy which contained overaged particles of γ' (Ni_3Ti). They also observed, through electron microscopy, only Orowan loops around these particles. Ashall and Evans (28) observed much better agreement of the yield stress results of Ni-ThO₂ with Orowan

and the elemental powder fragments are virtually absent. The finer, composite particles probably are fragments of similarly structured coarser powders. The elemental flake-like particles have mostly been captured by welding to other particles.

- iv) a random welding orientation is then generated wherein the weld seams of all the powder fractions become convoluted, as equiaxed powders cold weld together without any particular preference to the welding orientation.
- v) the final stage of the mechanical alloying occurs when a steady state is reached for the particle size distribution. The internal structure of the composite particles is refined to a sub-optical level. A saturation level of hardness of the particles and a narrow particle size distribution are the characteristic features in the final stage.

For mechanical alloying to be facilitated in the aforesaid manner, it is generally necessary that one of the constituents in the starting blend must be ductile enough to act as a 'cement' binding others during the process (116).

3.9 AREAS OF QUESTION AND SCOPE OF THE PRESENT WORK

While mechanical alloying has been exploited for producing a variety of novel composites of materials, there have been few investigations into the understanding of the process itself. Several questions relating to the process

therefore remain to be answered satisfactorily. An important question is whether mechanical alloying leads to homogeneous, true solid solutions. Benjamin (119) does consider this aspect and takes the view that alloying is deemed to be complete when the individual lamellae of the alloying elements are no longer seen in the optical microscope, at which point, he observes, the mechanically alloyed nickel and chromium powders had the same low level of 'magnetic response' as wrought nickel-chromium alloy produced by milling and working. According to Benjamin, the latter observation of low magnetic response indicates the formation of true solid solution rather than of a finely interdispersed mechanical mixture. This conclusion has been questioned by Wassel et al (130) as being based on inadequate evidence. Furthermore, White and Nix (131) have reached a somewhat different conclusion in their X ray diffraction study on Nb_3Sn compound formation by mechanical alloying, wherein they found that, although the individual phases could not be optically resolved, the milled powder was observed to be only an intimate mechanical mixture of the two elements. Wassel et al (131) on the same question conclude that there is only a limited homogeneity of alloying. This has been examined in the present work using a variety of analytical techniques including electron probe microanalysis and Scanning Auger Microprobe analysis.

Benjamin's results of 'magnetic response' are not spelt out clearly in his paper (119). The magnetic transformation in the alloy of our study here makes it amenable for a systematic investigation of this property in relation to mechanical alloying. Accordingly, in our investigations, magnetic coercivity measurements have been made on attritor milled powders and correlated with

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mechanical alloying with meaningful interpretations.

Inadequate homogeneity of alloying observed by Wassel et al (130) or White and Nix (131) may possibly be the result of a choice of incorrect operational parameters used for the mechanical alloying process. This takes us to a more general question of practical importance which has apparently received little scientific attention: are there any optimum values for the operational parameters to be applied for successful mechanical alloying? What attritor speed, for example, should be used for attritor milling of ODS alloys and for how long should the milling be done? What size of grinding balls are best for the purpose? Are there any threshold values for them? This dissertation considers these questions in detail by a systematic study involving variations in milling parameters using a specially designed attritor and a 'performance index' that quantifies the effectiveness of alloying.

If mechanical alloying is true alloying of the solute, what atomic level mechanisms are operative to bring about such alloying, and how do they relate to the mechanical energy input of the attritor? The mechanism suggested by Benjamin (123) which is more a phenomenological description of five stages in the process, occurring as a function of milling time, does not provide much insight into atomic level mechanisms that must be responsible for the alloying process. Surprisingly, there appears to be no other reported investigation into this aspect. The work carried out here therefore includes an attempt to understand the mechanism of alloying from a microstructural perspective, leading to an enhanced diffusivity mechanism as well as an 'energy-balance' model' based on some of the experimental results obtained.

CHAPTER IV

EXPERIMENTAL

CHAPTER IV

EXPERIMENTAL

4.1 DESIGN FEATURES OF THE EXPERIMENTAL ATTRITOR

This research work is directed towards understanding and optimising mechanical alloying in an attritor mill with reference to one typical alloy system, namely 2 volume % thoria dispersed in nickel-20% chromium alloy. It is therefore essential that an attritor be specially designed to meet the planned research requirements. Based on the limited information and clues available from Benjamin's (116,117) and Szegvari's (125) patents^{*}, and Chemical Engineering standard design principles of mixing agitators (132), the author has designed a laboratory model attritor for mechanical alloying.

Fig.15a shows the main design features with its list of parts as in Table 2 and Figs.15b and 15c show the design details of other main assembly parts. This attritor has the following features. A cylindrical, 18/8 stainless steel vessel was cast and machined to final dimensions of 170mm internal dia, 5mm wall thickness, 240mm flange and 30mm bottom radius all around inside and 180mm inside height. Such a large radius at the vessel bottom ensures that powder does not remain in pockets in the far-flung bottom corners as might

^{*}Being patents, full details of the attritor design are not available.

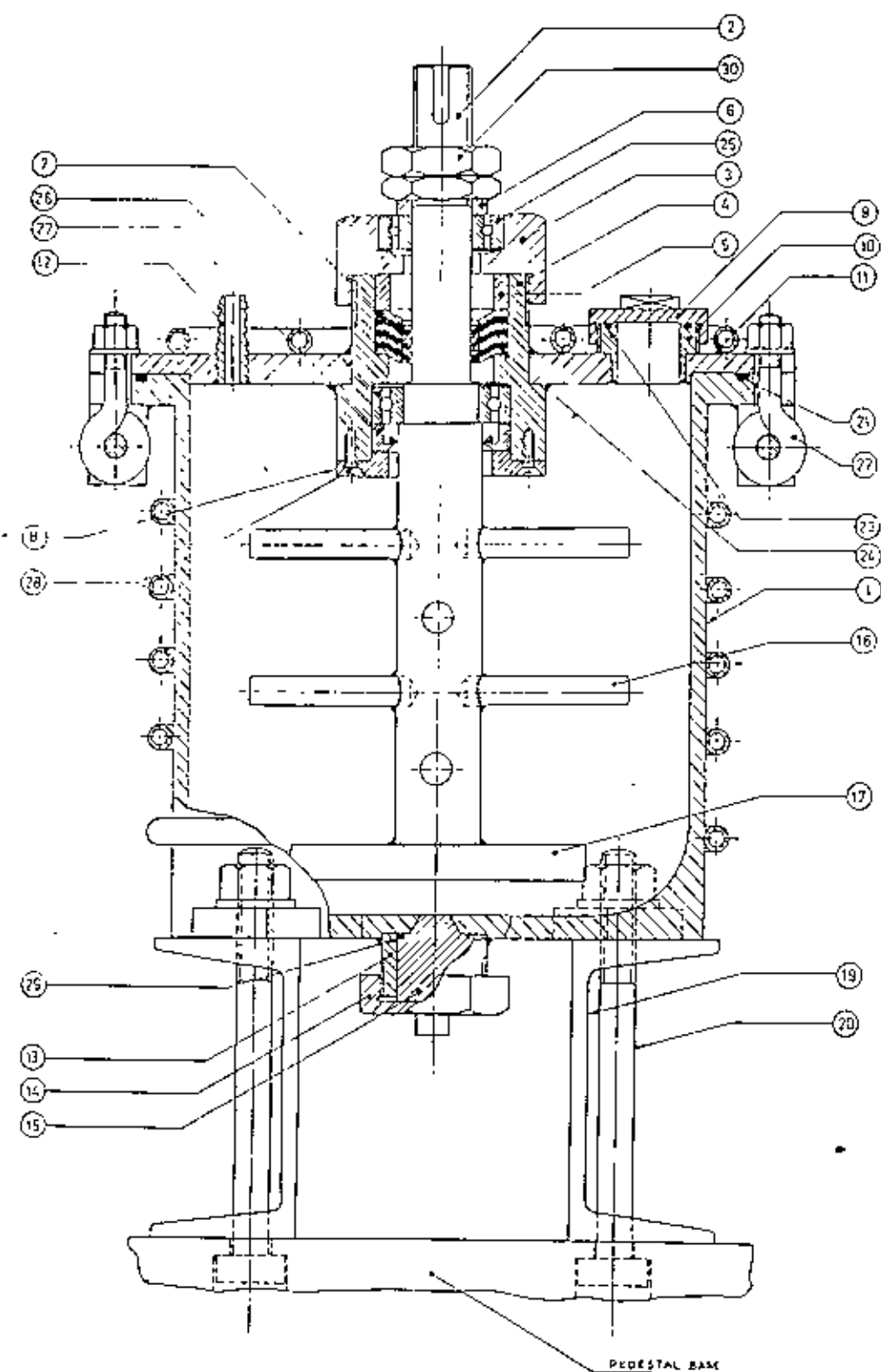


FIG 15 a DESIGN OF THE EXPERIMENTAL ATTRITOR
(ASSEMBLY VIEW)

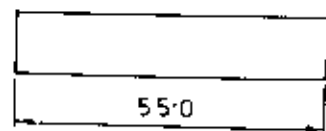
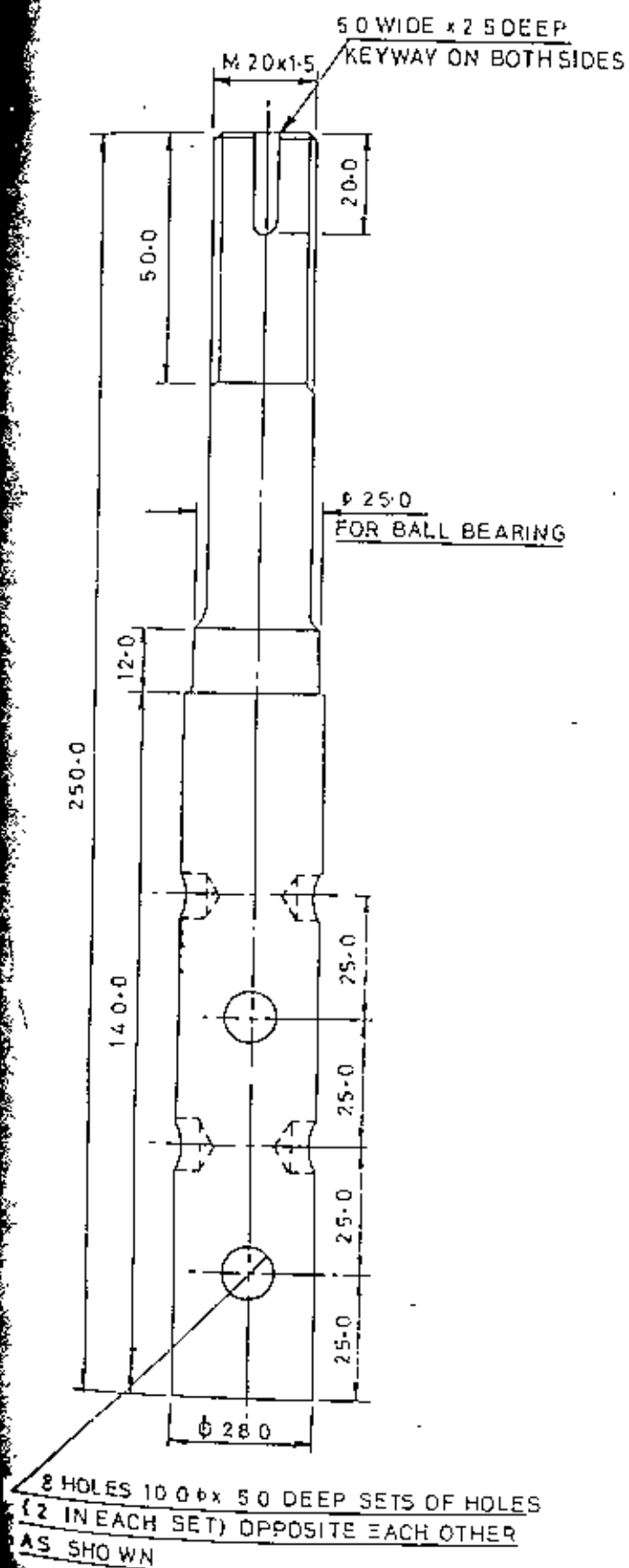
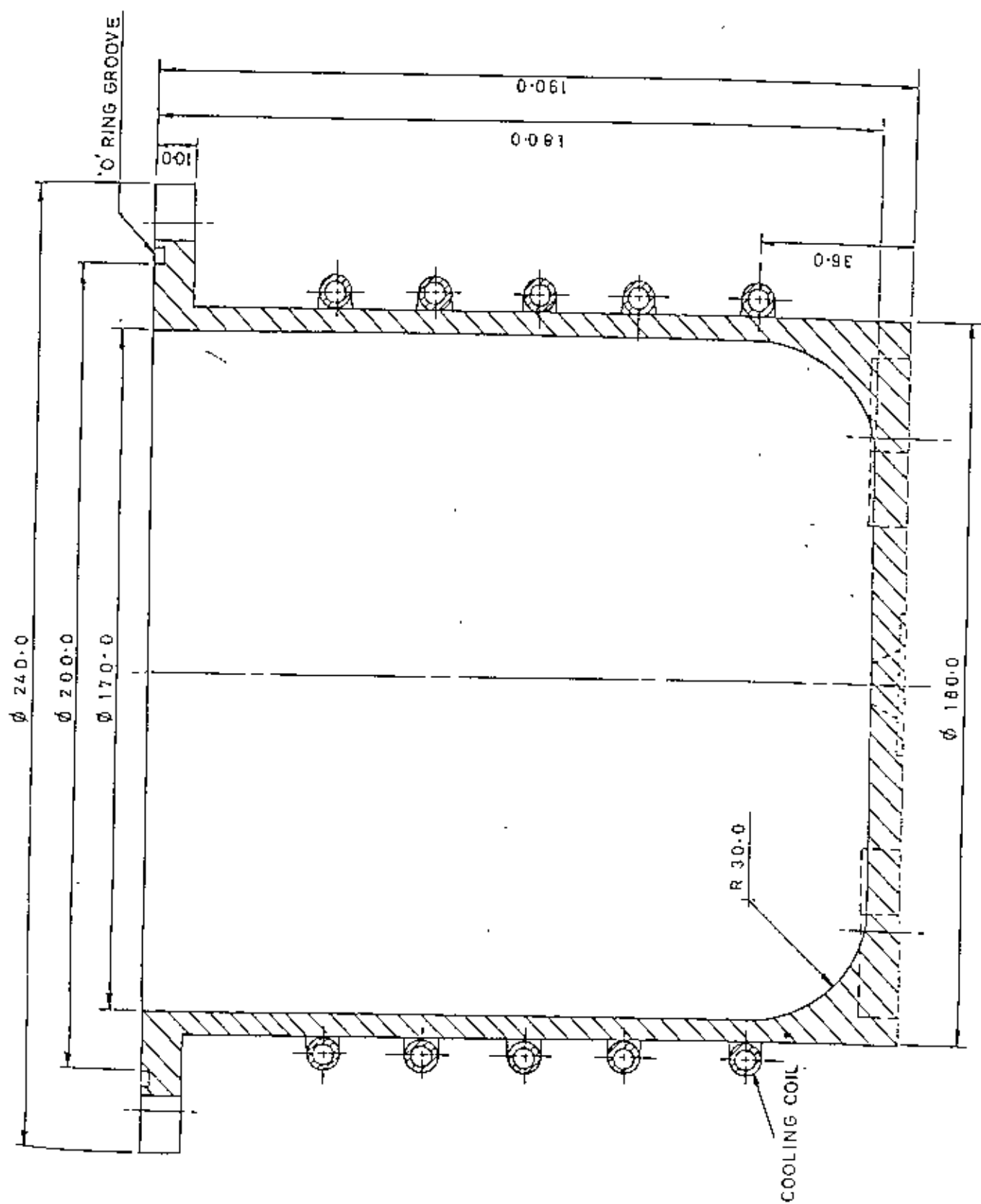


FIG 15 b DETAILS OF ATTRITOR SHAFT AND IMPELLERS



otherwise happen in a vessel with a sharp radius at the bottom. Copper tubing of 6mm internal diameter with 1mm wall thickness is brazed to the vessel in a spiral fashion to facilitate water cooling (attritor milling in the absence of water cooling is possible but the output or yield of the alloyed powder becomes too small because of excessive welding of the powder on to the balls).

To facilitate periodic removal of samples during milling, the vessel is provided with a 10mm diameter hole at the bottom offset from centre and to the hole is welded a threaded stainless steel bush into which an 'O' ring-sealed plug can be screwed to make it gas-tight. The vessel flange is grooved to seat an 'O' ring against which the 6mm thick top lid can be screwed to a gas-tight condition by eight perimetric bolts. Welded to the top lid in its central hole, is a water-cooled bush housing a ball bearing assembly with a set of Wilson seals which ensure gas tightness of the 30mm dia shaft passing through the housing. The Wilson seal arrangement consists of 4 alternate layers of thin, mild steel washers and neoprene gaskets hugging the shaft with sliding clearance. The seal assembly can be tightened by means of a hexagonal faced, threaded cap. The bottom ball bearing which comes below the top lid is seated in an oil-seal to protect the bearing from getting clogged with flying powder particles. The Wilson seal assembly comes above the top lid and below the top bearing. The shaft is thus supported above and below the top lid with two ball bearings, providing greater rigidity and support to the rotating shaft which has to remain freely hanging inside the vessel. The attritor shaft at its top is connected to the drive shaft by means of a modified universal coupling

that can be quickly disconnected for removing the top lid as and when required. The drive is provided from the vertical spindle of a variable speed drilling machine whose drill chuck has been removed to facilitate coupling of the spindle to the attritor shaft. To the sturdy base-frame of the drilling machine, the attritor is firmly bolted by means of two mild steel channel supports on the base-frame.

The impellers are fixed into the blind holes of the shaft by threaded ends of the impellers. By this arrangement, different types of impellers can be fixed and changed with ease. The overall thickness of the impeller is chosen to be in excess of the maximum size of the balls that may be used. The impeller rod diameter is thus fixed at 12mm. The length of the impeller arm in the ideal case can go as far as the vessel diameter would permit. However, with such lengthy impellers the possible misalignments in shaft assembly and eventual play of the shaft and the bearings can result in the impellers causing excessive loads on the drive and erosion of the vessel wall during rotation. The length is therefore maintained such that the clearance between it and the wall is more than two ball diameters to permit free passage of balls without causing blockade of the motion of balls. The bottom-most impeller, which may be called as 'scraper', has a rectangular cross section and is welded to the bottom face of the shaft. The distance of the scraper from the bottom of the vessel is such as to allow a clearance of a little over two ball diameters so that the balls are not blocked due to inadequate clearance. The top lid has a side hole with a bush welded to it which enables charging of the powder and the balls; the screw top of this bush can be closed gas tight by means of an O-ring located on the bush.

The 1-HP AC induction motor driving the pulley system of the machine is connected to the power supply via motor starter and a readily available 30 hours timer. The top lid has provision for gas inlet and gas outlet. A gas bubbler with a stop-cock is attached to the gas outlet nipple of the top lid of the attritor. The bubbler indicates, as and when desired, the presence of a positive pressure of argon which is found to be desirable to avoid oxidation of the elemental chromium powder in the charge. After flushing out air with argon flow, the stop-cock is closed to maintain a positive pressure of argon inside the vessel; a continuous flow of argon is not required. A general view of the apparatus is shown in Fig.16.

4.2 PREPARATION OF Ni-20Cr-2ThO₂

All the mechanical alloying experiments described in this study are aimed at the nominal composition of 20% chromium in solid solution in nickel with a dispersion of 2% thoria of less than 500Å average particle size. For this purpose commercially available nickel and chromium powders were used while thoria was prepared in the laboratory from a thorium salt. The details of preparation of thoria are given in Appendix 1.

4.2.1 Starting powder characteristics

For most of the experiments, nickel powder, supplied by M/s. International Nickel Co., U.K. was used. It has a purity of ~ 99.8%. Some of the

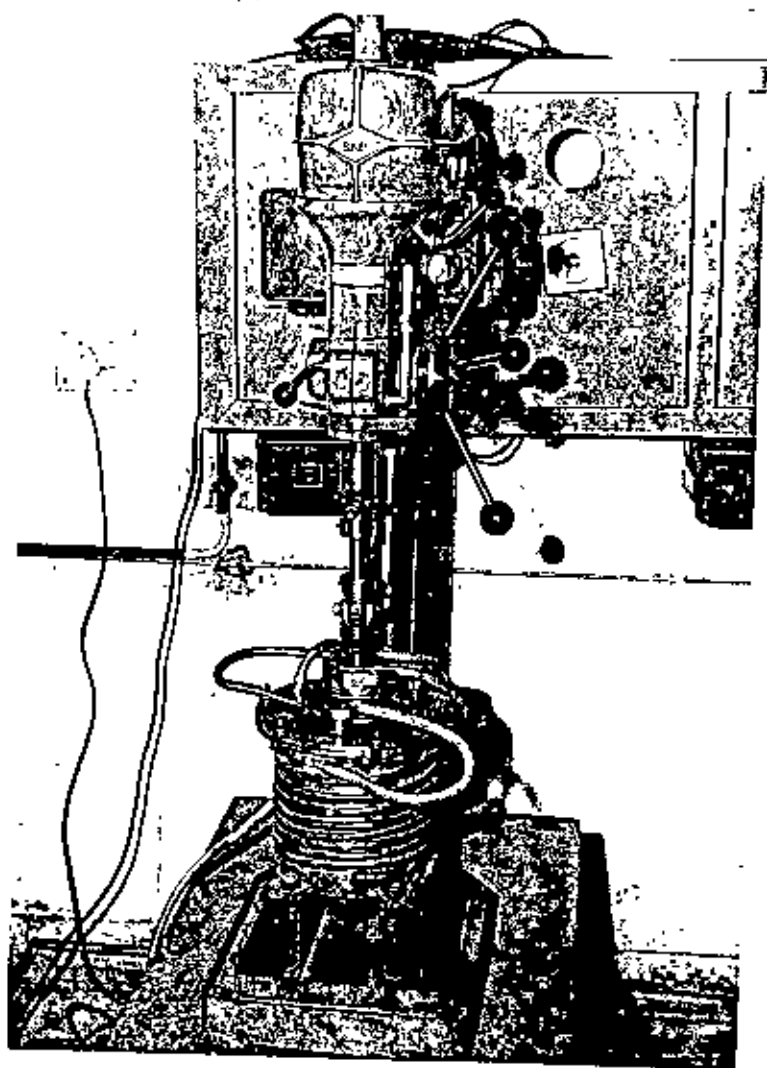
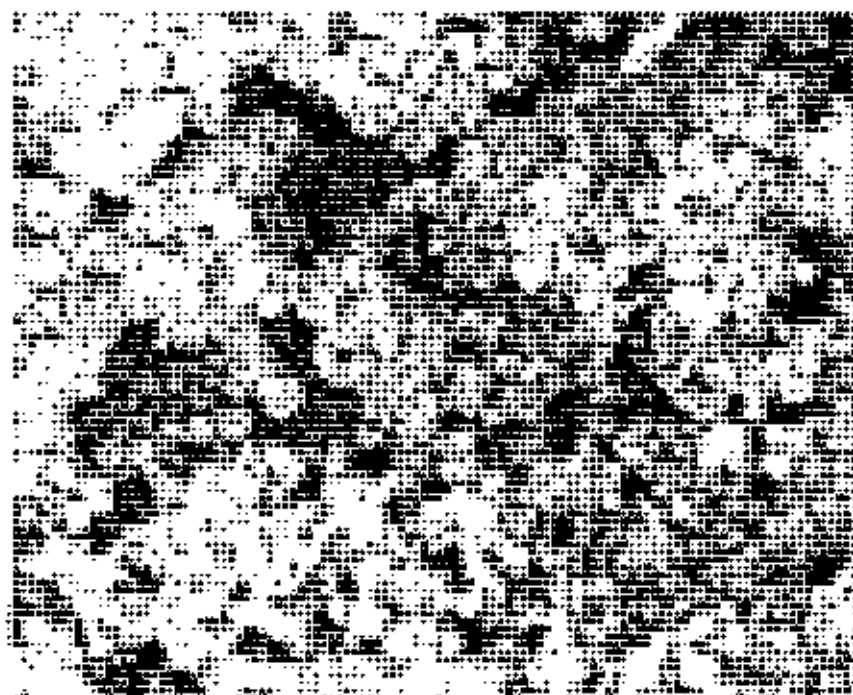


FIG 16 GENERAL VIEW OF THE ASSEMBLED ATTRITOR

impurity levels that could be determined in the laboratory are shown in Table 3. Its average particle size as determined in a Fisher sub-sieve sizer is 8 microns. The powder is spongy and spherical in appearance as shown in the Scanning electron micrograph in Fig.17a. Chromium powder was supplied by M/s. Goodfellow Metals Corp., USA. It is 99.5% pure and -200 Mesh. Its average particle size as determined by Fisher sub-sieve sizer is 45 microns. The powder particles are irregular and blocky in appearance as shown in scanning electron micrograph in Fig.17b. The impurity levels that could be determined in the laboratory are included in Table 3. In the experiments involving variations in starting particle size of nickel and chromium, powders of approximately similar purities but of different average particle size were used, as described in detail in Chapter V.

To determine the mean particle size of thorium powder which would be in the submicron range, X-ray diffraction line broadening technique described by Fergusson (133) was preferred to transmission electron microscopy as in the latter such fine particles may show up as agglomerated polymorphs, masking their true particle size. Furthermore X-ray diffraction line broadening method is a convenient technique recommended for ultrafine particle size measurement (134). A sample of the thorium powder was subjected to X-ray diffraction at 20 KV/30 mA with Cu K_{α} radiation in a Phillips X-ray diffractometer and the (111), (200), (220), (311) peaks were recorded. The instrumental broadening was obtained by using a silicon standard. The details of these results are tabulated in Table 4 from which it is seen that the average particle size of the



a NICKEL POWDER,

500 x



b CHROMIUM POWDER,

500 x

FIG 17 SCANNING ELECTRON MICROGRAPHS OF
NICKEL AND CHROMIUM POWDERS

thoria prepared may be taken as $330\text{\AA}$.

4.2.2 Charge preparation

Unless otherwise stated, all experiments were done with 305gm charge (254gm Ni, 60 gm Cr, 6gm ThO_2) and 6mm diameter ball-bearing quality steel balls (made out of SAE 52100 grade steel, and heat treated to a Rockwell-C hardness of 60-65). Samples were drawn at desired points of milling time through the sample discharge hole provided at the bottom of the attritor; appropriate number of balls were also removed along with powder sample to maintain the balls-to-powder ratio. In all the experiments, the powder constituents prior to charging into the attritor were pre-blended for one hour in a laboratory blender to obtain a well-distributed mixture of nickel, Chromium and thoria. The homogeneity of mixture was found to be satisfactory as revealed by the chemical analysis of three samples randomly drawn from different portions of a blended batch of the powder.

4.2.3 HIP consolidation

A limited experimentation was done on consolidating the powders only to facilitate preparation of samples for optical and electron microscopic study of the microstructure of the consolidated powder. HIP consolidated microstructure (optical) revealed an unexpected feature which was subsequently found to have a bearing on the optimisation of the milling process (see Section 5.3.9). In this connection the consolidation technique used was hot isostatic pressing

(HIP), a versatile technique known for its ability to produce 100% densities in powder compacts (135). The HIP utilised for this purpose was ASEA model QIH-32 and the HIP procedure was as follows: the powder was filled on a vibratory platform into a one-end closed, cylindrical 35mm^{dia} stainless steel capsule, evacuated to 10^{-5} torr and sealed off. The capsule was then loaded into the press. HIP was carried out at $1180^{\circ}\text{C} \pm 12^{\circ}\text{C}$ and 1.2 Kilobar argon gas pressure. The HIP'ed capsule was then skinned off on a lathe to expose the fully compacted powder sample.

4.3 TECHNIQUES USED TO CHARACTERISE MECHANICAL ALLOYING

Several instrumental techniques were used in the present work in order to follow the different aspects of mechanical alloying. The degree of alloying obtained under different milling conditions was monitored by magnetic coercivity measurements and Electron Probe Micro Analysis (EPMA). X-ray diffraction and Scanning Auger Electron Microprobe (SAM) analysis were used to determine whether mechanical alloying led to true solid solution of chromium in nickel. Scanning Electron Microscopy (SEM), average particle size measurements by Fisher Sub-Sieve Sizer and microhardness measurements were employed to monitor the course of mechanical alloying. Conditions and methods employed in all these techniques are briefly described below.

4.3.1 MAGNETIC COERCIVITY

In the case of Ni-Cr system, alloying can be monitored by following the marked change in magnetic behaviour: while pure nickel is ferromagnetic,

nickel alloyed with 20% chromium becomes non-magnetic. By following the change in magnetic coercivity, one can arrive at comparisons of the degrees of alloying with increasing attritor milling time and varied conditions of attritor parameters. While coercivity study can be very useful for qualitative comparisons, it cannot furnish quantitative and subtle distinctions of the degree of alloying between sample to sample, not only because the non-magnetic transition in nickel-chromium system begins from about 6% chromium in solid solution, as can be seen from the equilibrium diagram in Fig.18 (136) but also because of the inherent complications of coercivity variations with particle size, particle shape, cold work effects, dispersoid effects etc. (137). Nevertheless, since coercivity measurements can be readily and easily carried out directly on powder samples without any sample preparation, it is useful in a qualitative characterisation of the state of alloying in mechanical alloying of the system under study. The coercivity meter used in the present work is shown in Fig.19. The procedure of measuring coercivity with this instrument is briefly described in Appendix 2.

Study of coercivity variation with attritor milling time in all the experiments has revealed some general trends in the coercivity variation with progressive mechanical alloying of nickel, chromium and thorium. It will be seen in Chapter V that under conditions where alloying is reasonably rapid and homogeneous as evidenced by EMPA, coercivity rises initially to a peak value and drops down to a low value after which it tends to flatten out, as schematically depicted in Fig.20.

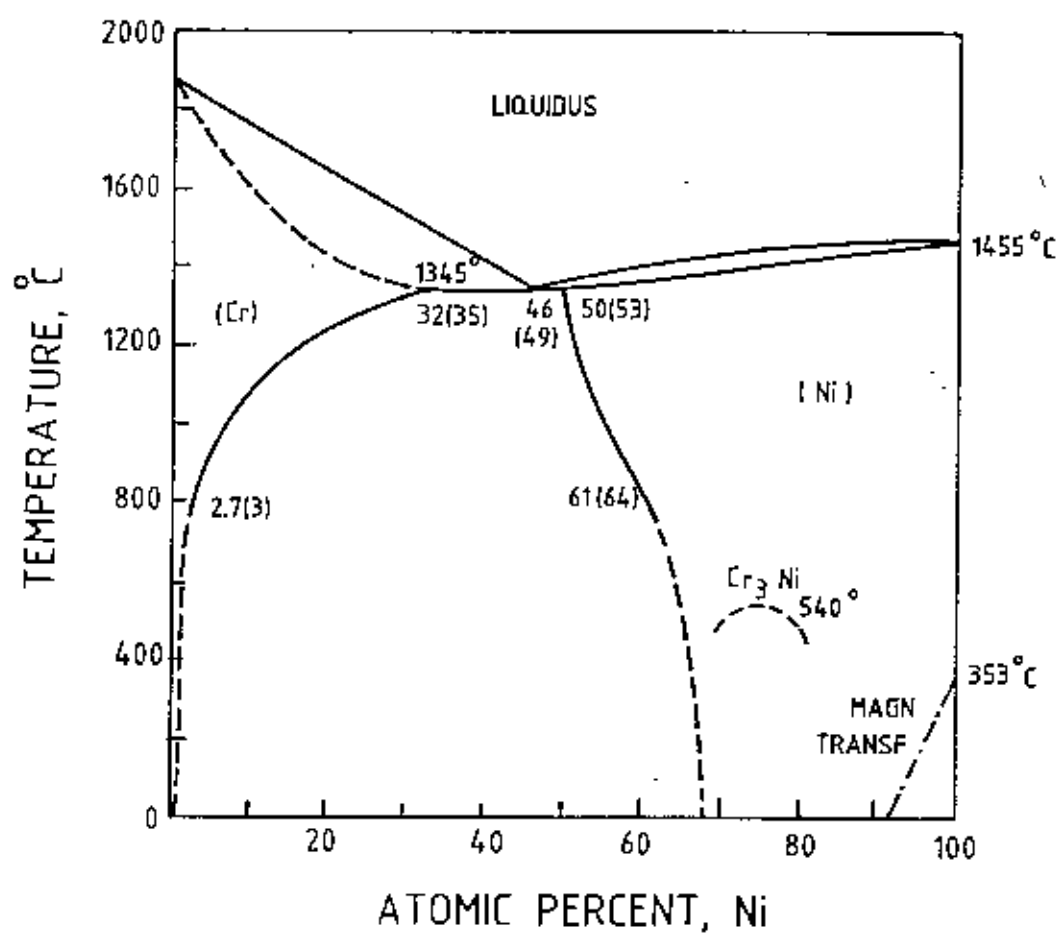


Fig. 18. EQUILIBRIUM DIAGRAM OF Cr-Ni SYSTEM, (Ref: 136)
(BRACKETED NUMBERS REFERS TO WEIGHT PERCENT)

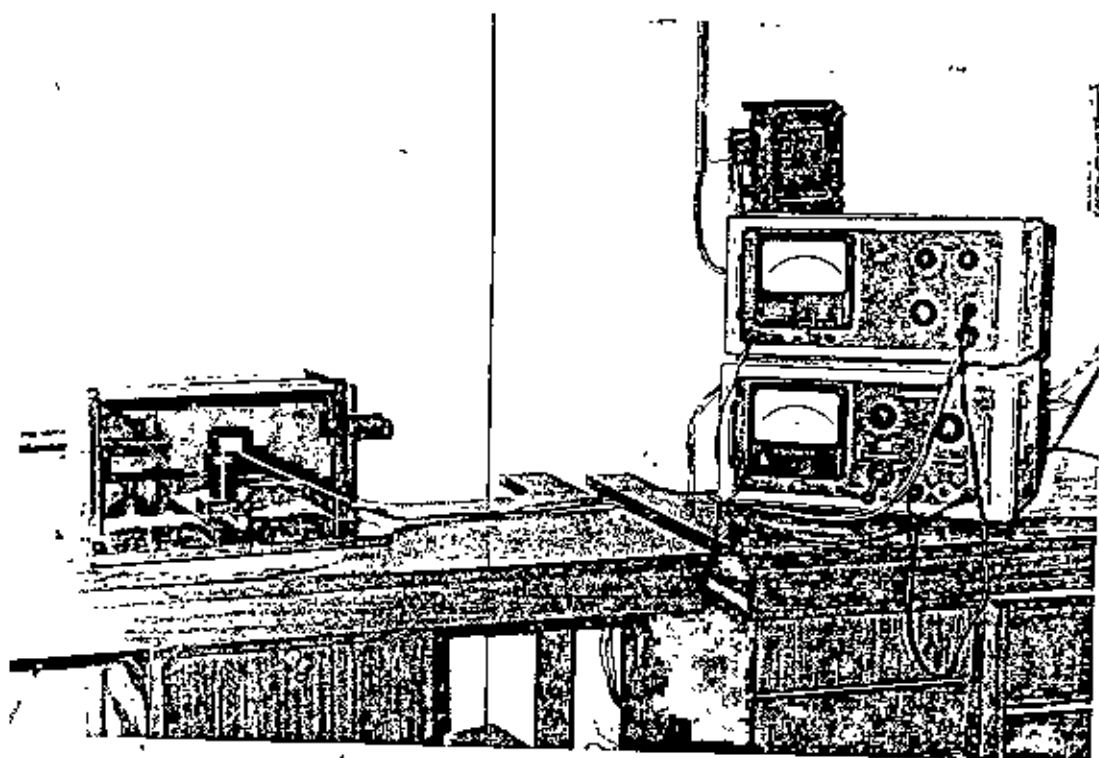


FIG 19 PRECISION COERCIVE FORCE METER

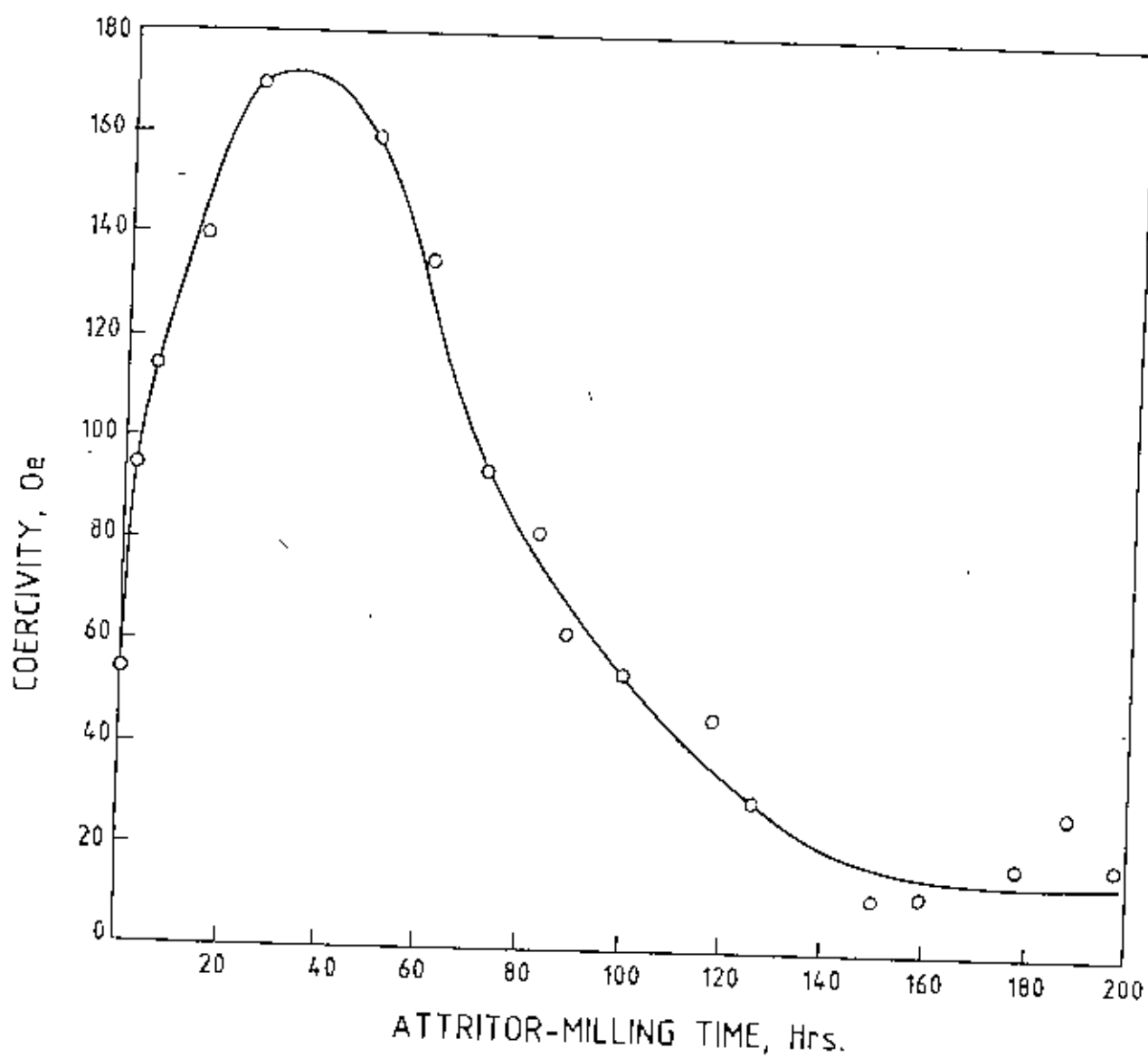


FIG 21 COERCIVITY VARIATION IN PROLONGED ATTRITOR MILLING OF Ni, Cr AND ThO_2

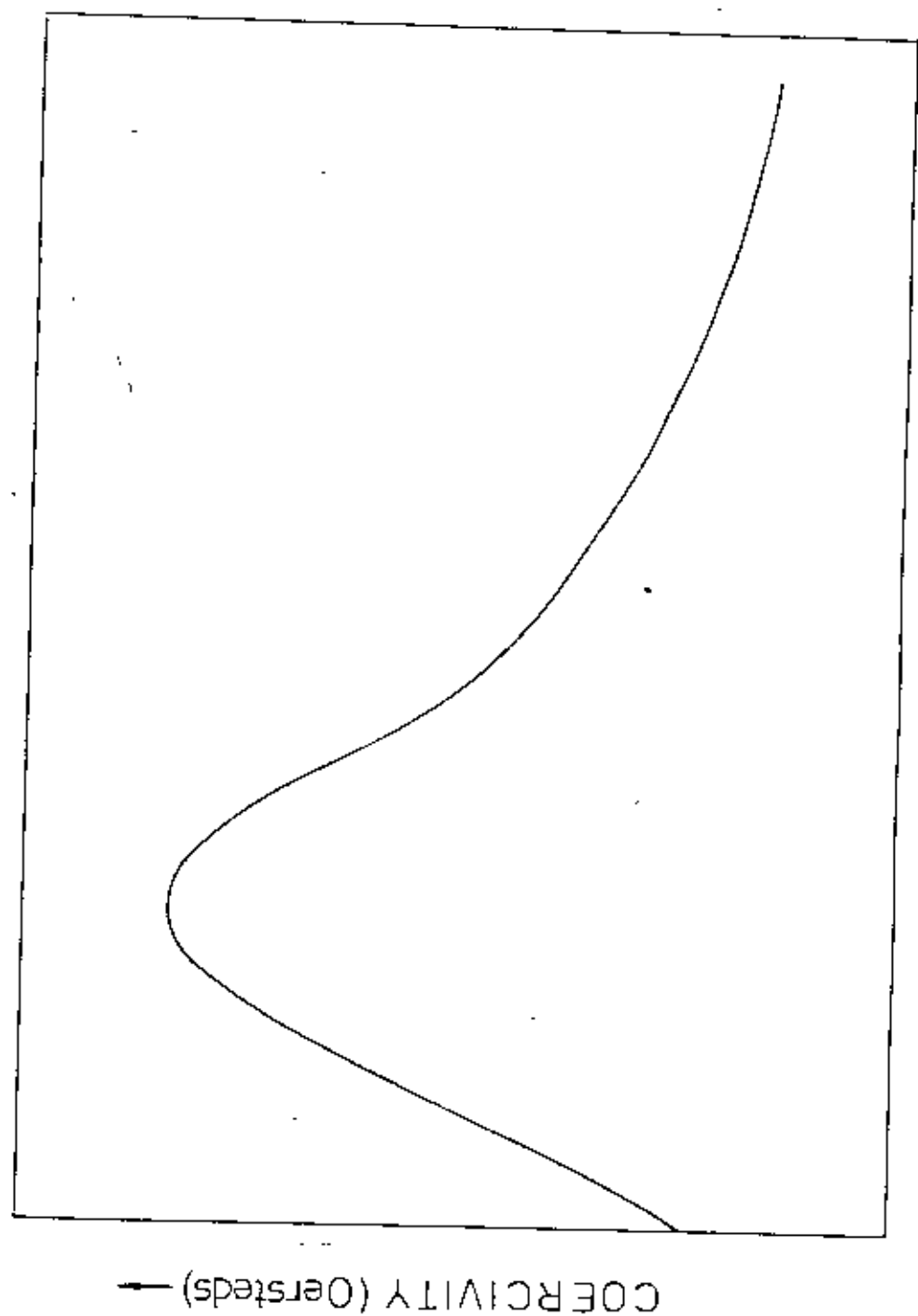


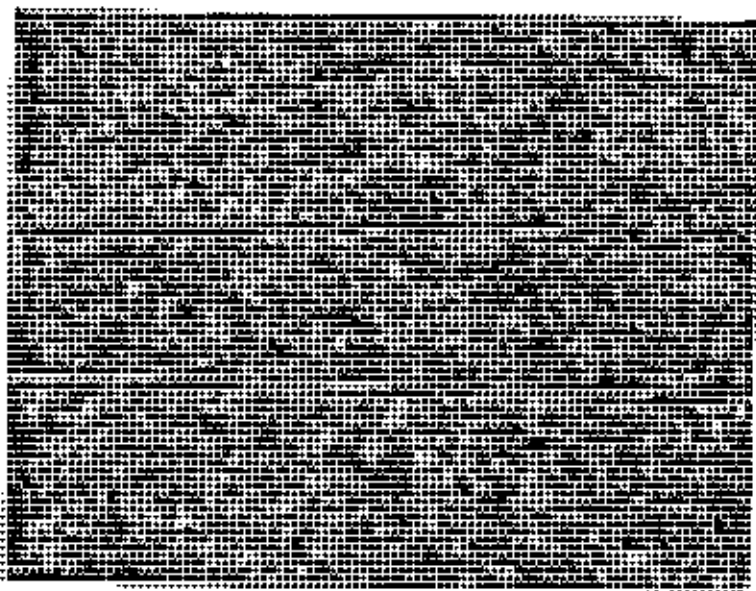
FIG 20 A SCHEMATIC DEPICTION OF COERCIVITY
VARIATION IN MECHANICAL ALLOYING OF

should show up as zero inhomogeneity (i.e. homogeneous solid solution). Both these indicators can be approximately quantified by Electron Probe Microanalysis (EPMA) on the powder particles using the line scan technique. The powder particles were bakelite-mounted, metallographically polished and vacuum coated with a flash of carbon to ensure electrical continuity of the sample. The line scan EPMA was carried out in a CAMEBAX Electron Probe MicroAnalyser under identical conditions of 10^4 counts for nickel scale, 3×10^4 counts for chromium scale, and a line magnification of 2000x. The electron beam voltage was maintained at 20 KV and beam current at 30 mA throughout for all the samples. The line scans obtained in all the samples represent a 50μ linear distance in the analysed particle which in most of the cases covers the entire particle.

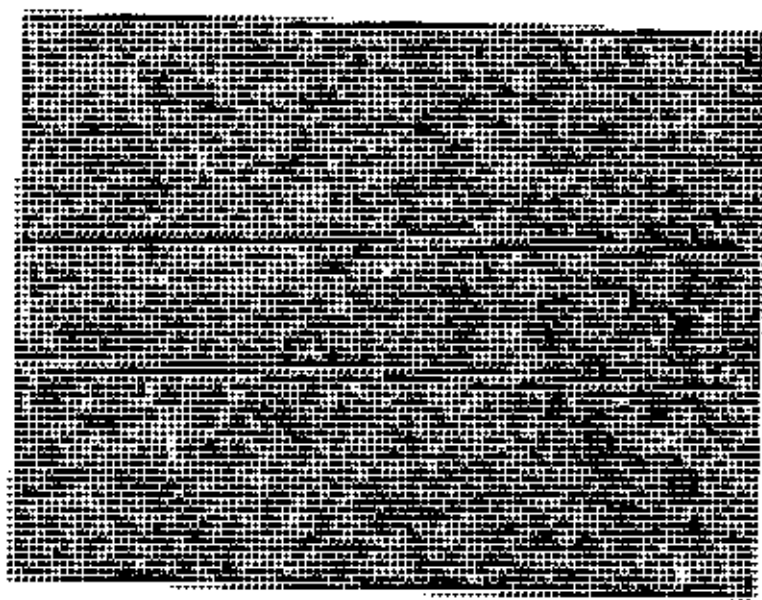
Since the line scan height of an element is directly proportional to the concentration of the element in the alloy, and since any variations in the line scan profile faithfully reflect the degree of inhomogeneity of the distribution of the element as present in the matrix, an approximately quantitative estimate of 'effectiveness of alloying' of chromium in nickel has been derived by analysing the EPMA line scan profiles in the following manner. A 'standard' powder sample was prepared by vacuum induction melting of Ni-Cr alloy (aimed at 20% Cr in solution) and subsequently argon atomising the same to spherical powders. Minus 200 mesh fraction of this powder was analysed and found to have 18.5% of chromium which was then vacuum annealed at 970°C for 8 hrs. EPMA line scan was obtained on this annealed powder (Fig.22a), and the

chromium line level in this scan represents 18.9% Cr in nickel. As a cross-check, a vacuum melted, homogenised, hot forged and annealed solid sample of Ni-Cr alloy having 19.0% Cr was prepared and its line scan (Fig.22b) shows that the homogeneity* of the 'standard' powder sample is as good as in the wrought 'standard'. The line scans for all samples were taken after confirming that the scans were representative of the nickel and chromium distribution in majority of the particles in a given sample. Thus the line scans obtained represent typical trends of the bulk sample. Since the alloying under study is that of chromium in nickel, only the chromium lines were compared with the chromium line of the powder standard. To arrive at an approximate estimate of the amount of chromium picked up in the sample, the mean height of the chromium line should be known so that it can be converted to Cr% with respect to the height of the homogeneous chromium line of the 'standard' sample whose chromium percentage is known. Since the experimental line scans were often wavy, the mean height of the chromium line was obtained by measuring the area under the wavy line and dividing this area by the scan-breadth of 95mm (equivalent to 50%) in all the cases. In effect, such a mean height is equivalent to the level of a line of same Cr%, had it been homogeneously distributed and is taken to represent the average percentage of chromium pick-up which

* A straight line scan of the element in EPMA line scan represents complete homogeneity of distribution of the element in the matrix alloy, within the limits of resolution of the EPMA technique.



a 'STANDARD' POWDER WITH 18.5 % Cr



b WROUGHT ALLOY WITH 19 % Cr

FIG 22 EPMA LINE SCANS OF NICKEL AND CHROMIUM FOR
'STANDARD' POWDER AND WROUGHT ALLOY

is then expressed in terms of percentage of chromium level of the standard powder. An approximate measure of the inhomogeneity of distribution of chromium in nickel in the particles has been obtained in terms of Cr% by calculating the scalar sum of positive and negative mean deviations of a wavy line with respect to its own mean line determined as described above and this total mean deviation is converted to Cr% from the known Cr% of the height of the chromium scan of the standard. The total mean deviation in chromium percentage represents the average inhomogeneity of chromium distribution in the sample: smaller the total mean deviation, less is the inhomogeneity. A more detailed description of this method of line scan analysis is illustrated in Appendix 3. We can now define maximum effectiveness of alloying as a result in which there is maximum chromium pick-up in the milled powder concomitant with the least possible inhomogeneity, as given by EPMA line scan analysis.

4.3.3 X-ray diffraction

X-ray diffraction profile analysis is one of the techniques used for investigating whether true solid solution of chromium in nickel is formed as a result of mechanical alloying. Details of the samples and the results obtained are presented in Section 6.2. Phillips X-ray diffractometer with filtered CoK_α radiation at 30kV and 50mA was used for all the samples. Slow scanning at 1/8 degree per minute and a chart speed of 1cm per minute were employed over a range of 2θ covering the (111) reflection which is the most intense peak for FCC crystals. The 2θ range was so chosen as to cover the tails

of the peak till they even out with the background. The powder samples were mounted with Canada balsam glue in aluminium holders.

4.3.4 Scanning Auger Microprobe analysis

Another technique employed for investigating the nature of solid solution formed by mechanical alloying is the Scanning Auger Electron Microprobe Analysis (SAM) of chromium and nickel. A Physical Electronics Model 545-C Scanning Auger Microprobe has been used. Here the sample which is in powder form cannot be placed in a mount of organic chemical material such as bakelite. Therefore, a special mounting technique was employed: the powder particles were pressed onto a thick indium foil which was held in the sample holder. Two types of analysis were carried out: i) fixed depth analysis in which the Auger analysis was done at preselected depths of the surface by sputter etching the surface layers to the desired depth with a beam of argon ions, and (ii) continuous depth profile analysis in which the analysis was continuously obtained as the particle surface was continuously sputter etched with the ion beam.

The following conditions of SAM were employed for fixed depth analysis:

Primary beam voltage	:	3kV
Primary beam current	:	3 μ A
Etching gun voltage	:	1kV
Etching current	:	10mA
Etching rate	:	20Å ² /min.

The following conditions were employed for continuous depth profile analysis:

Primary beam voltage	:	3kV
Primary beam current	:	3 μ A
Etching gun voltage	:	30kV
Etching current	:	30mA
Etching rate	:	420 $\text{\AA}$ /min.

4.4 MICROSCOPY AND MICROHARDNESS

Transmission Electron Microscopy (TEM) was employed to compare the thorium distributions obtained in the milled Ni-Cr-ThO₂ powders under different attritor milling conditions. Philips EM 300 electron microscope was used for this purpose, mostly at 80 keV. It has not been possible to prepare specimens for TEM directly from the powder particles themselves. It has therefore become inevitable to consolidate the powders by HIP and it is reasonable to assume that thorium distribution and particle size do not alter by the consolidation process of HIP carried out at 1180°C.

Same HIPing procedure as described previously in Section 4.2.3 was adopted to make small solid rods for the purpose of TEM study. The HIPed and skinned rods were sliced into about 2mm thick discs in an abrasive cut-off machine. The 2mm thick discs were first chemically thinned to about 0.5mm thickness in a solution of the following composition:

HCl	:	780 ml
HNO ₃	:	240 ml
H ₃ PO ₃	:	114 ml
FeCl ₃	:	90 gm

Bath temperature : 85°C

The discs were subsequently hand-polished to about 0.25mm thickness. From these discs 3mm diameter discs were punched out for jet polishing for TEM. Jet polishing was done with a solution of the following composition and conditions:

Methanol	:	78%
H ₂ SO ₄	:	7%
HF	:	2%
HNO ₃	:	3%
Lactic Acid	:	10%
Voltage	:	12V
Current	:	40mA
Temperature	:	-20° to -40°C

Scanning Electron Microscopy was done in a ISI - 100A microscope (which has EDAX attachment) at about 20kV. EDAX was used to analyse the milled powder and powder welded to balls for relative assessment of Cr & Ni contents as a ratio of Cr/Ni.

Optical microscopy was done in a Leitz microscope. Powder samples were mounted in bakelite and polished through standard grits of increasingly fine emery paper and then wheel-polished on Sylvet cloth with coarse alumina followed by wheel polishing with 2 μ diamond paste. For obtaining etched microstructure, the mounted samples were immersion etched for 15 to 60 seconds in a solution of:

FeCl_3 : 5gm
HCl : 50ml
 H_2O : 100ml

Microhardness was measured using a Lertz microhardness tester with a Vickers diamond indenter. The load was maintained either at 50gm or at 100gm. In case where the 50gm load gave indentations too small to measure accurately, the load was changed to 100 gm. The load was maintained constant in all the samples where comparison among themselves was necessary.

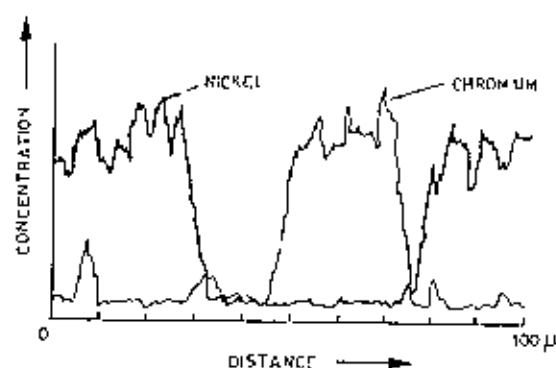
CHAPTER V

OPTIMUM PARAMETERS OF ATTRITOR MILLING

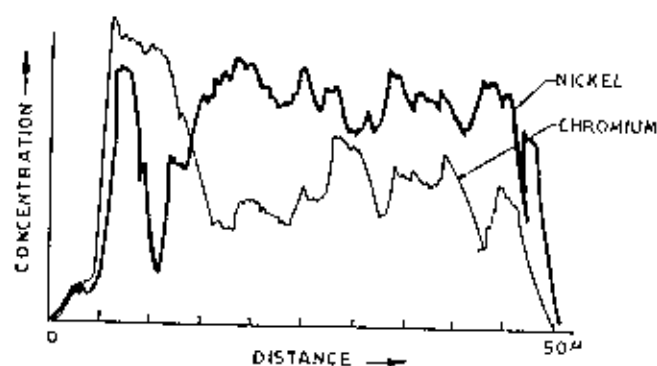
carbon replicas were made from rolled strips of the powder. The strips were obtained by a process of die-compaction, encapsulated hot-rolling and subsequent cold rolling with intermittent hydrogen annealing.

Fig.23 compares the line scan EPMA of nickel and chromium of 90 hr ball-milled samples with 16 hr and 40 hr attritor milled samples. It can be seen that while 90 hrs of milling in a ball mill fails to achieve even a semblance of homogeneity of either chromium or nickel, 40 hrs of milling in an attritor is sufficient to produce fairly homogeneous alloying of Cr in Ni. Electron micrographs in Fig.24 show the non-uniformly distributed and agglomerated clusters of thorium particles in the 90 hr ball-milled sample, while the samples attritor milled for only 6 hrs shows much better distribution of thorium with much finer size. The 48 hr attritor milled sample (Fig.25) shows a satisfactory distribution of thorium with an average size of about $370\text{\AA}$.

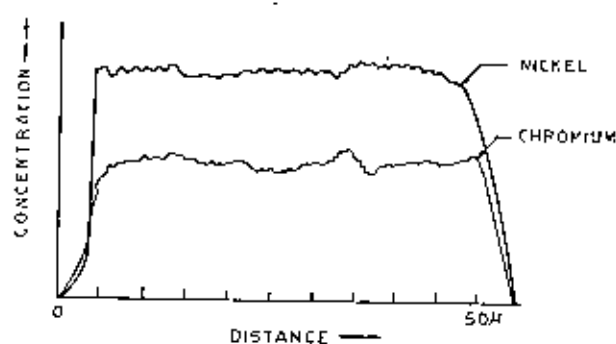
The basic limitation of a ball mill in terms of its failure to achieve the desired alloying of the powder constituents can be seen to lie in the low 'critical' speed of a ball mill; 'critical' because it is the upper limit beyond which the grinding balls get centrifugally pinned to the surface of the rotating drum, or, is the theoretical speed limit at which the centrifugal force on a ball in contact with the drum becomes equal and opposite to the force on it due to gravity (132, 139). The necessarily low speeds of rotation imply low kinetic energy to the balls which, although sufficient to cause comminution by the 'cascade/cataract' mechanism (132), becomes ineffective for mechanical alloying.



a SAMPLE BALL MILLED FOR 90 HRS

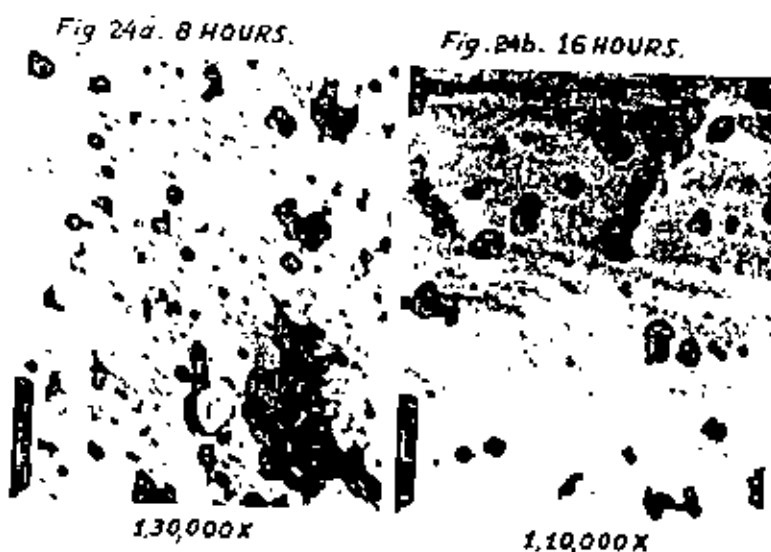


b SAMPLE ATTRITOR MILLED FOR 16 HRS

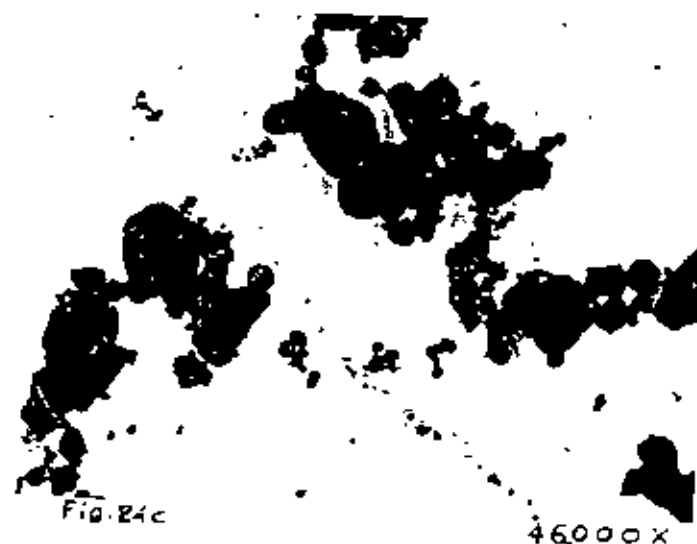


c SAMPLE ATTRITOR MILLED FOR 48 HRS

FIG 23 EPMA LINE SCANS OF NICKEL AND CHROMIUM
OF BALL MILLED AND ATTRITOR MILLED POWDERS



a, b THORIA DISTRIBUTION IN ATTRITOR MILLED SAMPLES



c THORIA DISTRIBUTION IN BALL MILLED SAMPLES

FIG 24 ELECTRON MICROGRAPHS SHOWING THORIA DISTRIBUTION IN ATTRITOR MILLING AND BALL MILLING



FIG 25 ELECTRON MICROGRAPH SHOWING THORIA DISTRIBUTION
AFTER 48 HRS ATTRITOR MILLING, 30000 x

With an attritor, where the vessel is stationary and the balls are kept in colliding motion against each other by the rotating impellers, there is no dependence on any 'catacting' or 'cascading' effect of the balls for achieving comminution or blending. The centrifugal and gravitational forces on the balls in an attritor act at right angles to each other. It is therefore possible to operate the attritor at RPMs much higher than an equivalent capacity ball mill without encountering the disadvantages of centrifugal pinning of the balls to the vessel wall. Thus, in the experiments described here, while the ball mill could not be operated at speeds more than 60 RPM, the attritor was run at 170 RPM and can in fact be operated at even higher speeds with better results.* While in a ball mill the drum itself rotates to impart energy to the balls, in the attritor the energy to the balls is derived by the passage of the rotating impellers through the ball charge with the vessel remaining stationary. The random ball motion induced by contact with the impellers and the ball-to-ball collisions are responsible for the grinding action. The high speeds possible in an attritor impart a high level of kinetic energy to the balls which bring about mechanical alloying of the powder constituents. A detailed account of mechanism for mechanical alloying in attritor milling is covered in Chapter VII.

5.2 VARIABLES IN ATTRITOR MILLING

Since an attritor can prima facie impart unlimited kinetic energy to the balls by its ability of being operable at virtually unlimited speeds, the question arises whether there at all exists any optimum speed of operation that can be

selected for a given set of constituents to be mechanically alloyed under a given set of other operating conditions. Furthermore, what are the other parameters that can influence the extent and homogeneity of alloying and what optimum values can be chosen for them? It can easily be visualised that the features of the grinding media, i.e. the balls, can have significant influence such as the total weight of balls in relation to the weight of the powder to be milled (balls-to-powder weight ratio) and the diameter of the ball. The shape and material of the balls may also be important. Since the velocity of the balls and hence the kinetic energy of the attritor is derived by the motion of impellers, the shape and the number of vanes could also have some influence on mechanical alloying. In addition, the average starting particle size of the constitutive powders can have a bearing on the effectiveness of mechanical alloying since the attritor energy is mostly expended in particle welding and de-welding in the course of alloying. There have been hardly any systematic investigations on such lines, although mention can be made of the limited study by Wassel¹ and Himmelf (130) who observed increased rates of mechanical alloying when either the speed was increased from 150 to 300 RPM, or when balls-to-powder ratio was changed from 8.5:1 to 17:1. Detailed study of the influence of varying the above mentioned parameters on mechanical alloying - should lead to the optimisation of the attritor operational parameters including milling time.

For the purpose of this study, the following parameters of attritor operation have been chosen:

- i) RPM of the attritor
- ii) The balls-to-powder weight ratio
- iii) The diameter, shape and density of the ball
- iv) The shape and number of the impellers, and
- v) Average starting particle size of nickel and chromium

In order to study the effect of the above parameters on mechanical alloying, the constituent powders of nickel, chromium and thorium were milled in the attritor under varying operational conditions. In all these experiments while one parameter was varied, other parameters were kept the same. Unless otherwise stated, the values of the fixed parameters common to all the experiments are as follows:

Attritor RPM	:	154
Balls-to-powder weight ratio	:	18/1
Ball diameter	:	6mm
Impeller shape	:	round
Number of impellers	:	8
Average particle size of nickel	:	8 μ
Average particle size of chromium	:	45 μ

Since the attritor is driven by a multi-speed drilling machine drive, the choice of speed is arbitrarily fixed by the speeds available in the drive, of which five speeds have been selected for study: 154, 260, 450, 850 and 1880. The balls-

to-powder weight ratio was varied in seven different proportions by varying on the powder quantity so that the total height of the bed of the balls remain the same in all cases of the variation. The ratios studied are: 12/1, 18/1, 24/1, 40/1, 50/1, 100/1 and 150/1. The ball diameter variations studied are: 4mm, 6mm, 8mm and 10mm diameter steel balls. In addition, 6mm diameter tungsten carbide balls have also been tried in one of the experiments. 6mm x 6mm cylinders have been tried in another experiment. The effect of impeller shape has been studied by considering three different cross sections. The number of impellers have also been varied in two configurations keeping the shape same. Finally, the average starting particle sizes of nickel and chromium have been varied in four different combinations of coarse and fine sizes, whose details are included in Section 5.3.8.

The effect of varying these parameters on the degree and effectiveness of mechanical alloying was followed by magnetic coercivity measurements and EPMA, while thoria distribution was studied by TEM. Details of these analytical tools have already been described in Chapter IV. Besides giving confirmation of the qualitative trends of alloying shown by coercivity, EPMA provided a quantitative distinction between different degrees of alloying and thus a performance index could be obtained, as already explained in Chapter IV.

5.3 EFFECTS OF PARAMETRIC VARIATIONS ON MECHANICAL ALLOYING

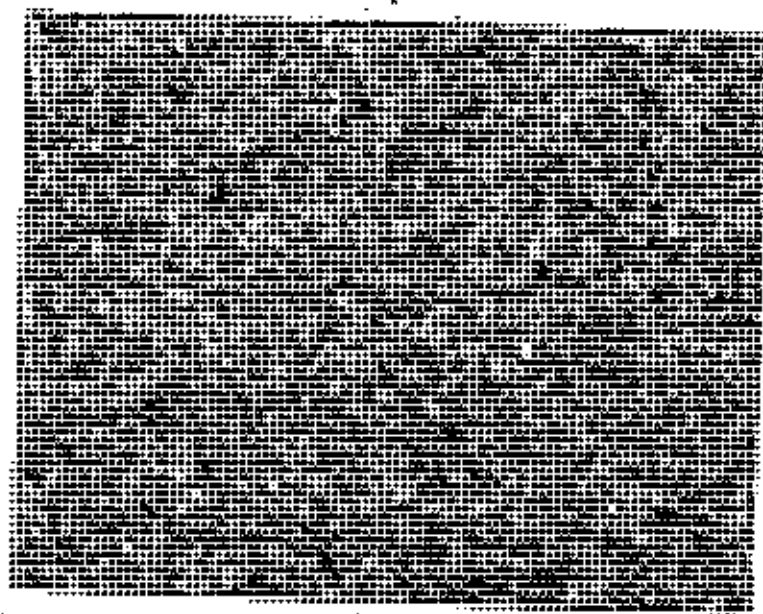
In this section, the results of the experiments of varying the chosen attritor milling parameters and their effects on mechanical alloying kinetics

are described. A detailed discussion and interpretation of these results with respect to each of the parameters are covered in Section 5.4

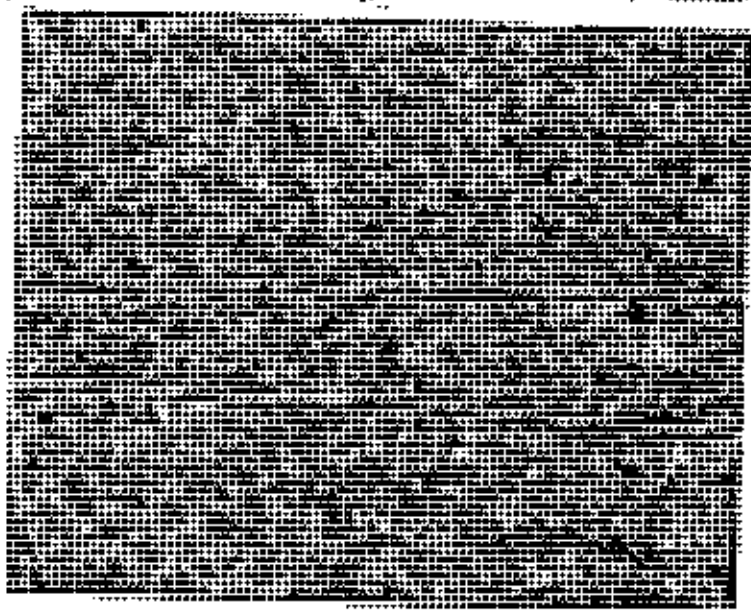
5.3.1 Effect of attritor speed

Fig.26 shows the variation of coercivity with increasing milling time for four different attritor speeds namely 154, 260, 450 and 850 RPM. Coercivity does not show any peak-crossed drop in the 154 RPM run upto a milling time of 60 hours although a tendency to peak does begin after 42-48 hours. In contrast, in the 260 RPM run, there is a coercivity peak (150 Oe) at 12 hrs milling time and this drops to 100 Oe at 24 hrs decreasing further to about 40 Oe for milling time of 36 hrs. Progressively faster rise and faster drop in coercivity can be seen as RPM is increased from 260 to 450 and 850.

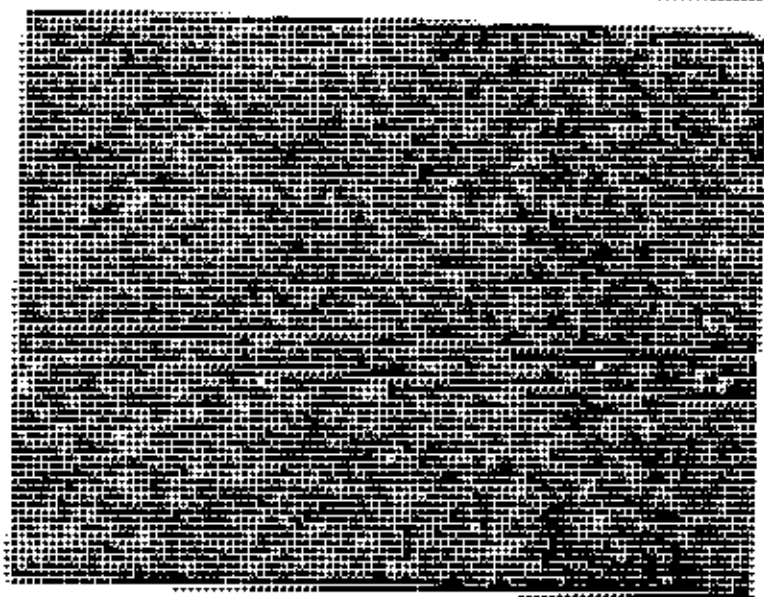
EPMA line scans carried out on samples drawn after 24 hrs and 42 hrs of milling time in all the four RPM runs are presented in Figs.27 and 28 respectively. The effectiveness of alloying in terms of average chromium pick-up and the inhomogeneity, calculated from EPMA results of Figs.27 and 28, for the different RPM runs at the 24th and 42nd hour milling time are shown in Table 5. It is clear from Table 5 that the average chromium pick-up and the homogeneity of its distribution in the 260 RPM run are significantly better than in 154 RPM. The EPMA result thus confirms that a peak-crossed drop in coercivity observed for the 260 RPM run (Fig.26) represents a well-alloyed state as against the almost flat coercivity curve for 154 rpm run for which effectiveness of alloying is seen (Fig.28) to be comparatively weak in the observed milling time. A similar trend is seen for the higher RPMs too wherein a peak-crossed



154 RPM

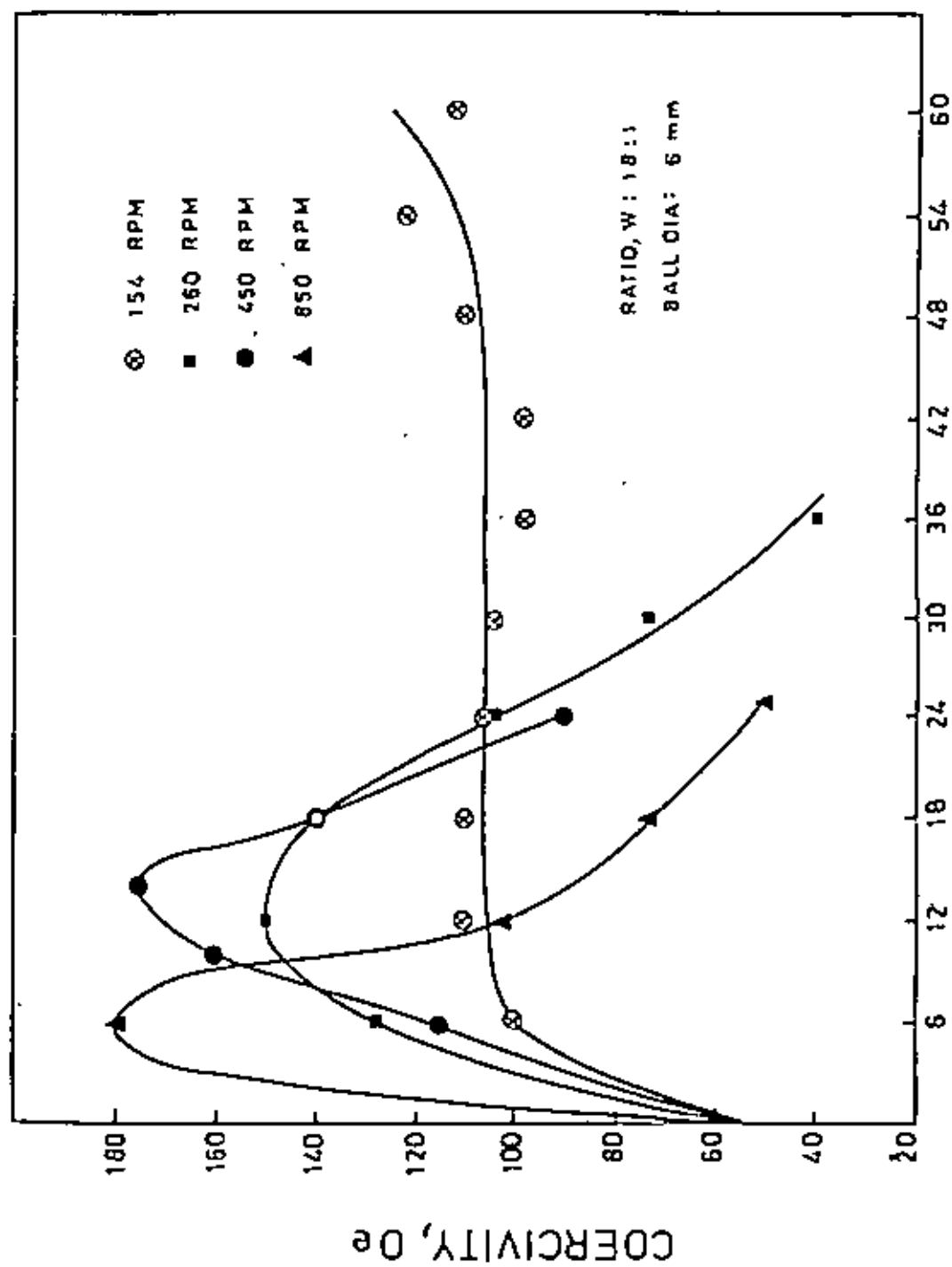


260 RPM



450 RPM

FIG 28 EPMA LINE SCANS AFTER 42 HRS MILLING



drop in coercivity occurs and it occurs earlier as the speed is higher indicating faster alloying.

Table 5 shows that chromium pick-up as well as the homogeneity of alloying increase as the RPM increases, but the improvement of alloying is seen to become marginal at higher and higher speeds; thus, there is only negligible difference in the effectiveness of alloying between the 260 RPM run sample and 850 RPM run sample, and both represent a well-alloyed condition almost at par with the 'standard' sample.

Data of Table 5 of all the four different RPM samples for the constant milling times of 24 hours and 42 hours are graphically plotted as isochronal curves in Fig-29 which shows as a function of RPM, the effectiveness of alloying in terms of the two indicators, namely, average chromium pick-up percentage with respect to the chromium in the 'standard' sample, and the average inhomogeneity in Cr%. For a constant milling time of 24 hrs it is seen that the 'maximum effectiveness of alloying'^{*} is reached at about 800 RPM, whereas for constant milling time of 42 hrs, the maximum effectiveness of alloying is realised at about 300 RPM itself.

A better distinction and comparison of the efficacy of alloying at the different speeds of attritor milling can be made by comparing samples drawn

* As already defined in Section 4.3.2

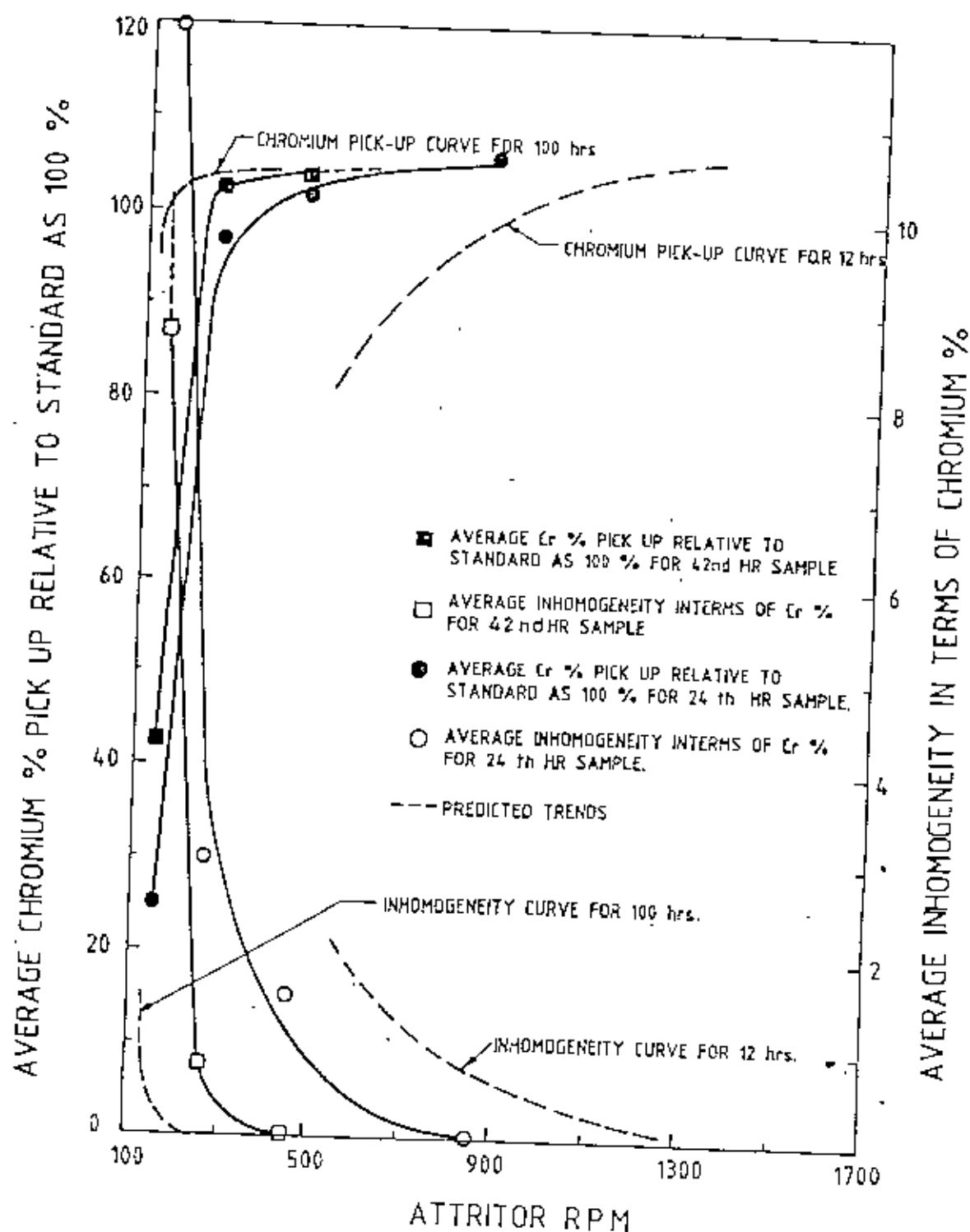
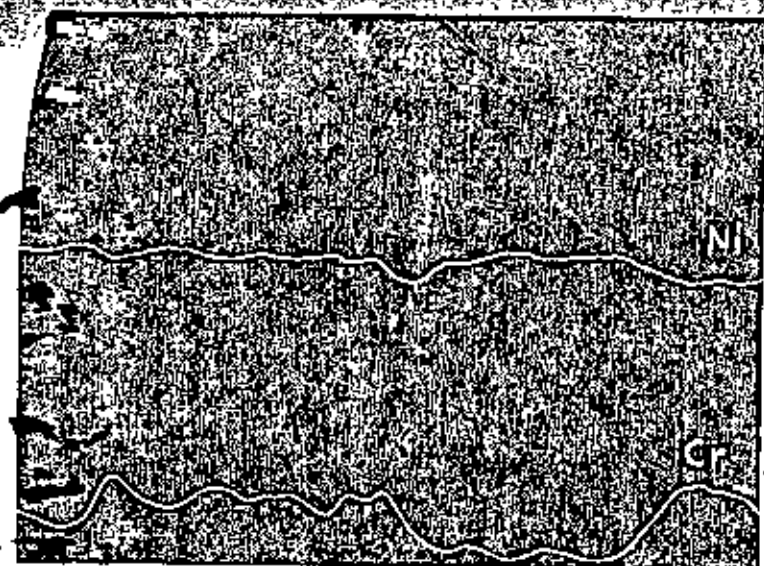


FIG 29 EFFECTIVENESS OF ALLOYING WITH INCREASING RPM FOR CONSTANT MILLING TIMES

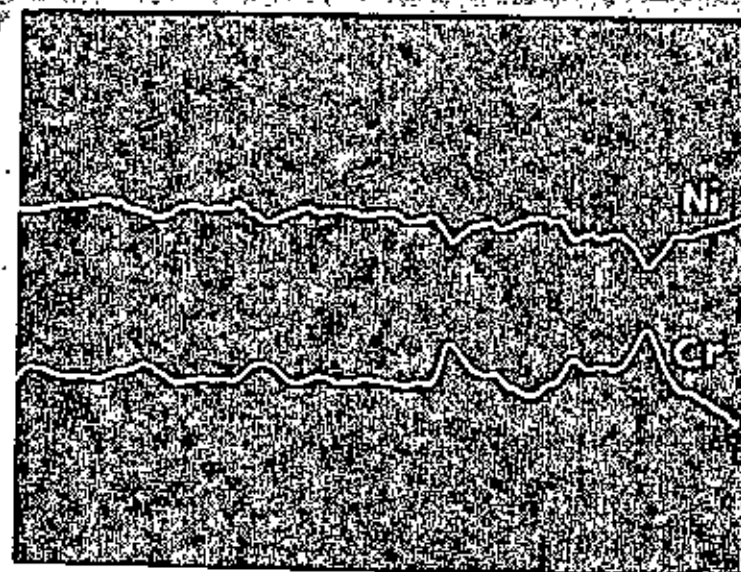
at about the same, total number of revolutions (given by the product of RPM and milling time). Table 6 shows the number of revolutions at the sampled points of milling time for the four different speeds under study. The four samples (underlined in Table 6) at nearly identical number of revolutions of about 3.6×10^5 for the four different speeds, designated as A, B, C and D in Table 6 were subjected to EPMA and these line scans are presented in Fig.30. Similarly, EPMA line scans of samples drawn at about 6.2×10^5 revolutions for the four different speeds designated as F, G, H and J in Table 6 are shown in Fig.31.

From the EPMA line scans, the chromium pick-up and inhomogeneity calculated for samples A, B, C, D, F, G, H and J are presented in Table 7. For about the same number of revolutions of either 3.6×10^5 or 6.2×10^5 the 260 RPM sample has higher level of chromium pick up although with slightly more inhomogeneity than in the 450 sample, while the sample of the still higher RPM of 850 has even less chromium pick-up and more inhomogeneity than that of either the 450 RPM or 260 RPM sample. A similar trend is observed in coercivity variations when they are replotted against number of revolutions, as shown in Fig.32; it can be seen here that the peak-crossed coercivity drop for the 260 RPM run occurs earlier than for the higher speeds of 450 and 850 RPM.

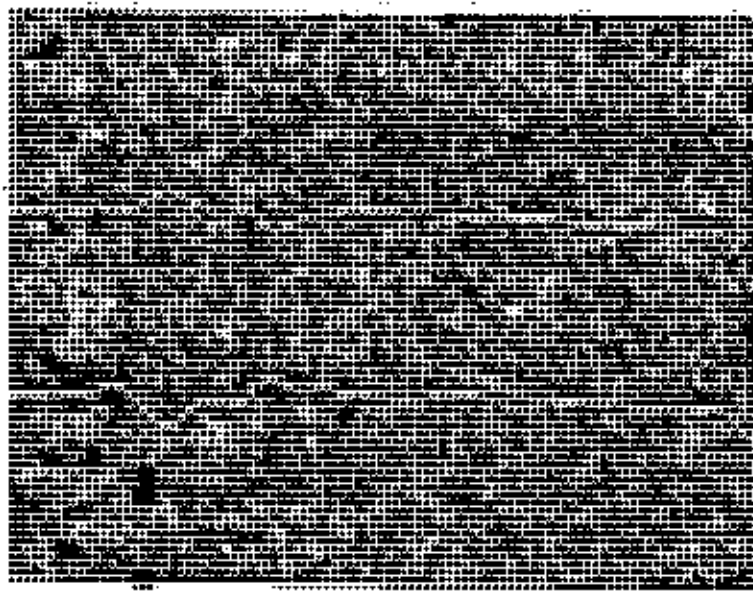
The attritor used for this work is not designed for continuous operations at speeds in excess of approximately 1000 RPM. However, a short run has been attempted at 1880 RPM for which an appropriate pulley drive is available in



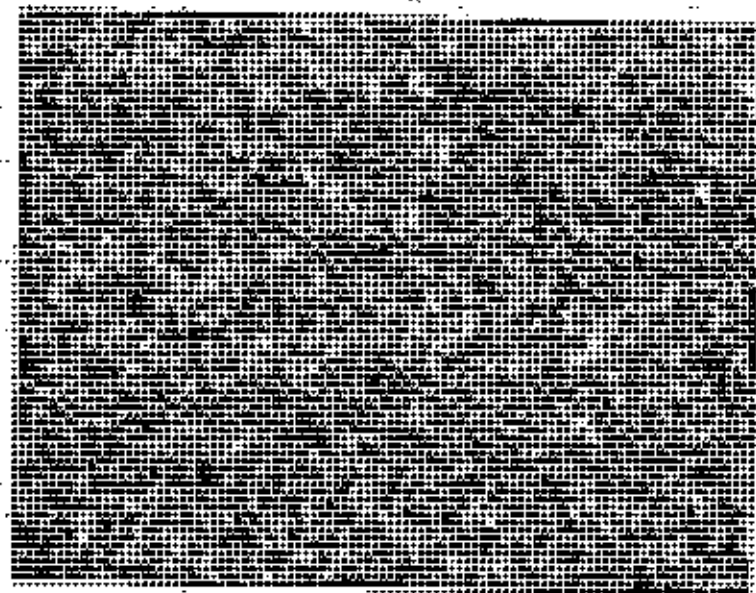
154 RPM



260 RPM



450 RPM



850 RPM

FIG. 30. EPMA LINE SCANS OF ATTRITOR MILLED SAMPLES AT
CONSTANT NUMBER OF REVOLUTIONS OF $\sim 3.6 \times 10^5$

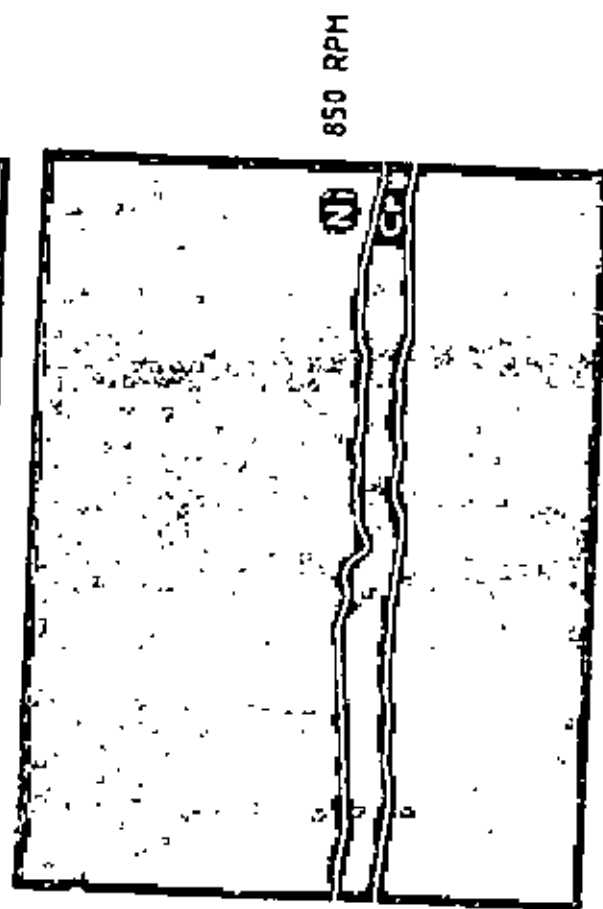
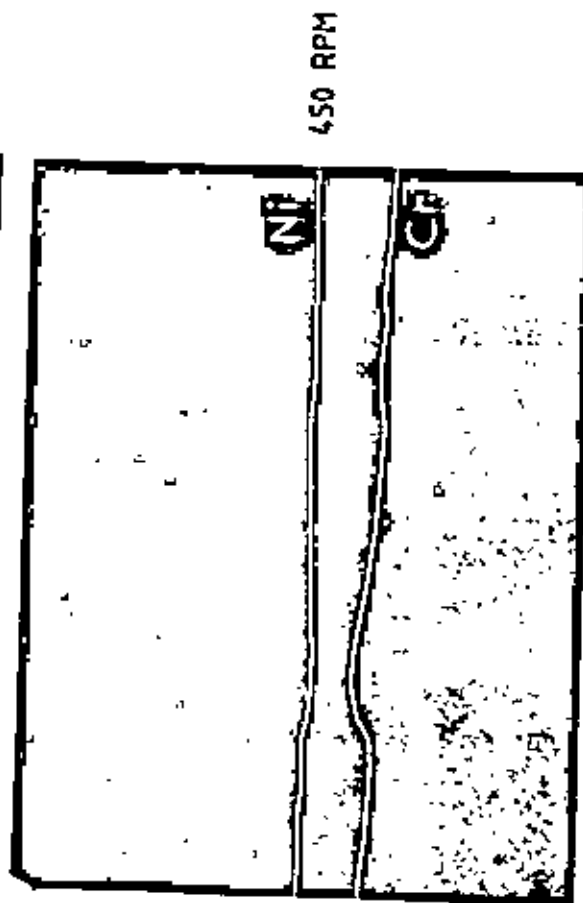
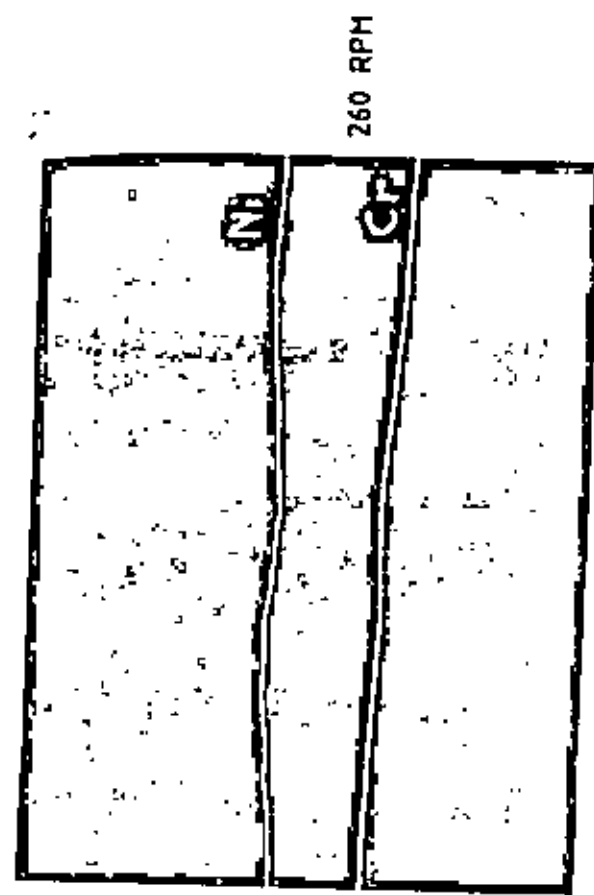
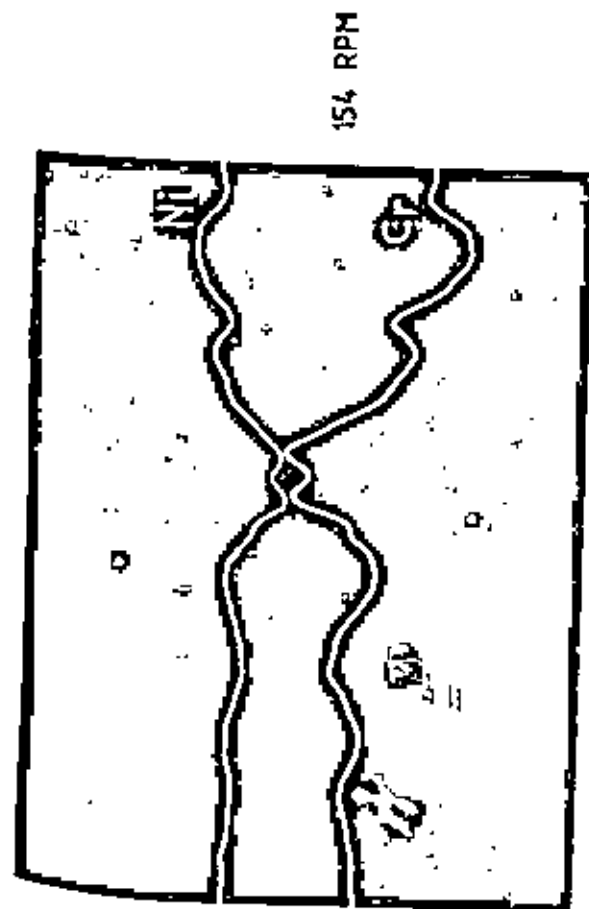


FIG 31 EPMA LINE SCANS OF ATTRITOR MILLED SAMPLES AT CONSTANT NUMBER OF REVOLUTIONS OF $\sim 6.2 \times 10^5$

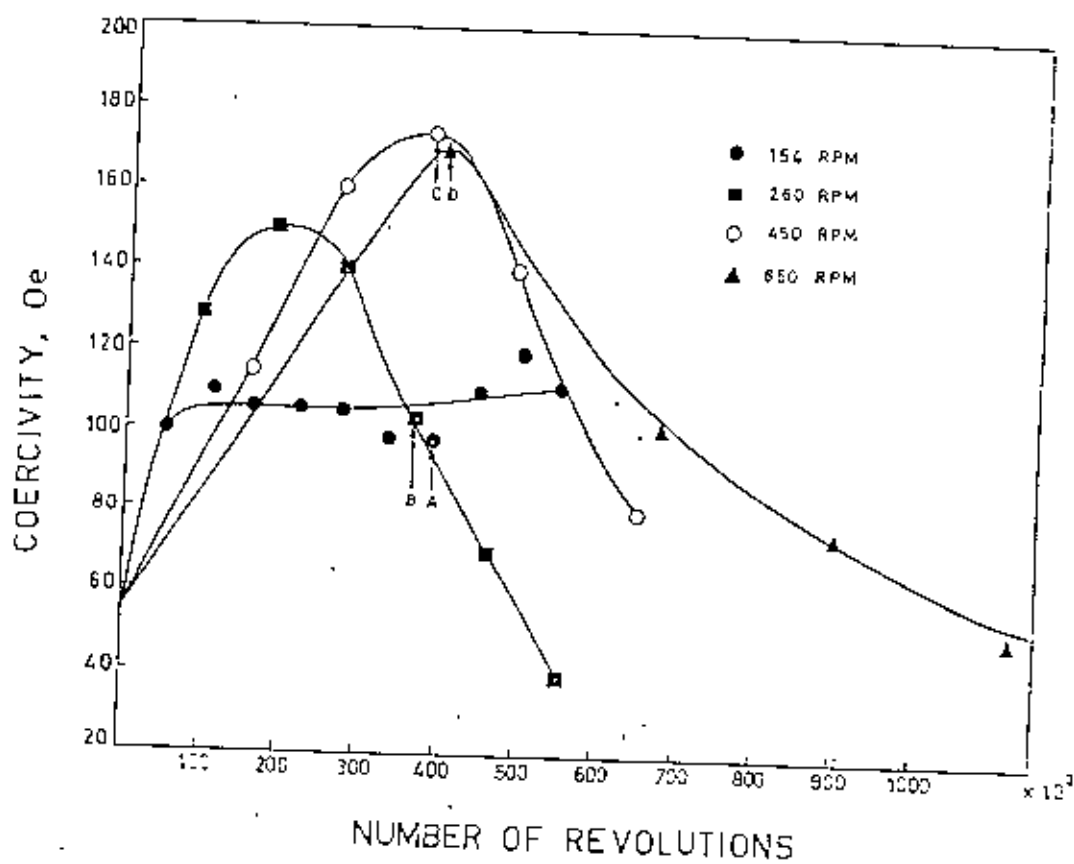


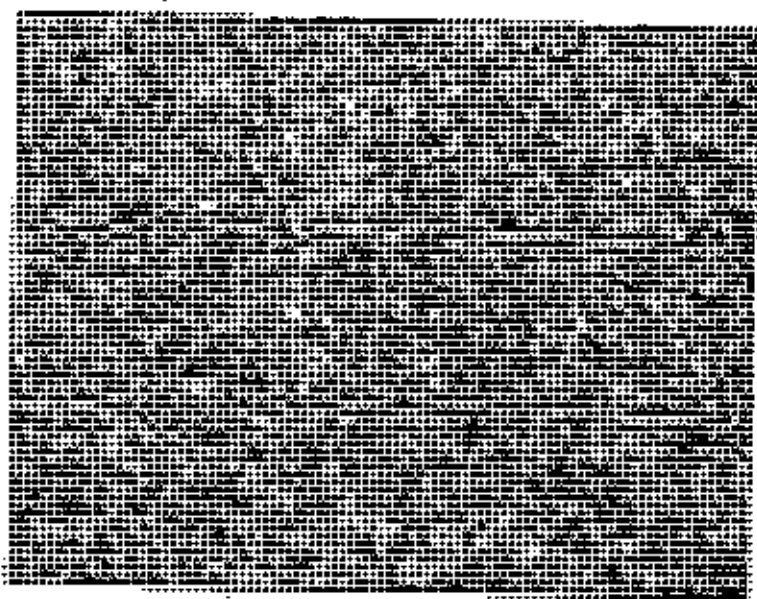
FIG 32 EFFECT OF ATTRITOR RPM ON COERCIVITY IN TERMS OF NUMBER OF REVOLUTIONS

the attritor. Using a charge of 300 gm with 6mm diameter steel balls in 18/1 balls-to-powder ratio, milling was carried out for 3.5 hours to match approximately its number of revolutions of samples A, B, C and D. The sample is designated as E in Table 6. The EPMA line scans of this sample E are shown in Fig.33b in comparison with that of a sample from 450 RPM run at about the same number of revolutions (Fig.33a). The EPMA line scan analysis of sample is included in Table 7. A comparison of the EPMA line scan analysis of this sample with all the others, as can be seen from Table 7, reveals that the % chromium pick-up in 1880 RPM is lower and also has much less homogeneity than either the 250, 450 or 850 RPM sample, although number of revolutions are essentially the same in all. All the data of Table 7 are plotted in Fig.34 as curves of effectiveness of alloying for constant number of revolutions. It reveals that for a constant number of revolutions of $\sim 3.6 \times 10^5$ the effectiveness of alloying is maximum at about 350 RPM; RPMs either less or more than this value tend to produce less effective alloying. Even for a higher number of $\sim 6.2 \times 10^5$ revolutions, while the inhomogeneity is comparatively reduced over the entire RPM range, the maximum effectiveness of alloying is still seen to occur at about the same 350 RPM (shown as shaded areas in Fig.34).

The results on the effect of attritor speed described above are discussed in detail in Section 5.4.1.

5.3.2 Effect of balls-to-powder weight ratio

The coercivity variation with respect to attritor milling time is plotted



a 450 RPM SAMPLE AT $\sim 3.8 \times 10^5$ REVOLUTIONS



b 1880 RPM SAMPLE AT $\sim 4 \times 10^5$ REVOLUTIONS

FIG 33 EPMA LINE SCANS OF SAMPLE FROM 1880 RPM RUN
COMPARED TO SAMPLE FROM 450 RPM RUN

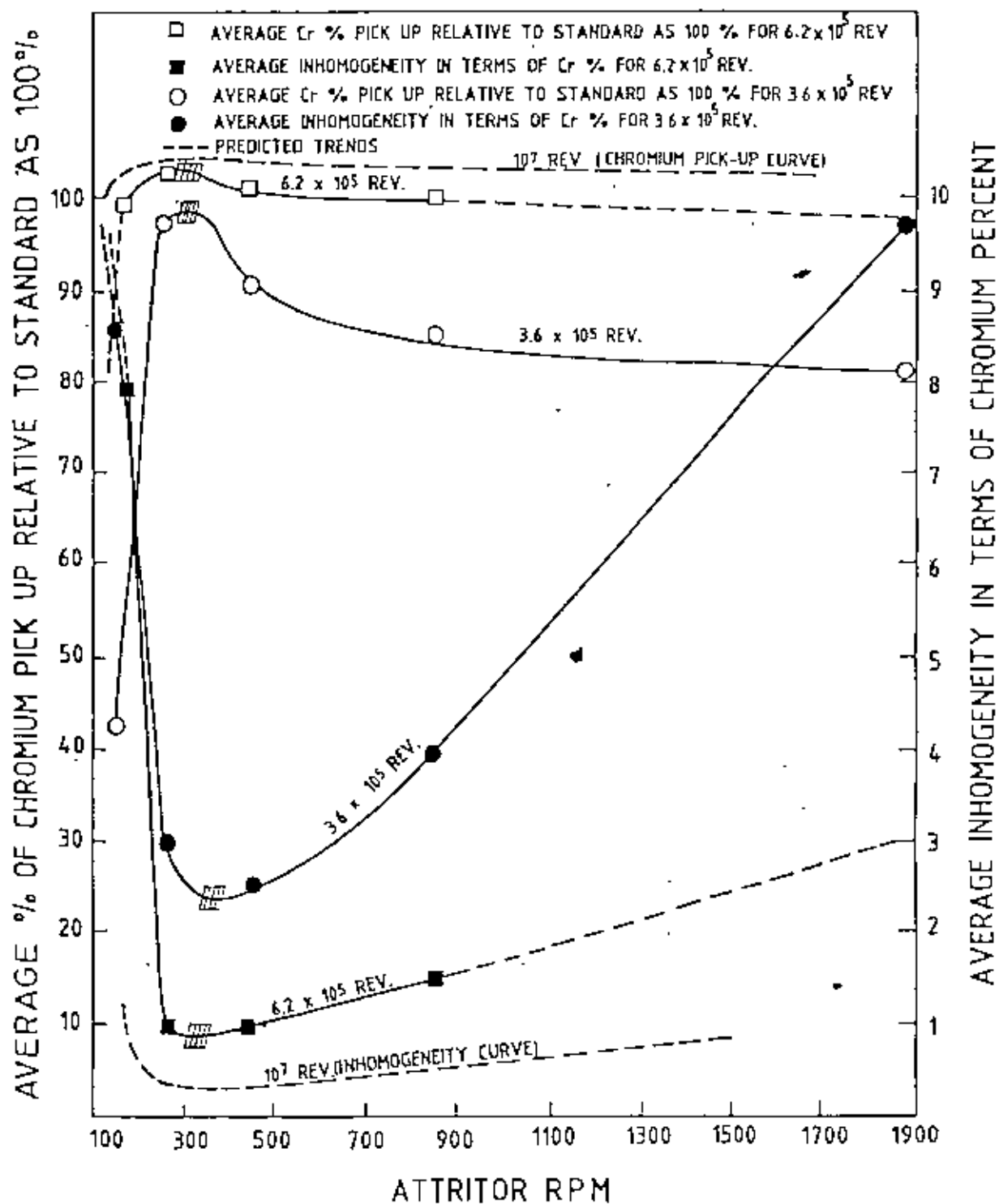


FIG 34 EFFECTIVENESS OF ALLOYING WITH INCREASING RPM FOR CONSTANT NUMBER OF REVOLUTIONS

in Fig.35 for six different balls-to-powder weight ratios (hereafter referred to as ball ratios, for convenience) ranging from 12/1 to 100/1. While the 12/1 ratio run shows neither a peak nor peak-crossed drop in coercivity within 48 hours and 18/1 ratio run slowly tends towards a peak, all the other runs show peak-crossed drop in coercivity to different extents. This should mean lack of any alloying in the 12/1 run while alloying to varying extents must be occurring in the runs with other ratios. The actual state of alloying was verified by conducting EPMA line scan analysis on samples of all the six runs, drawn at the 42nd hour of milling time. EPMA was also done on the sample drawn at the 42nd hour of milling time from the run conducted with 150/1 ball ratio. The line scans are shown in Fig.36a* & b and the line scan analysis in Table 8. Samples were also drawn at the 24th hour for all the seven different ball ratio runs. In Figs. 37a* & b and Table 9 are presented the EPMA line scans and the line scan analysis respectively of the samples drawn from 12/1, 18/1, 40/1, 50/1, 100/1 and 150/1 runs at the 24th hour milling time. The results of average chromium pick-up and inhomogeneity (Tables 8 and 9) are plotted as a function of ball ratio in Fig.38 as isochronal curves for 42 hours and 24 hours of constant milling time. Fig.38 reveals, in general, a progressively improving effectiveness of alloying with

* In the EPMA, the Cr line scans for 12/1 ratio run in Fig.36a as well as for 18/1 ratio run in Fig.37a were recorded relative to 10^4 counts, instead of the commonly used 3×10^4 counts scale, in order to boost the feeble Cr signal in these samples. This change is taken into account in the relevant calculations in Table 10.

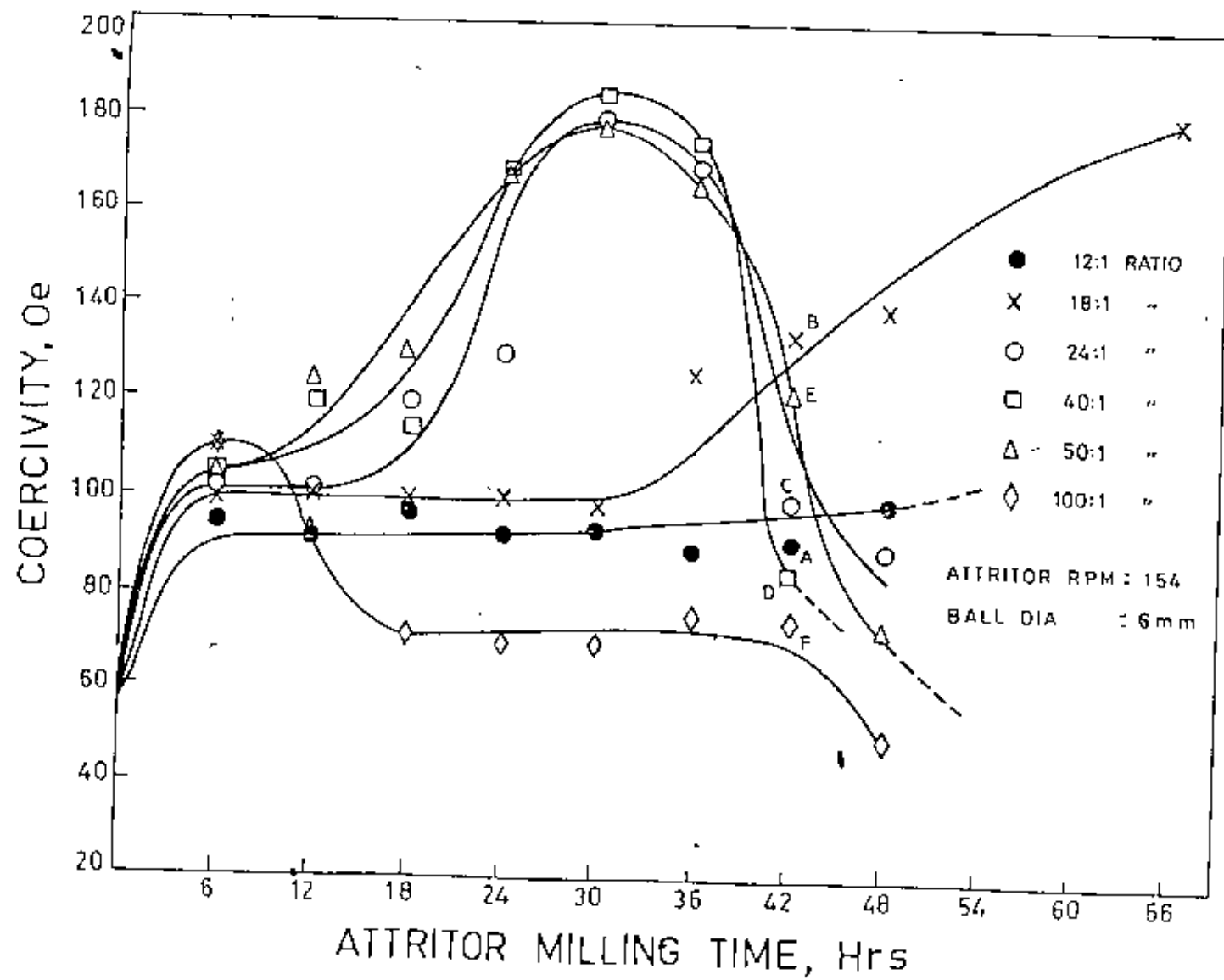
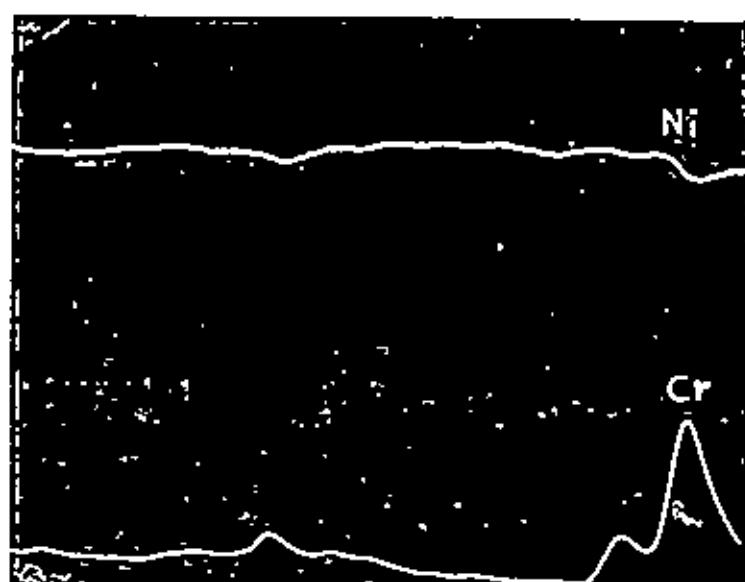
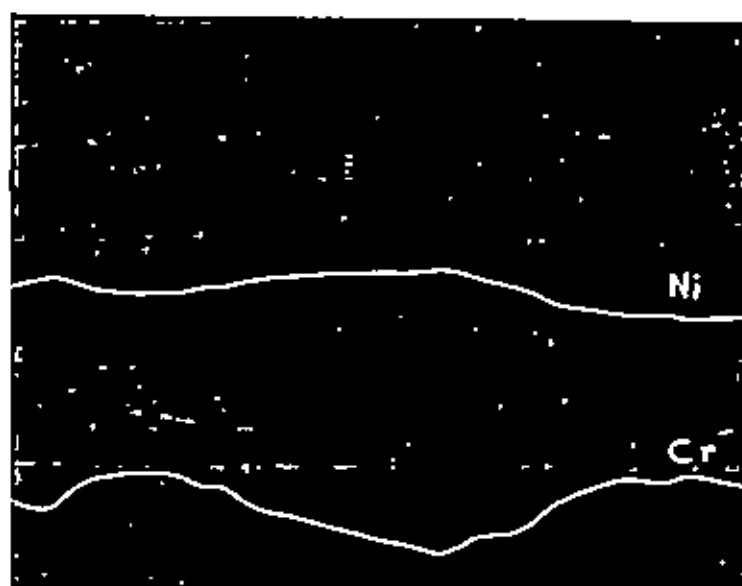


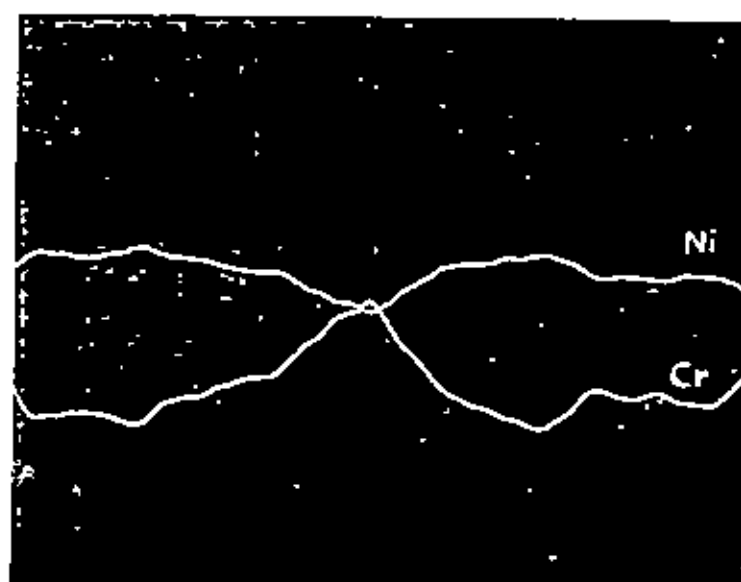
FIG 35 EFFECT OF BALLS - TO - POWDER RATIO ON COERCIVITY VARIATION



12 / 1 BALL RATIO



18 / 1 BALL RATIO



24 / 1 BALL RATIO

FIG 36a EPMA LINE SCANS AFTER 42 HRS MILLING (CONTD)

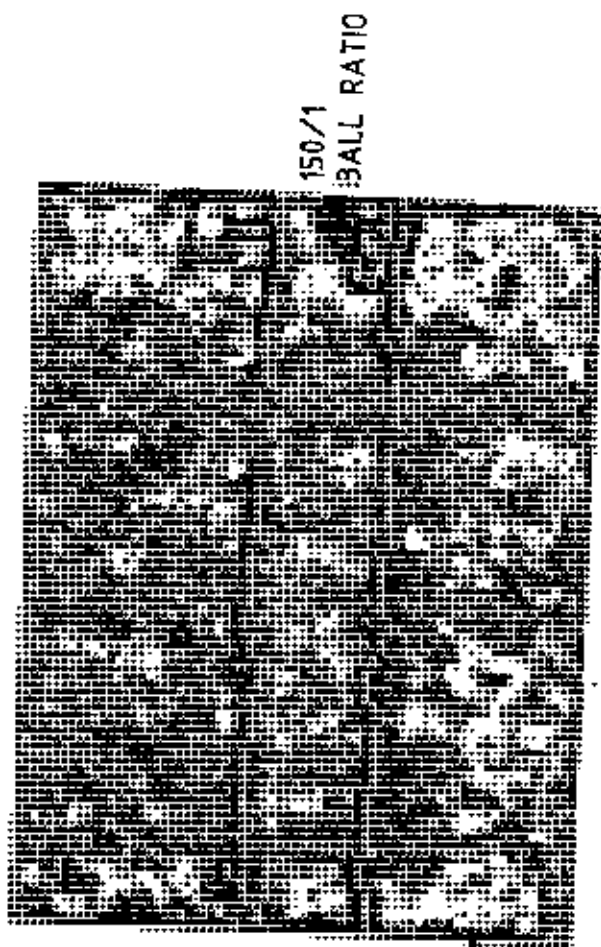
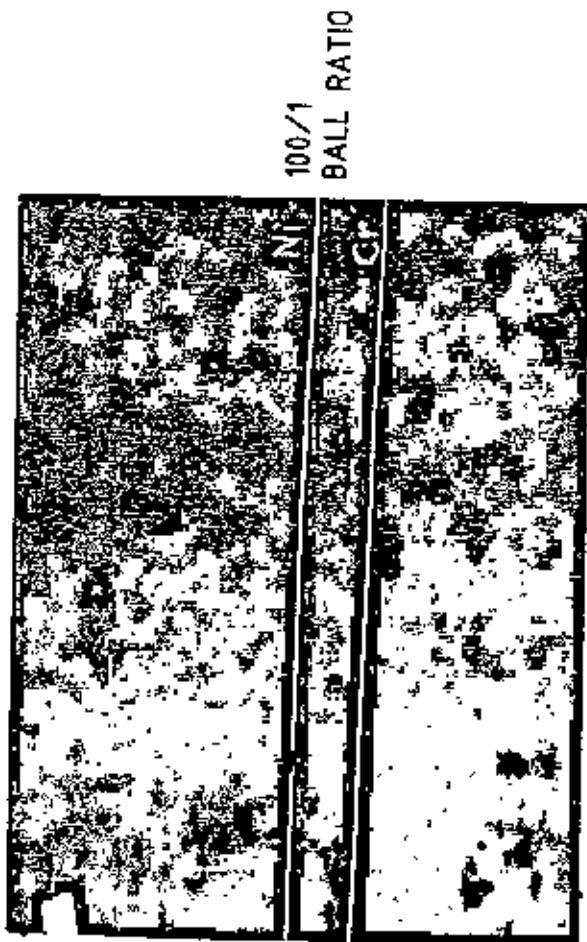
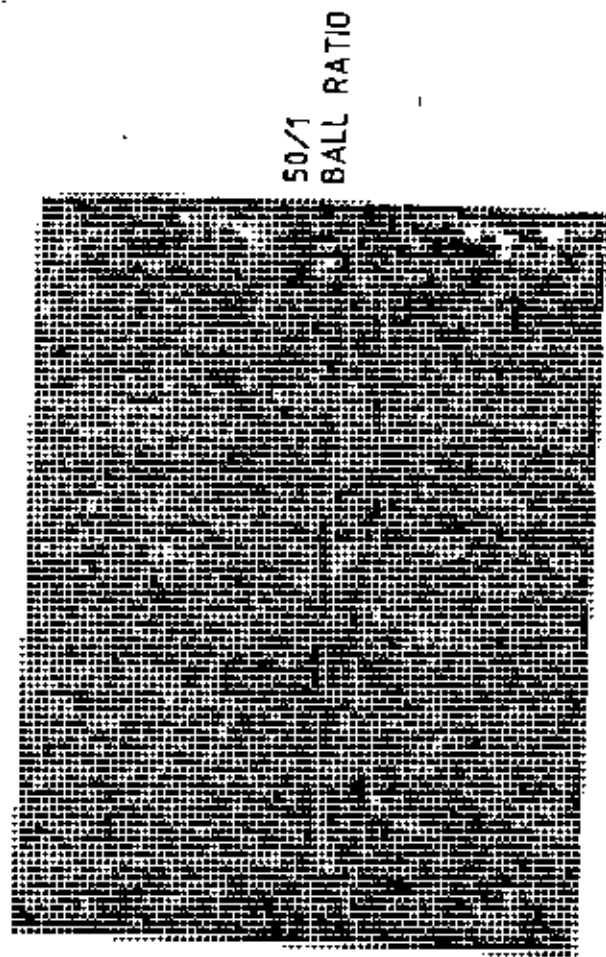
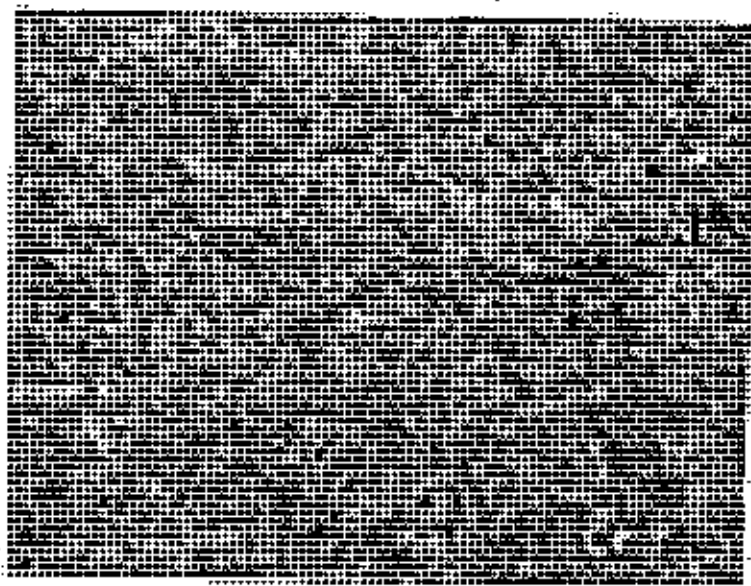
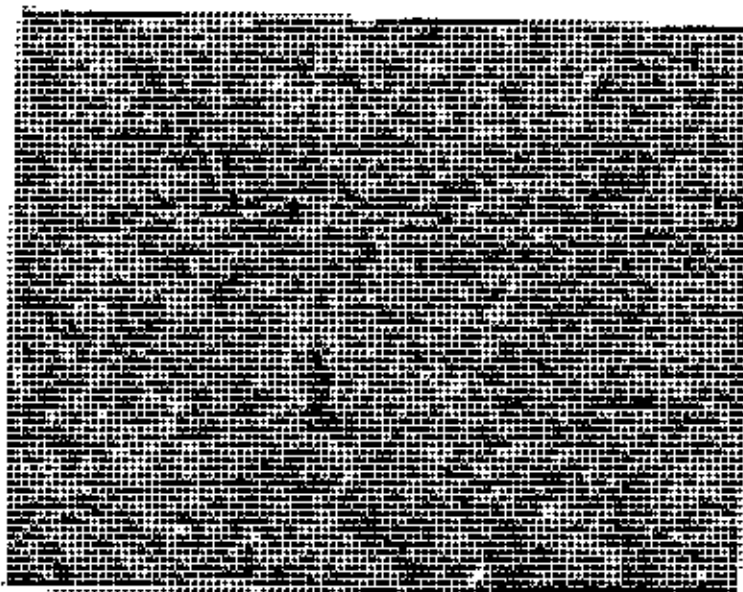


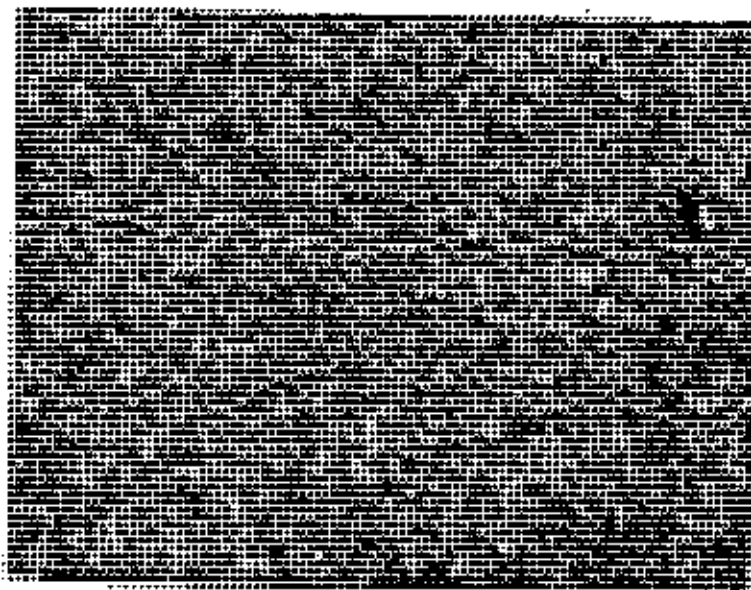
FIG 36 b EPMA LINE SCANS AFTER 42 HRS MILLING



12/1 BALL RATIO

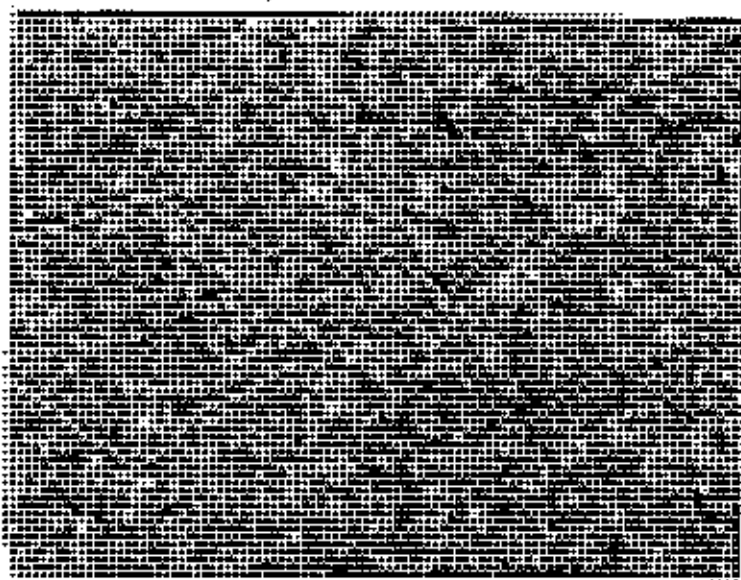


18/1 BALL RATIO

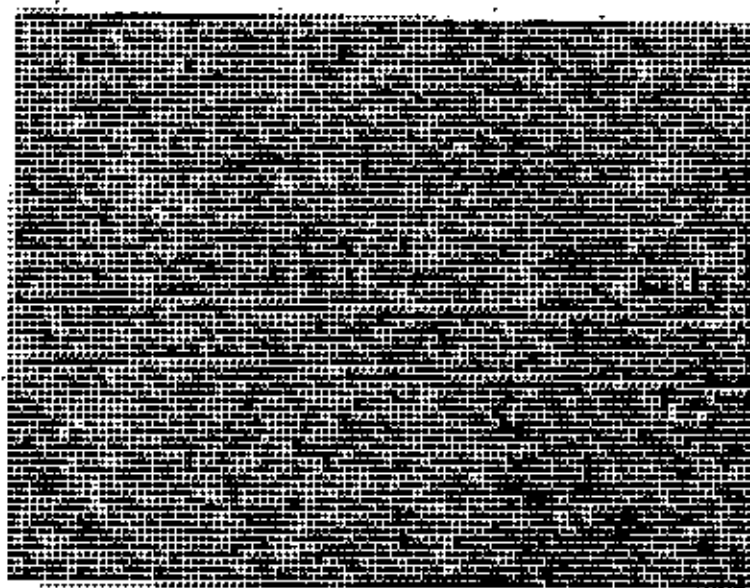


40/1 BALL RATIO

FIG 37 a EPMA LINE SCANS AFTER 24 HRS MILLING (CONTD)



50/1 BALL RATIO



100/1 BALL RATIO



150/1 BALL RATIO

FIG 37 b EPMA LINE SCANS AFTER 24 HRS MILLING

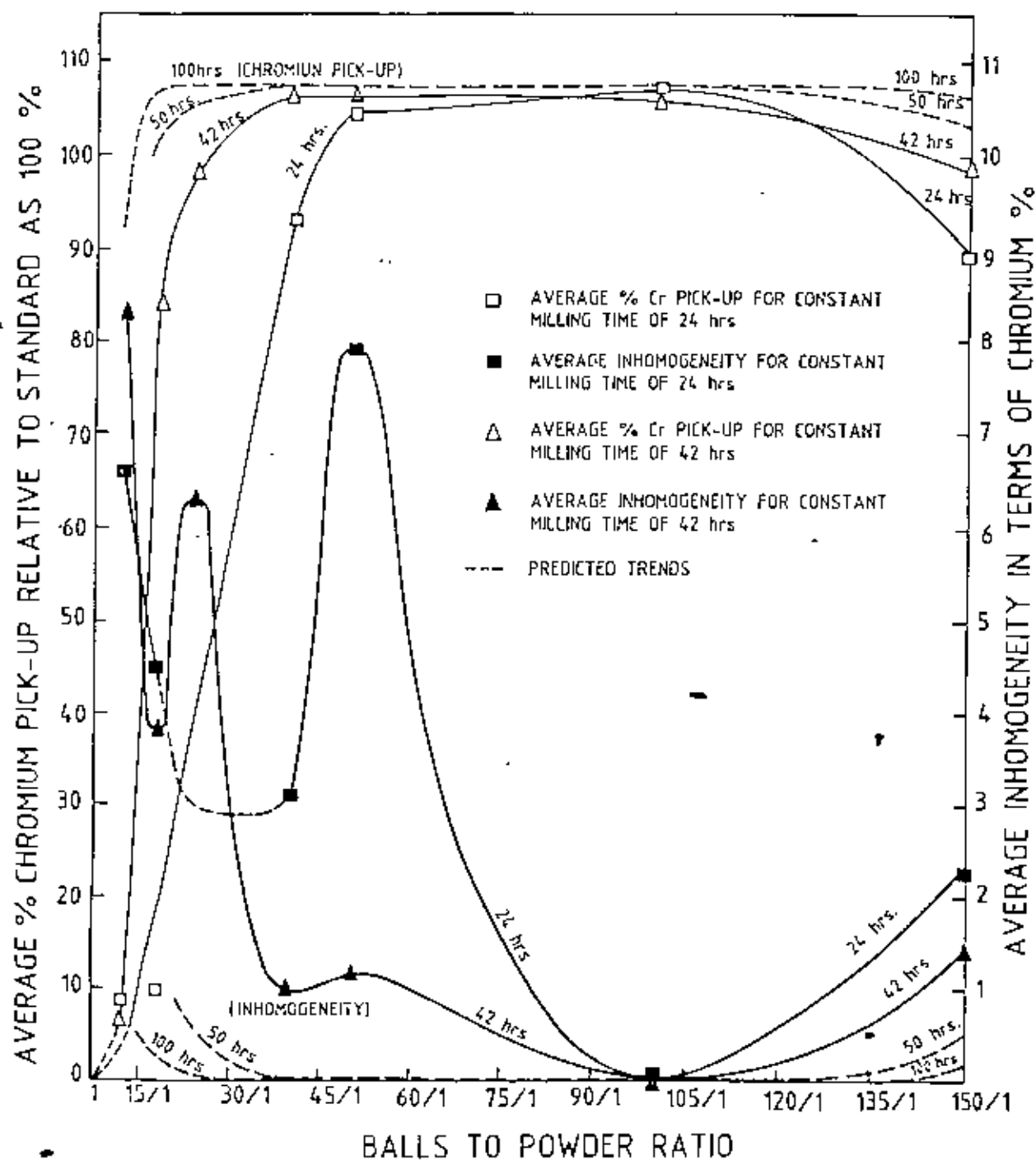


FIG 38 EFFECTIVENESS OF ALLOYING AS A FUNCTION OF BALLS-TO-POWDER WEIGHT RATIO FOR CONSTANT MILLING TIMES

increasing ball ratio for constant milling times. While both milling times show maximum effectiveness of alloying about 100/1 ball ratio, the effectiveness of alloying in the case of 42 hours milling may be taken as satisfactory even from a ball ratio of about 40/1 onwards. Alloying tends to be less effective at ball ratios less than these values. Furthermore, the inhomogeneity curves are marked by peaks of inhomogeneity at certain ball ratios. There is also seen to be no further gain in effectiveness of alloying at ball ratios higher than these values; in fact, at the very high ball ratio of 150/1, the effectiveness of alloying is seen to decrease.

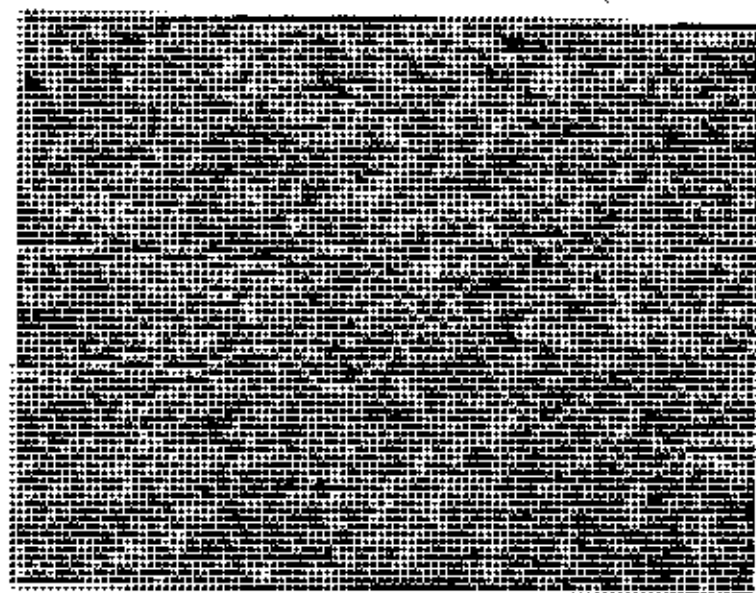
Let us now consider a different method of comparison of efficacy of alloying with varying balls-to-powder weight ratio. Since RPM is the same for all these experiments, the number of revolutions at any given milling time remain the same for all the ball ratios. However, with higher ball ratios obtained through decreasing the powder charge weight, the intensity of collisions experienced by the powder particles will increase. We can thus think of a factor such as NtW (number of performed revolutions $\times$ ball ratio), where

N = RPM of the attritor

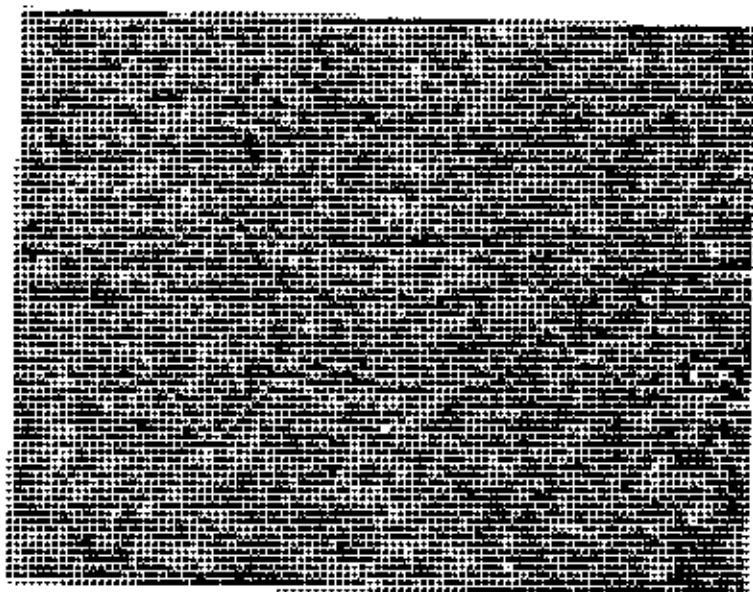
t = time of milling in minutes

W = balls-to-powder weight ratio,

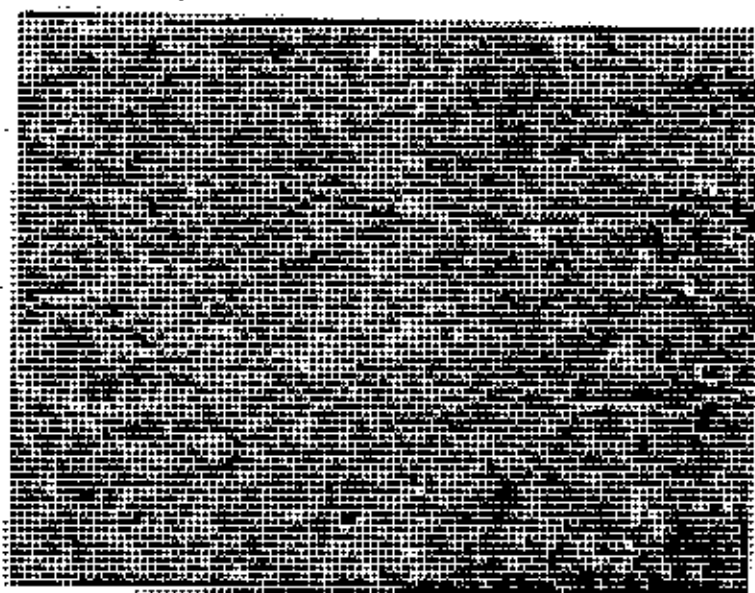
as representing the intensity of collisions. This number becomes different for different ratios for the same milling time, as shown in Table 10. Samples marked A, B, C, D & E in Table 10 — which have approximately the same NtW factor of about 1.1×10^7 — were subjected to EPMA line scan analysis



18/1 BALL RATIO



24/1 BALL RATIO



40/1 BALL RATIO

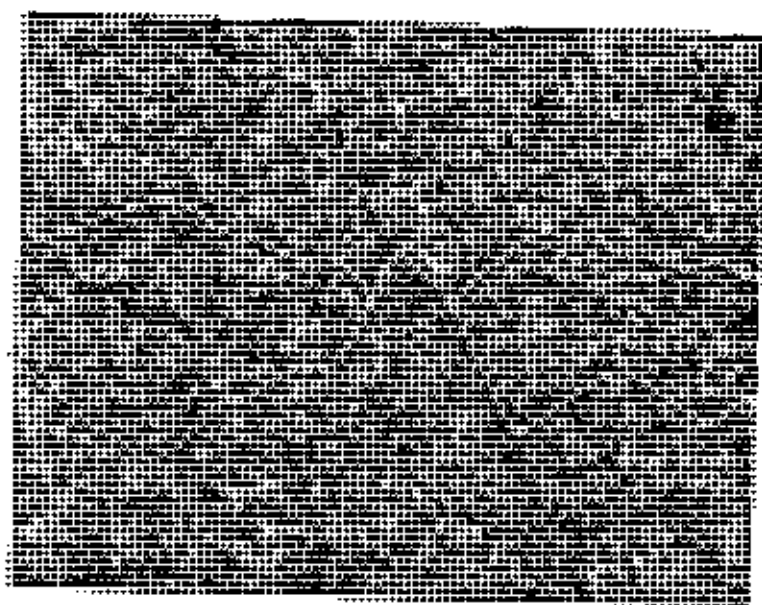
FIG. 39 a EPMA LINE SCANS OF SAMPLES AT
CONSTANT NEW OF $\sim 1.1 \times 10^7$ (CONTD)

whose results are presented in Figs.39a and 39b and Table 11. Similarly samples which have approximately a value of 1.7×10^7 for NtW and marked F, G, H, J, K, L, in Table 10 were analysed by EPMA with their line scans shown in Figs. 40a and 40b, and line scan analysis in Table 12. The data of Tables 11 and 12 are plotted in Fig.41 as ball ratio versus effectiveness of alloying in terms of mean chromium pick-up and inhomogeneity: it is seen that for both 1.1×10^7 and 1.7×10^7 values of NtW, the maximum percentage of average chromium pick-up occurs at about 50/1 ratio but maximum inhomogeneity also occurs at 50/1 ratio. Although the inhomogeneity is very low at the ball ratio of 100/1, the chromium pick-up is seen to diminish at 100/1 ratio. From the shaded areas marked in Fig.41, it will be noticed that a maximum in the chromium pick-up consistent with least inhomogeneity (i.e. maximum effectiveness of alloying) occurs at the same ratio of about 35/1 for both the NtW curves.

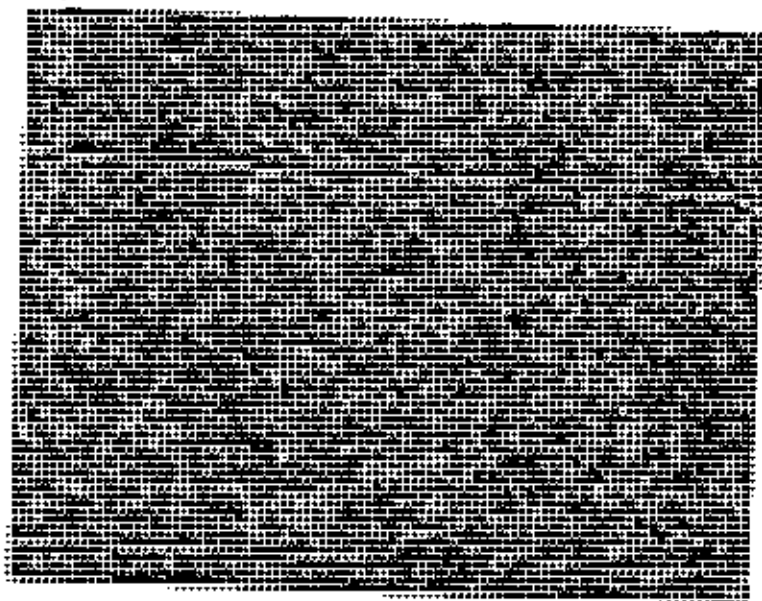
A detailed discussion of these results of the effect of ball ratio is presented in Section 5.4.2.

5.3.3 Effect of ball diameter

The coercivity versus milling time behaviour has been studied for four different ball diameters namely, 4mm, 6mm, 8mm and 10mm. The results are presented in Fig.42. The 4mm and 6mm ball experiments do not show peak-crossed drop in coercivity within 48 hours of milling time while the 8mm and 10mm ball runs do. This indicates a better degree of alloying for ball diameters of

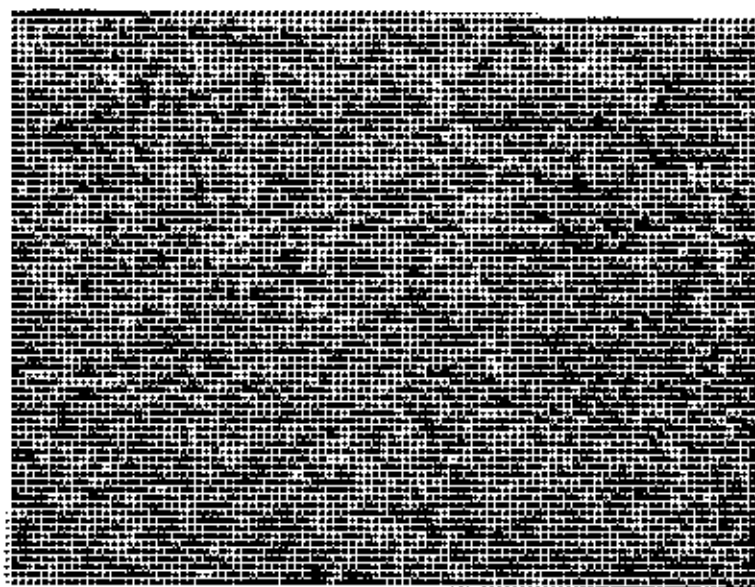


50/1 BALL RATIO

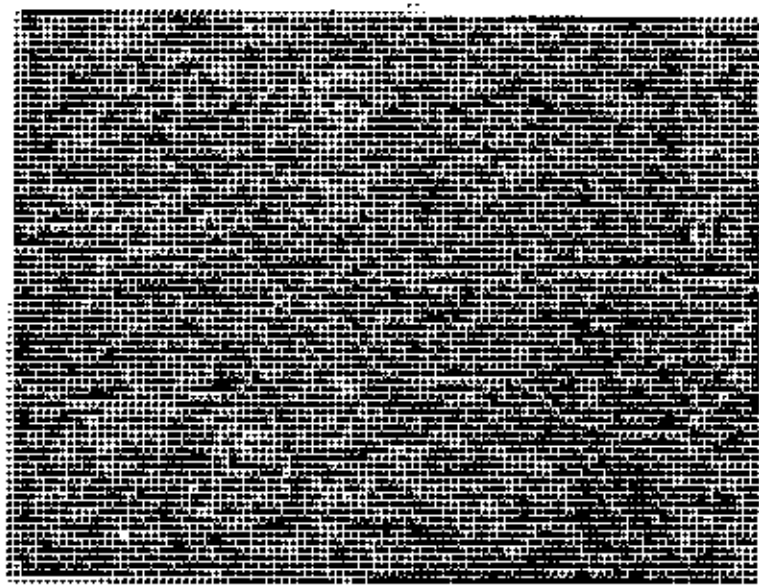


100/1 BALL RATIO

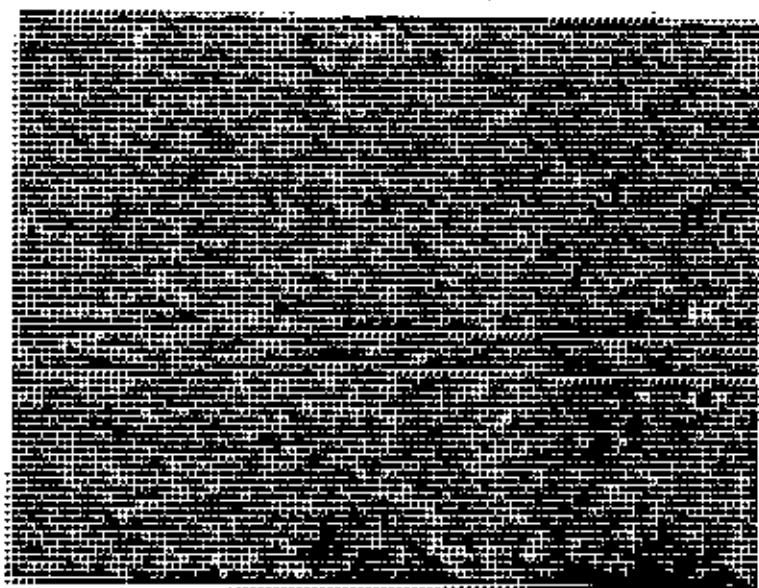
FIG 39 b EPMA LINE SCANS OF SAMPLES AT CONSTANT
NTW OF $\sim 1.1 \times 10^7$



18/1 BALL RATIO

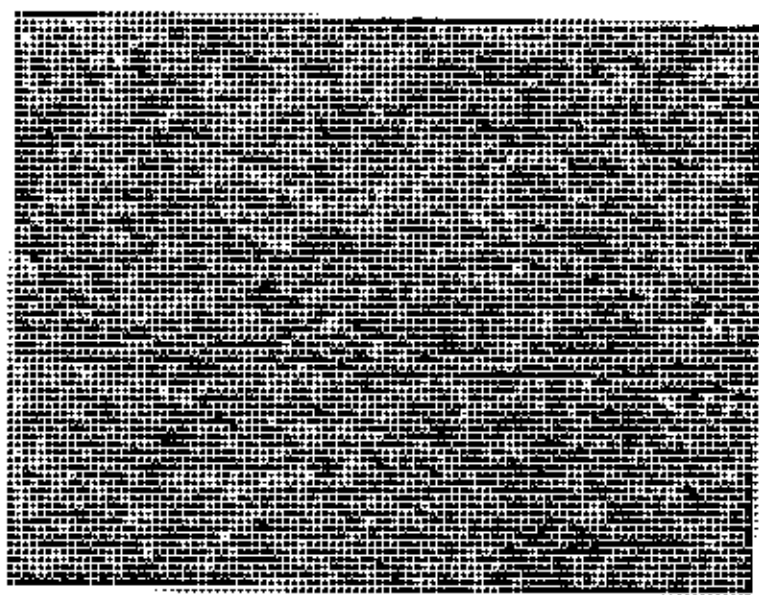


24/1 BALL RATIO

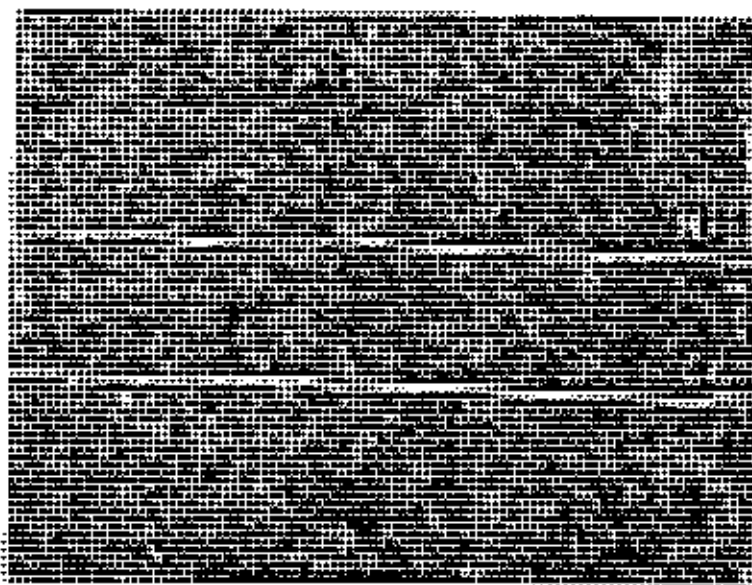


40/1 BALL RATIO

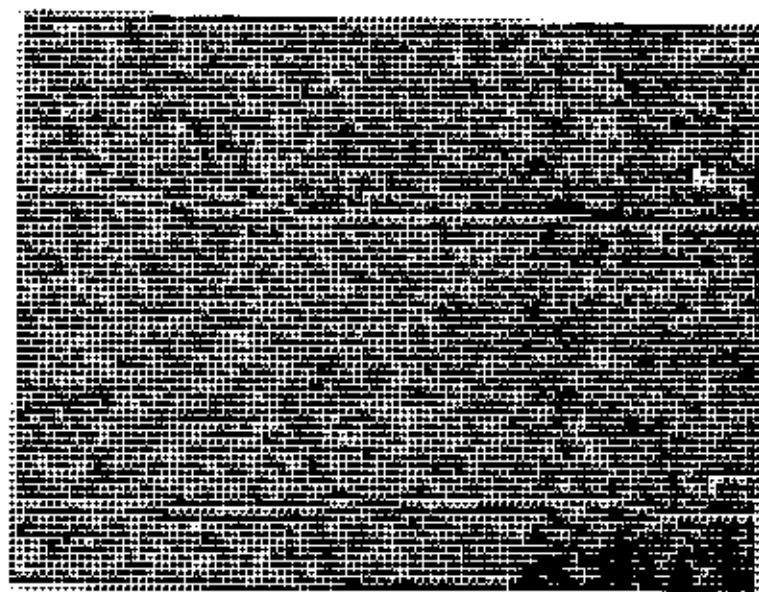
FIG 40 a E. M. LINE SCANS OF SAMPLES AT CONSTANT
NEW OF $\sim 1.7 \times 10^7$ (CONTD)



50/1 BALL RATIO



100/1 BALL RATIO



150/1 BALL RATIO

FIG 40 b EPMA LINE SCANS OF SAMPLES AT CONSTANT
NtW OF $\sim 1.7 \times 10^7$

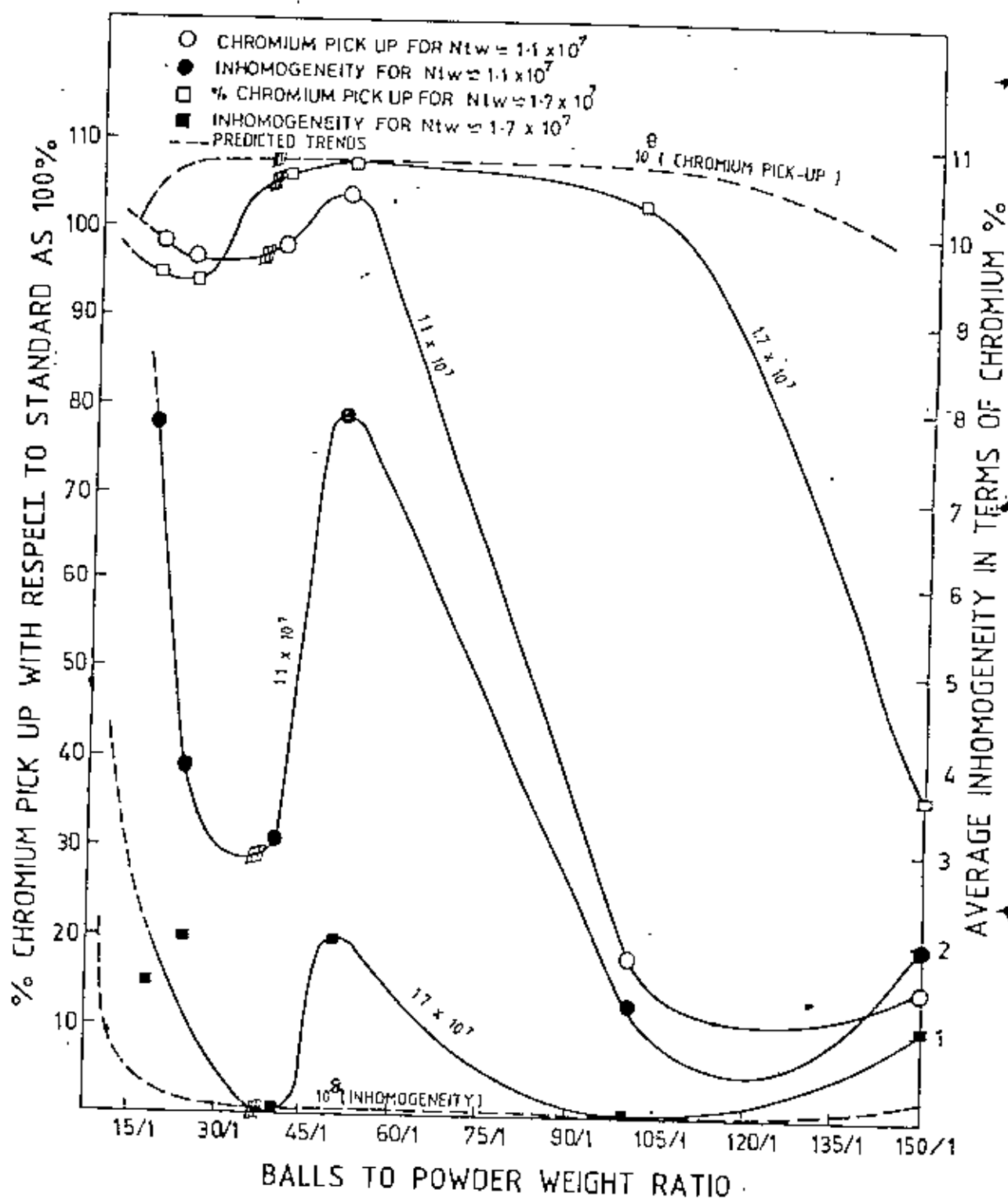


FIG 41 EFFECTIVENESS OF ALLOYING AS A FUNCTION OF BALLS-TO-POWDER WEIGHT RATIO FOR CONSTANT VALUES OF NtW

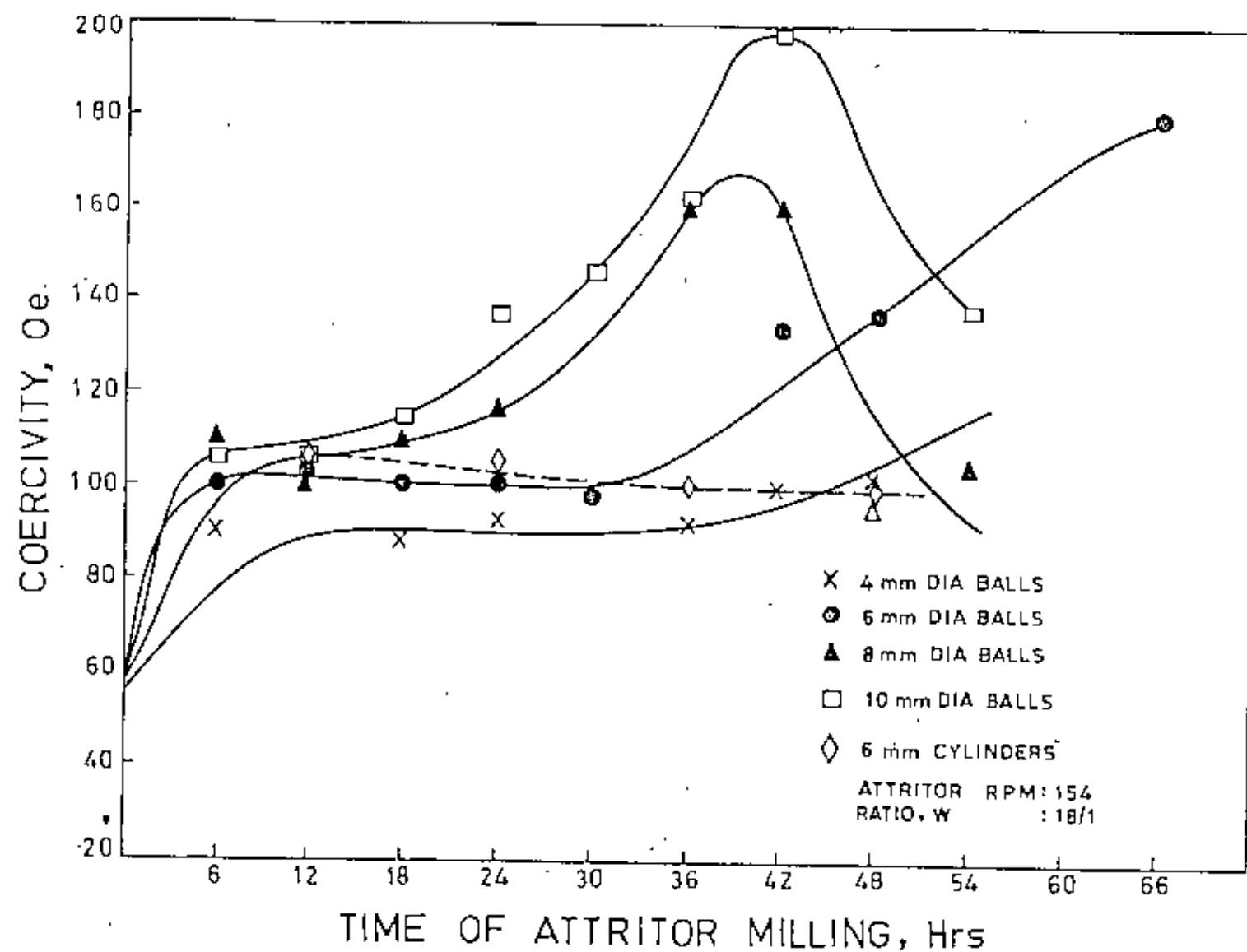


FIG 42 EFFECT OF BALL DIAMETER ON THE COERCIVITY
VARIATION IN ATTRITOR MILLING

8mm and 10mm. The value of the peak-crossed drop in coercivity for 8mm ball run is lower than the value for 10mm ball run, suggesting more effective alloying in the former case.

The EPMA line scans and line scan analysis of samples drawn after 42 hours milling for the four ball diameter experiments depicted in Fig.43 and Table 12 respectively clearly bring out the generally increasing degree of alloying of chromium in nickel as the ball diameter increases, vindicating the coercivity trends. The results of Table 12 are plotted in Fig.44 as ball diameter versus effectiveness of alloying. While the chromium pick-up curve reaches a maximum at 6mm ball diameter and remains approximately at that level from then onwards, a minimum in the inhomogeneity curve can be seen to occur at about 8mm diameter. This indicates that the maximum effectiveness of alloying in 42 hours milling time can be realised with the use of 8mm diameter steel balls.

5.3.4 Effect of shape and material of balls

In addition to a study of the ball size effect, the alloying behaviour with grinding media differing in shape and material from the hardened steel spheres was examined. 6mm dia x 6mm height cylinders of stainless steel have been chosen as a case of a different shape. This shape has a surface area larger than that of a 6mm diameter ball. The constituent powders were attritor milled with these cylindrical elements in 18/1 ball ratio at 154 RPM for which the coercivity versus milling time curve (Fig.42) shows no peak in 48 hours indicating

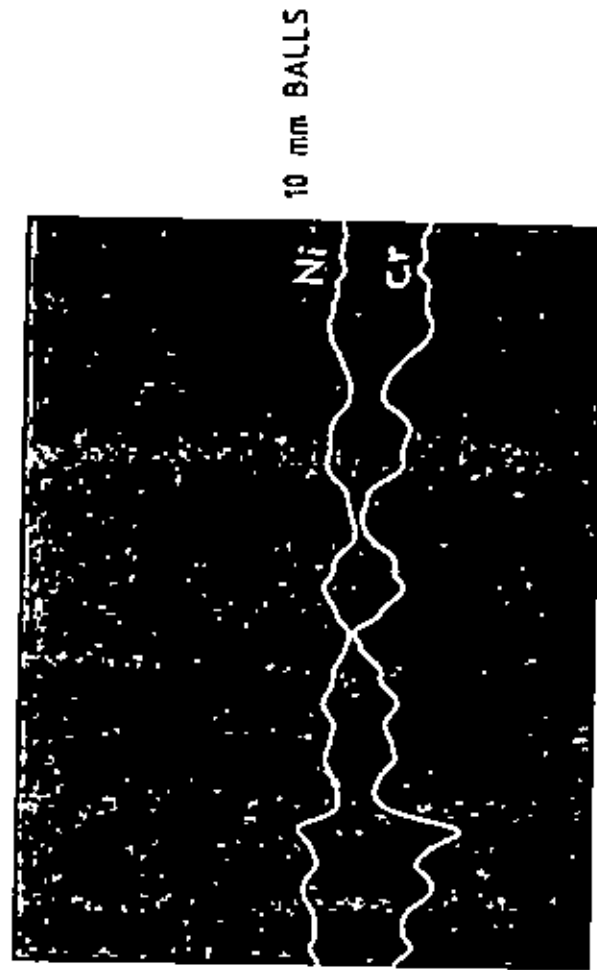
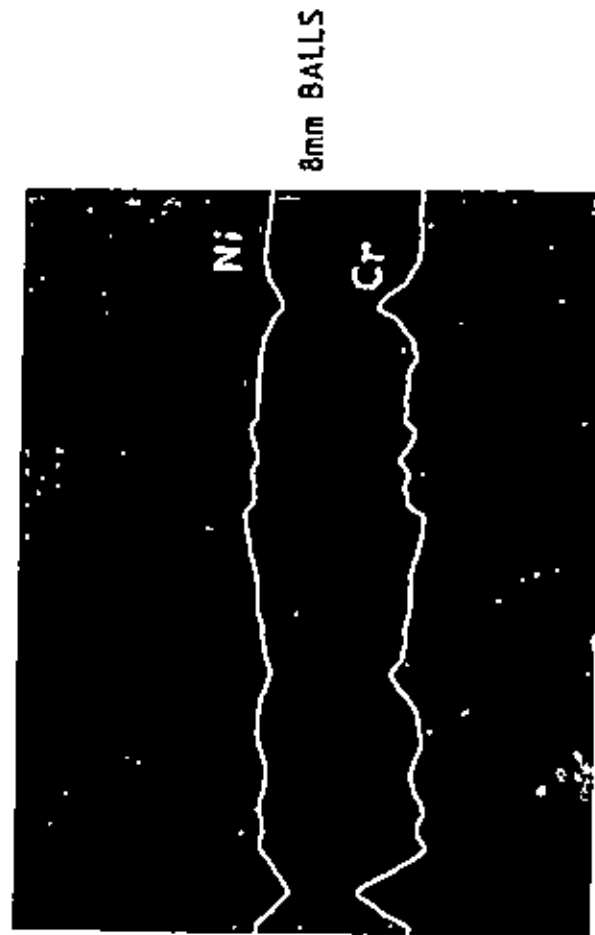
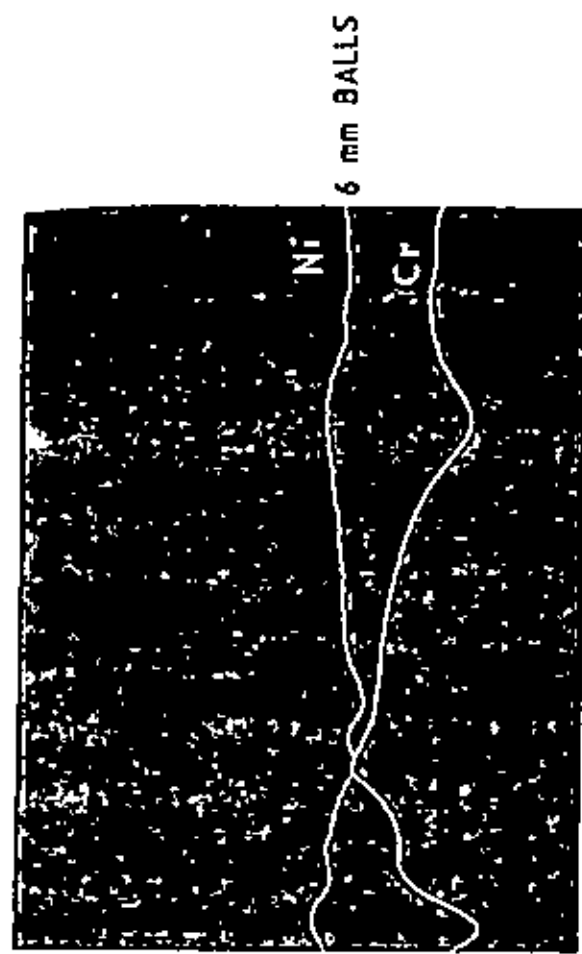


FIG 43 EPMA LINE SCANS OF SAMPLES AFTER 42 HRS MILLING

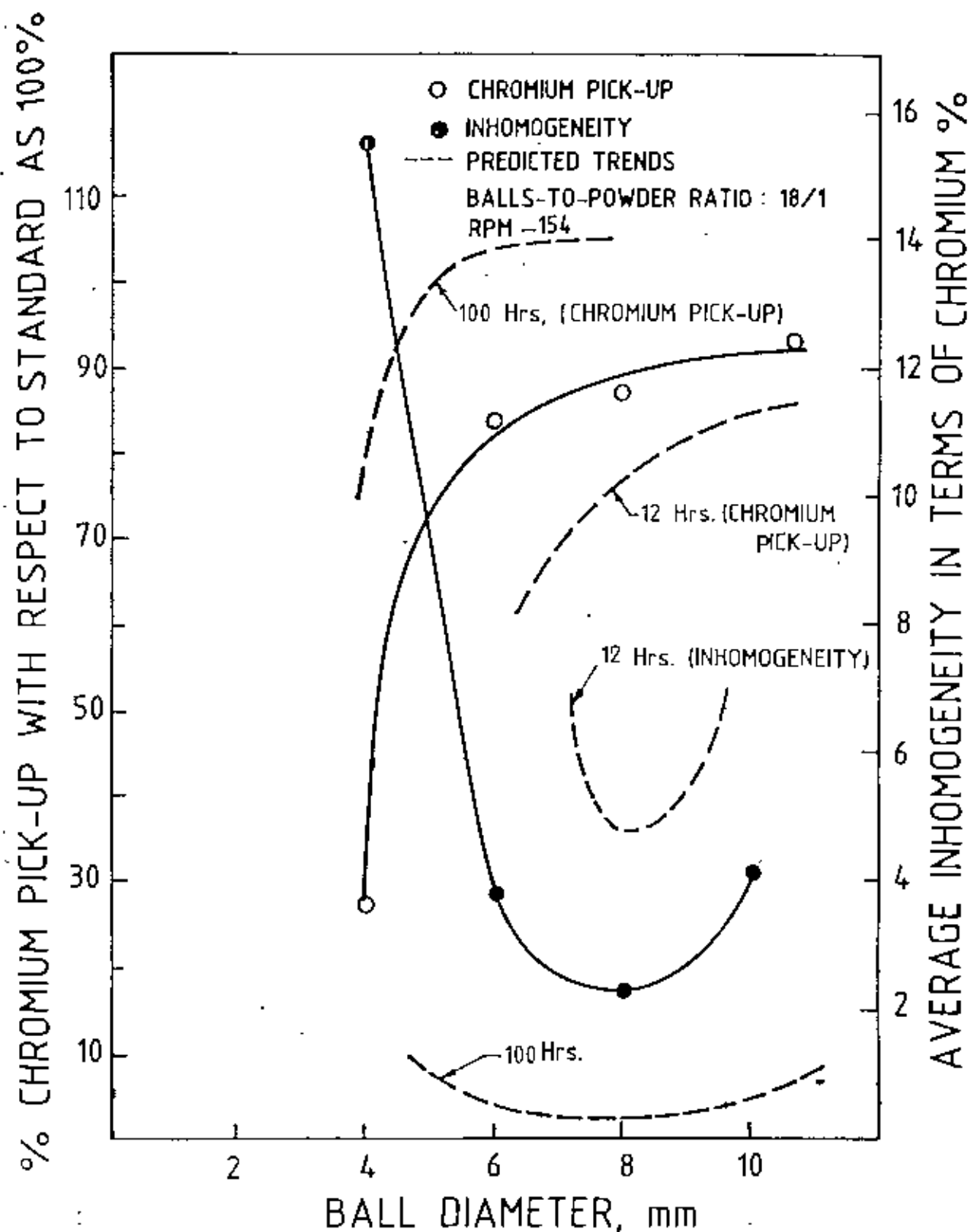


FIG 44 EFFECTIVENESS OF ALLOYING WITH INCREASING BALL DIAMETER AFTER 42 HRS MILLING

An attempt has been made in gaining this understanding by conducting attritor milling experiments with a few variants of impeller shapes. Three experiments were done in which the attritor was run using round, triangular and flat impellers (Fig.46). All the three experiments were done with 6mm balls in 18/1 ratio and at an attritor speed of 154 RPM.

The coercivity variations with attritor milling time for the three shapes are plotted in Fig.47 which shows the absence of any peak for flat impellers and a tendency for coercivity to peak but not to a peak-crossed drop for round vanes, and a peak-crossed drop in coercivity for triangular shape vanes within the observed milling time frame of about 54 hours. The EPMA line scans and the EPMA line scan analysis of samples drawn at the 48th hour milling time from the three experiments are presented respectively in Fig.48 and Table 13. These results indicate that the triangular impeller does bring about higher level of chromium pick-up and with much less inhomogeneity than the other two shapes considered here.

5.3.6 Number of impellers

In a given length of shaft, how many impellers are required for mechanical alloying? To attempt an answer to this question, two basic configurations have been tried. Configuration 'A', where 8 round impellers in sets of two impellers opposite each other are placed one set above the other, each set being placed at 90° to the neighbouring set as shown in Fig.49. Another configuration (Fig.50)

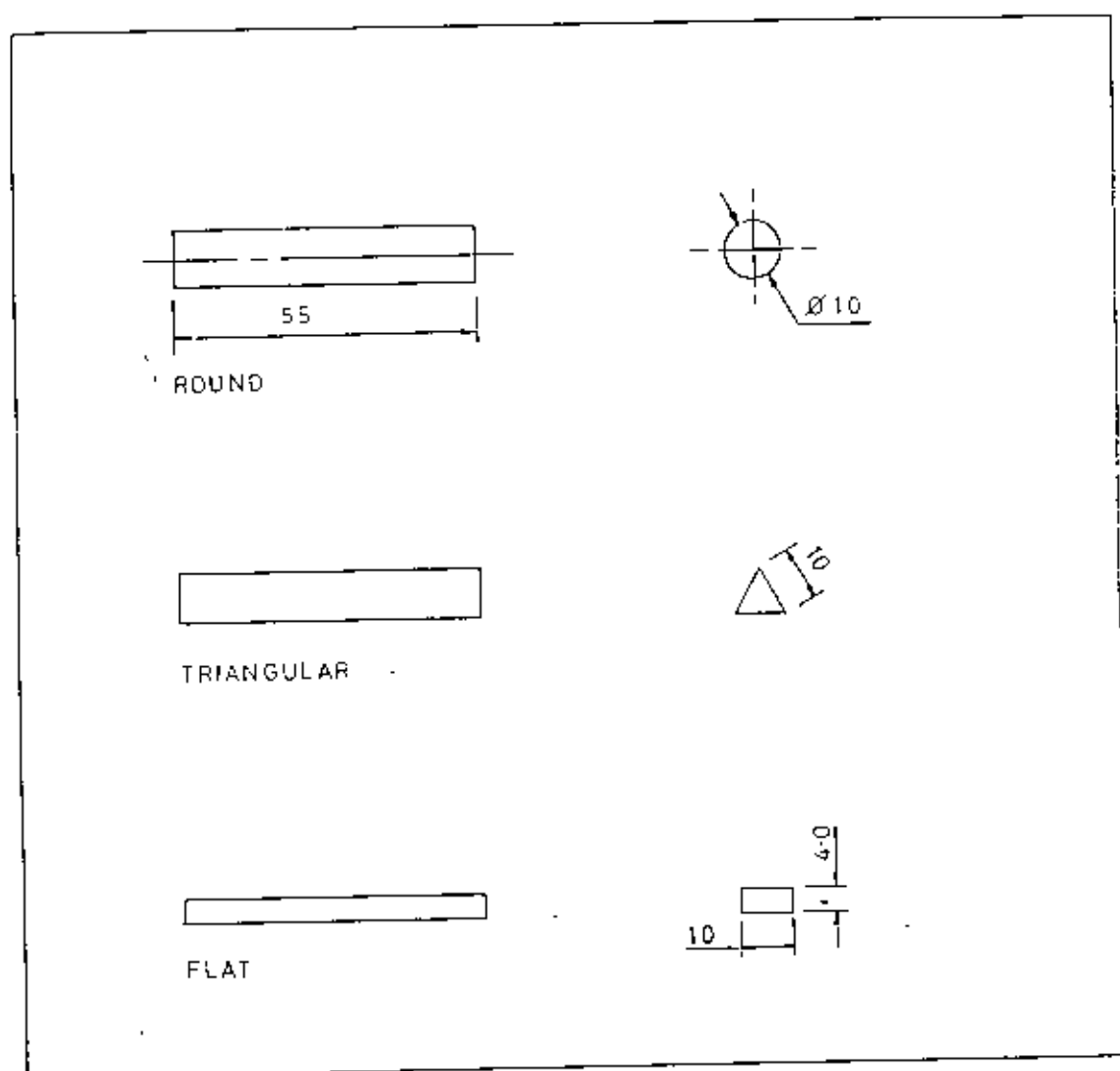


FIG 46 THREE SHAPES OF IMPELLERS TRIED
IN THE ATTRITOR

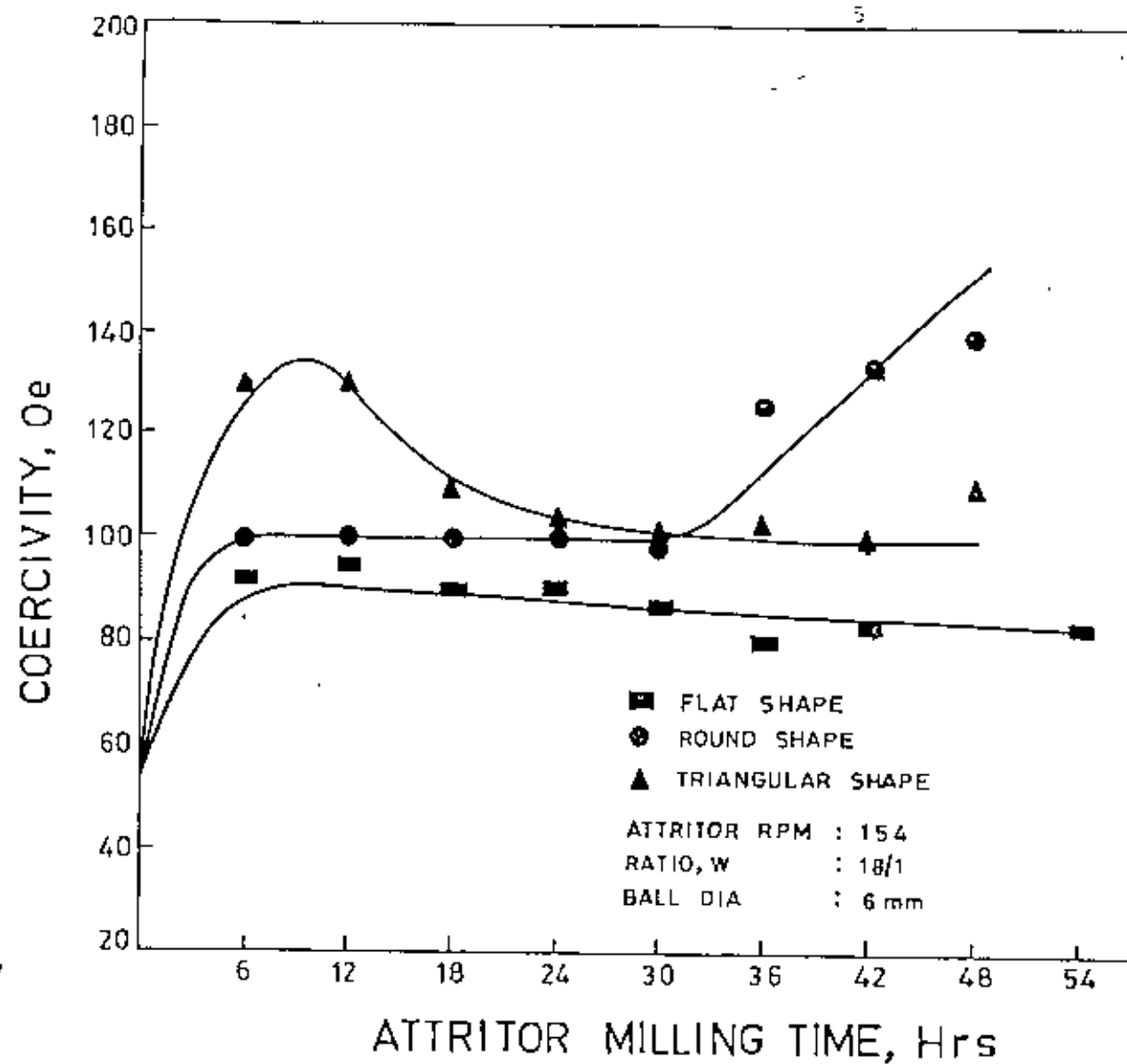
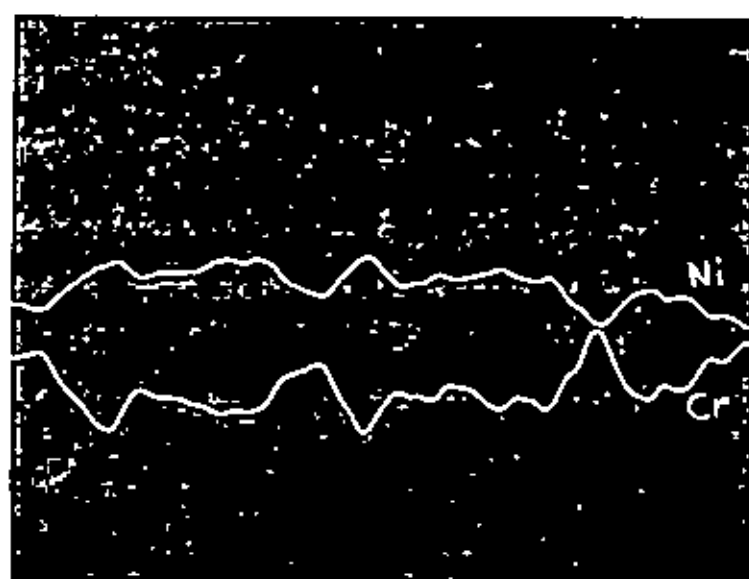


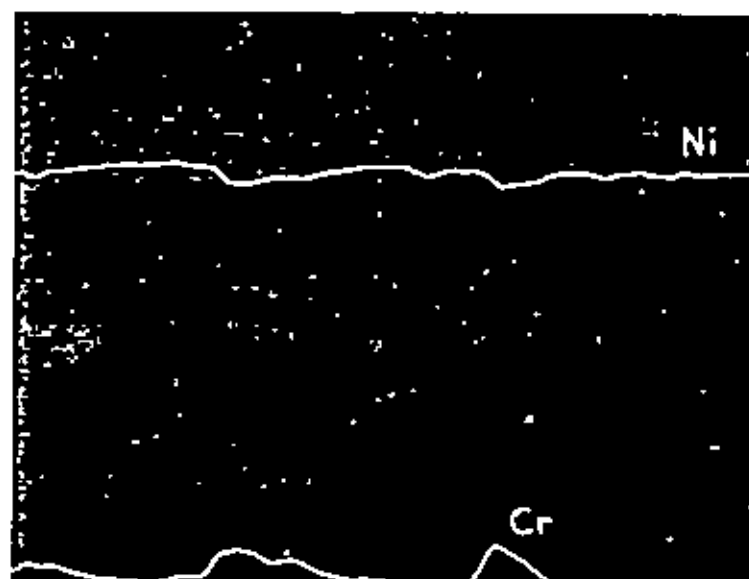
FIG 47 EFFECT OF IMPELLER SHAPE ON COERCIVITY VARIATION IN ATTRITOR MILLING



ROUND IMPELLERS



TRIANGULAR IMPELLERS



FLAT IMPELLERS

FIG. 48 EPMA LINE SCANS AFTER 42 HRS MILLING

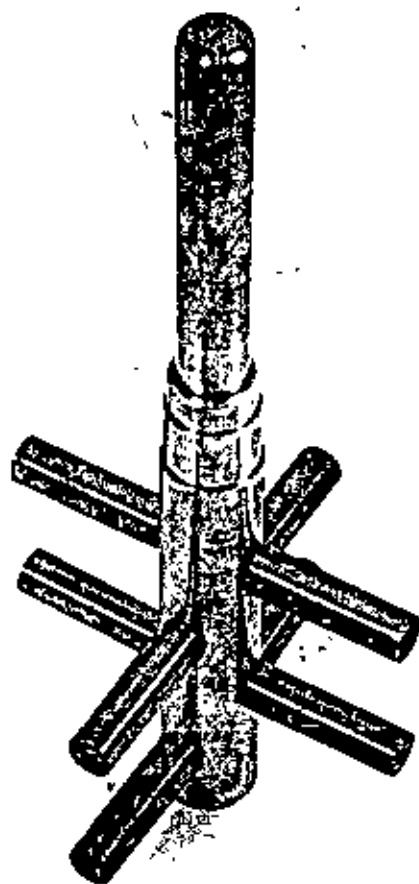


FIG 49 8 - IMPELLER CONFIGURATION OF ATTRITOR
SHAFT ASSEMBLY

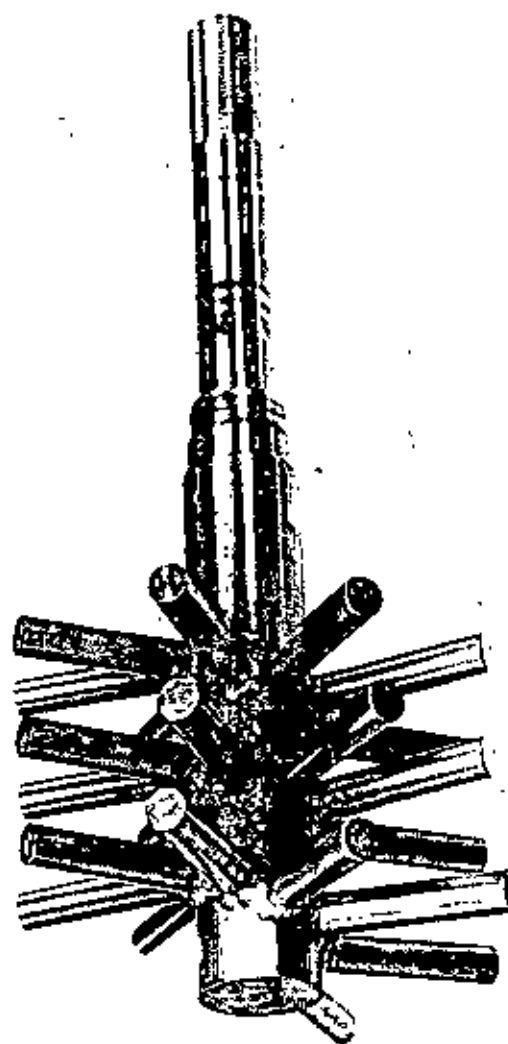


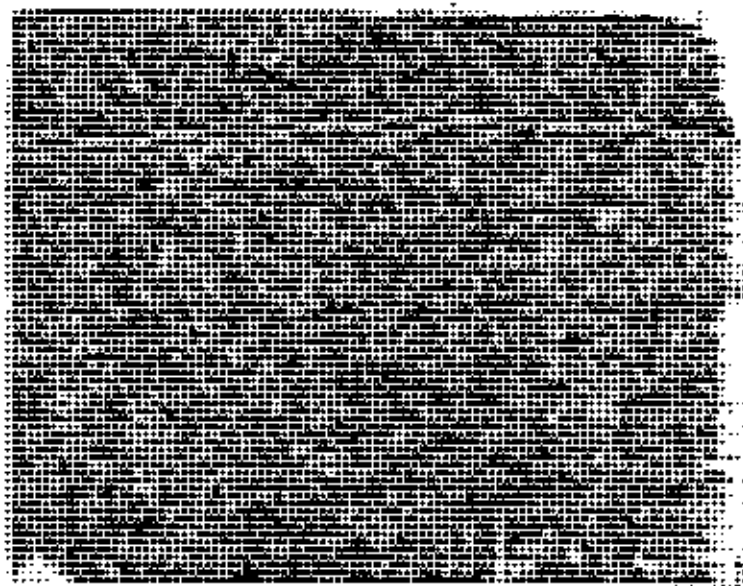
FIG 50 21 - IMPELLER CONFIGURATION OF ATTRITOR
SHAFT ASSEMBLY

denoted as 'B' is fabricated with 21 round impellers along the length of the shaft, arranged in a helical fashion; this is almost triple the number of vanes in the same length of the shaft as compared to the former configuration. The constituent powders were attritor milled under identical conditions (154 RPM speed, 6mm ball diameter and 18/1 ball ratio) in two successive runs of 48 hours with these two different impeller configurations. The EPMA line scans and the line scan analysis of the powder samples drawn at the 48th hour milling time for both A and B runs are shown in Fig.51. The total absence of Cr signal in Fig.51b reveals the poor state of alloying for 'B' configuration.

5.3.7 Baffled attritor

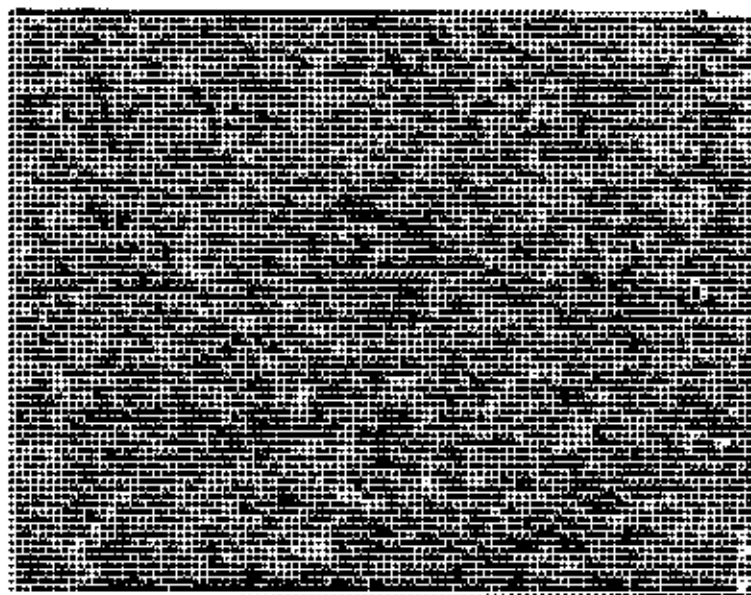
The use of baffles in agitator tanks is common in chemical engineering practice whereby a well-mixed condition of the constituents is ensured because these baffles help in eliminating vortex formation of the solid-liquid/liquid-liquid blends, break up the eddies and thus bring a greater degree of mixing of the constituents (132). A question that arises in this context is whether baffling of the attritor is desirable for mechanical alloying.

To answer this problem, standard design parameters for baffled agitator tanks have been applied to the attritor. Although several variations of design for different applications prevail, it is generally prescribed in chemical engineering practice of design of baffled agitators that:



a

21 IMPELLERS.



b

8 IMPELLERS

FIG 51 EPMA LINE SCANS AFTER 48 HRS MILLING

i) Height of tank (H_T)	=	Diameter of the tank (D_T)
ii) Diameter of impeller	=	$1/3 D_T$
iii) Height of impeller from tank bottom=		Diameter of impeller
iv) Width of baffle	=	$1/10 D_T$
v) Length of baffle	=	Height of tank
vi) Number of baffles	=	4

The attritor used in this work, which already has a vessel height almost equal to the vessel diameter thus satisfying the first requirement, has been modified to provide for the impellers and baffles according to the above standard features shown schematically in Fig.52. The vessel wall of the experimental attritor was tack-welded inside with four narrow strips of stainless steel at diametrically opposite positions. The attritor was then run with the same charge of nickel, chromium and thorium at 154 RPM using 6mm diameter balls in 18/1 weight proportion. The attritor milled sample at the 48th hour was subjected to EPMA line scan whose result is shown in Fig.53 which can be compared with a line scan of a similarly attritor milled powder sample from an unbaffled attritor (Fig.51b). This clearly indicates that the baffled attritor yielded a very poor result in terms of degree of alloying.

These results of the effects of impeller shape, number of impellers and baffles in the attritor are discussed in some detail in Section 5.4.4.

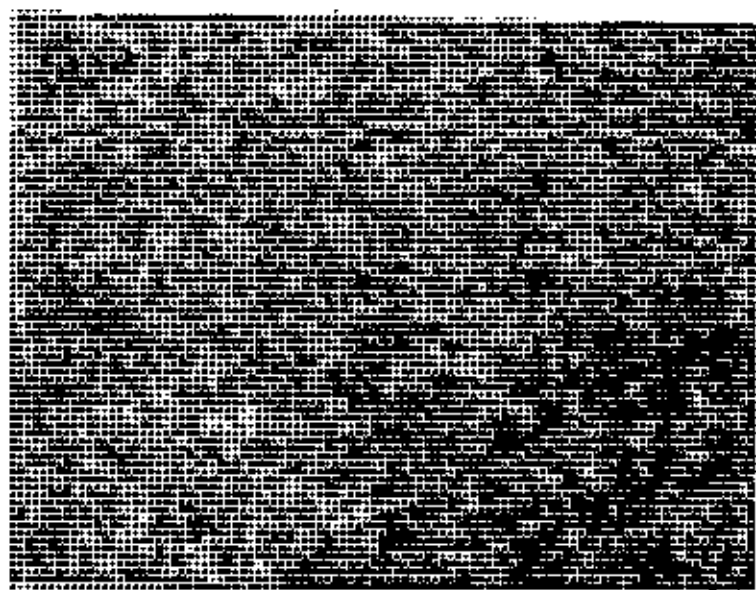


FIG 53 EPMA LINE SCANS AFTER 48 HRS MILLING
WITH BAFFLES IN THE ATTRITOR

5.3.8 Effect of starting particle size

Since attritor milling for mechanical alloying involves particle comminution and particle welding, one would expect the alloying kinetics to be influenced by the starting average particle sizes of nickel and chromium powders. Four different size combinations of nickel and chromium powders as given in Table 15 were tried out in order to study the influence of particle size on mechanical alloying. The powder-sizes selected are arbitrary, as per their ready availability in the laboratory. Table 5 reflects a scheme of combining the available coarse and fine powders of nickel and chromium in four combinations which are designated as 8/45, 8/12, 25/45 and 25/12; (in each of these designations, the first number denotes the average particle size of nickel powder and the subsequent number denotes the average particle size of chromium powder).

The above combinations of nickel and chromium were attritor milled for about 54 hours except for run 8/12 which had to be terminated at the 48th hour. The coercivity-versus-milling time plots for these experiments are presented in Fig.54. Samples drawn at the 48th hour were subjected to line scan EPMA. The EPMA line scans of 8/45 & 8/12 runs are shown in Fig.55a and of 25/45 & 25/12 in Fig.55b. Their line scan analysis is presented in Table 16.

It is seen from Fig.54 that peak crossed drop in coercivity occurs for runs 8/12, 25/12 and 25/45 while there is only a tendency towards peak in coercivity for the 8/45 run within the common milling time of 48 hours. These trends indicate effective alloying for the former three combinations and poor alloying for the latter one. Same trends of alloying are confirmed in EPMA too (Figs.55a and

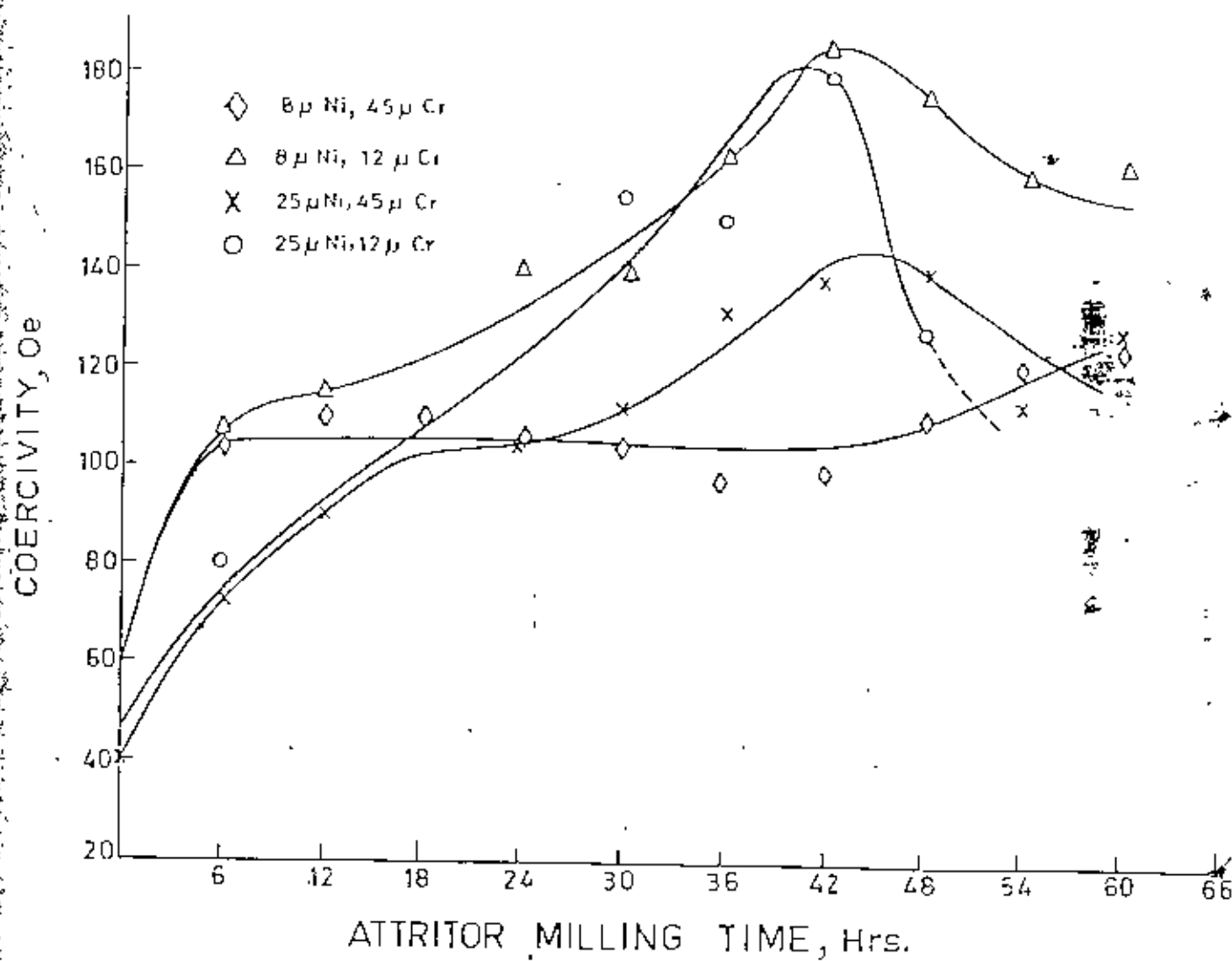
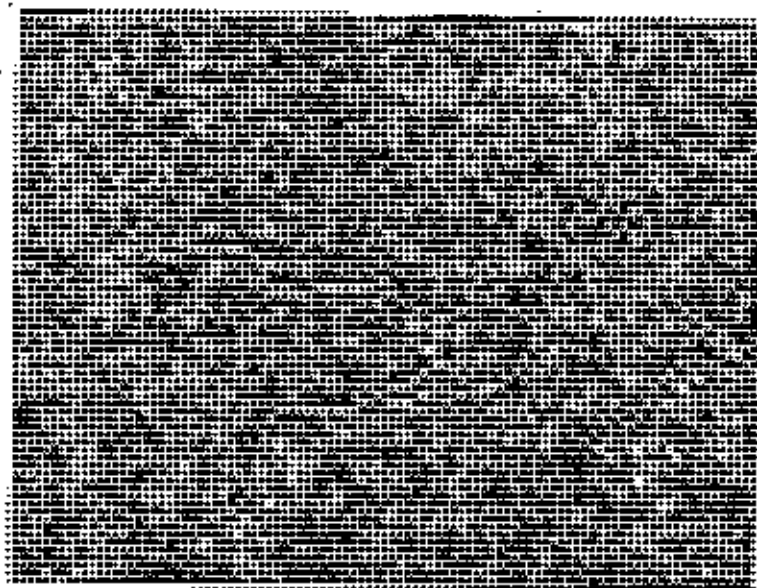
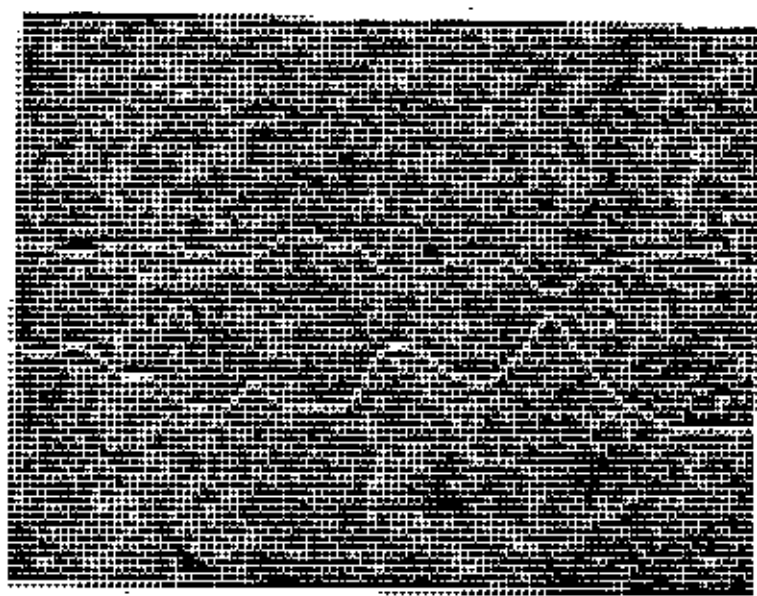


FIG 54 EFFECT OF STARTING PARTICLE SIZE OF Ni AND Cr ON COERCIVITY VARIATION

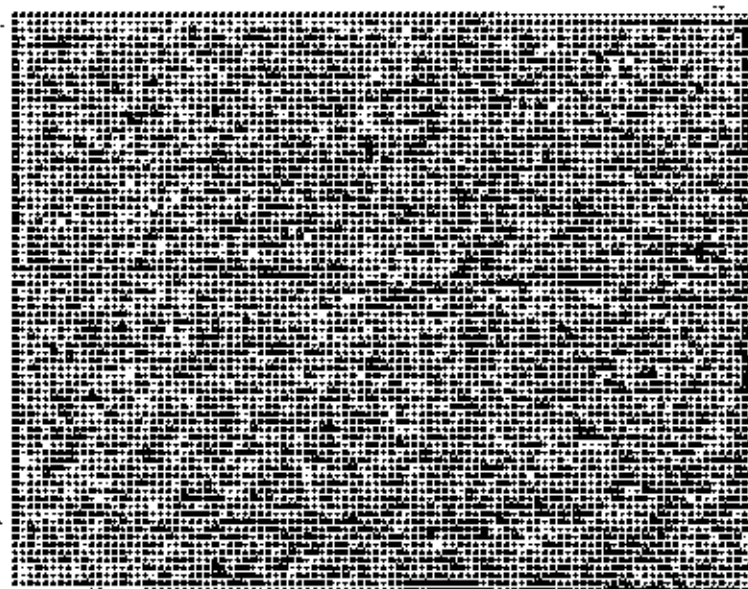


25 μ Ni, 45 μ Cr



25 μ Ni, 12 μ Cr

FIG 55 a EPMA LINE SCANS AFTER 48 HRS
MILLING WITH DIFFERENT STARTING
PARTICLE SIZES (CONTD)



8 μ Ni, 45 μ Cr



8 μ Ni, 12 μ Cr

FIG 55 b EPMA LINE SCANS AFTER 48 HRS MILLING
WITH DIFFERENT STARTING PARTICLE SIZES

55b and line scan analysis in Table 16). These experiments thus reveal that more effective alloying is possible in combinations where fine chromium powder is used, whereas coarse nickel appears to be more effective in alloying than fine nickel powder out of the two nickel powder sizes that have been tried. Discussion on these results is presented in Section 5.4.5.

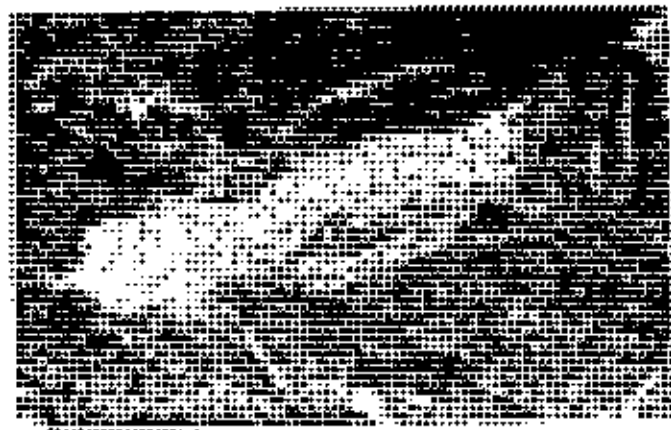
5.3.9 Effect of sequence of alloying additions

An important problem noticed in the optical microstructures of the HIP consolidated Ni-20Cr-2ThO₂ alloy is discussed here. Fortunately, it could be solved by a modification in the attritor milling procedure indicating the importance of milling procedures.

The HIP-consolidated compacts of Ni-20Cr-2ThO₂ attritor milled under various milling conditions described previously have revealed a peculiar feature in their microstructure, a typical example of which is shown in Fig.56a. As seen here, a light-etching phase (appearing white) is present in a network fashion, whereas the optical microstructure should reveal a single-phase solid solution of Ni-20Cr, thorium particles being in the sub-optical range. At higher magnification, the light etching phase in the HIPed microstructure reveals recrystallised type of equiaxed, fine grain structure (Fig.56b). Several quantitative measurements of this phase in EPMA have shown that it contains nearly 80% nickel and 20% chromium while the dark-etching matrix contained the aimed composition of approximately 20% chromium and 78% nickel. Thorium



a



b



c



d

FIG 56a NETWORK OF LIGHT ETCHING PHASE IN HIP CONSOLIDATED POWDER , 100X

FIG 56b RECRYSTALLIZED GRAIN STRUCTURE IN THE LIGHT ETCHING PHASE, 500X

FIG 56c LIGHT ETCHING PHASE IN PRESSED AND SINTERED POWDERS , 100X

FIG 56d THORIA-FREE REGION , 50000X

content in the light and dark-etching phases could not be analysed in EPMA due to its low concentration in the alloy.

In order to investigate this further, same batch of the attritor-milled powders were sintered in hydrogen at 1100°C for 4 hours to produce porous compacts. The typical microstructure obtained on the sintered compacts is shown in Fig.56c. Because of the incomplete densification, the original powder particle boundaries can be seen. It will also be noticed that while the interior of the particles etched dark, the particle boundaries are seen to contain the light-etching phase similar to that seen in the HIPed microstructure. It can therefore be surmised that HIP consolidation has led to a network of this light-etching phase delineating the prior particle boundaries. A similar feature of a light etching phase with enrichment of chromium in it was observed in Fe-Cr-Al-Y₂O₃ alloy by Wilson et al (140) who however did not indicate any attempt of eliminating it.

What could be the reason for this feature in the microstructure? Since the nickel and chromium contents in the light-etching phase as analysed by EPMA are tallying approximately to 100% in contrast to the nearly 98% tally in the dark-etching phase, it is reasonable to think that the light-etching phase is thorium-free. This is also supported by the observation that recrystallised grains are seen in this phase at high magnification (Fig.56b), because thorium, if present in these regions, would have made the matrix resistant to recrystallisation. Further confirmation could be obtained by TEM of the HIP compacts

of the powder which revealed (Fig. 56d) 'islands' which are relatively thoria-free and these might correspond to the light-etching areas. Since this feature is originating from the sites of particle-boundaries, it would imply that somehow the outermost layers of the attritor-milled particles are ending up without any thoria in them.

The exact process by which this odd phenomenon is occurring could not be established with certainty in this study. However, a logical conjecture is made as follows. The attritor milling is done by pre-blending the entire powder charge of nickel, chromium and thoria and then loading into the attritor for mechanical alloying. In the process of composite particle formation in the early stages of milling, thoria particles (as also the chromium particles) are embedded in the nickel particle agglomerates. Since the volume percent of thoria is rather small, most of what has been added would get 'fixed' in the initial composite particle formation. Under the 'kneading' action of cold welding and fracturing, the composite particles undergo continuous refinement of their internal structure. The dispersoid particle distribution to the desired fineness and uniformity is supposed to be a result of weld-fracture cycles (129). Even though the thoria distribution would have become uniform, the weld-fracture cycles continue and this might lead to a coating of only nickel and chromium on the periphery of the composite particles which have already got dispersed in their interiors with almost all the thoria. This explains a relatively thoria-free Ni-Cr material in the outer layers of the composite particles.



FIG 57a HIP CONSOLIDATED POWDER MADE WITH LATE ADDITION OF THORIA, 100 x

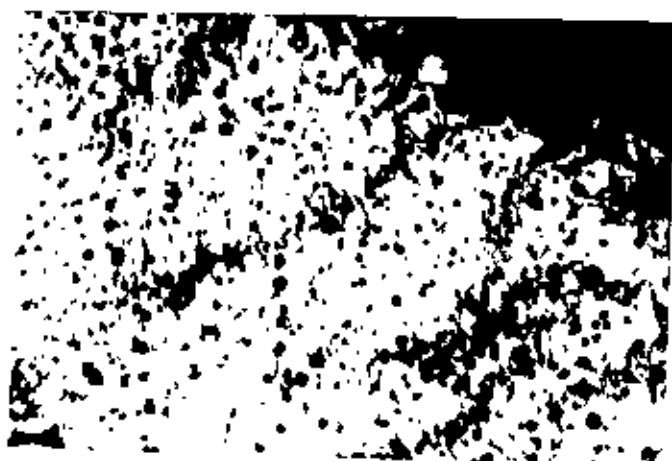


FIG 57 b THORIA DISTRIBUTION IN THE SAMPLE DESCRIBED ABOVE, 63000 x

If this explanation is correct, then the omission of thorium particles in the initial blend and its addition at a later stage should eliminate the light-etching, thorium-free phase. This in fact is the case as seen in the experiments with late thorium addition. Fig.57a is the HIP-consolidated microstructure of an attritor-milled batch where thorium is added at about half-time interval (that is, around 20th hour of milling time out of the 40-50 hours of total milling time, typical for a normal run) and it shows elimination of the light-etching phase. It may also be pointed out that nickel and chromium powders attritor milled without any thorium also result in the elimination of the light-etching phase. The modified procedure of late addition of thorium does not hinder attaining a satisfactory dispersoid distribution as may be seen from the transmission electron micrograph in Fig.57b.

5.4 OPTIMISATION OF OPERATIONAL PARAMETERS

5.4.1 Attritor RPM

It was seen in Section 5.3.1. that the attritor RPM has a remarkable influence on the state of alloying: higher the RPM, faster is the completion of alloying. However, as seen from Figs.29 & 34 a minimum speed seems to exist (at about 100 RPM) for the given set of attritor operational conditions, above which only mechanical alloying is realisable in practical time periods. At less than this minimum speed, either alloying is not feasible or very prolonged milling extending presumably to several hundreds of hours becomes necessary

to cause satisfactory alloying. Increasing RPM indefinitely beyond a certain limit is of no benefit either, because, as can be seen from Fig.33, there can be no further gain in the chromium pick-up as well as homogeneity both of which have reached their maximum values, for a given number of hours of milling. However, with an increased level of milling time, the upper limit of RPM for maximum effectiveness of alloying shifts to a lower value as can be seen in Fig.29. Although not verified experimentally, the trends observed here can be expected to apply even for milling times shorter than 24 hours and longer than 42 hours; this is illustrated in Fig.29 itself for two arbitrary milling time periods of 12 and 100 hours as the predicted trends.

An optimum value for RPM becomes more strongly evident when we compare the effectiveness of alloying versus RPM at constant number of impeller revolutions denoted as R' , as illustrated in Fig.34. The chromium pick-up curves for both 3.6×10^5 and 6.2×10^5 revolutions reach a maximum at about the same speed of 350 RPM. The inhomogeneity curves also show a minimum at about the same RPM of 350. For speeds higher than this, the chromium pick-up decreases as RPM increases for a constant value of R' , while it increases for higher values of constant R' , at a constant RPM. Since the maximum chromium pick-up cannot be more than 100% of the aimed composition, it is logical to predict from the trend of the curves of chromium pick-up and inhomogeneity for the two values of constant R' , curves corresponding to still higher R' would continue to show the maximum chromium pick-up and also minimum in inhomogeneity.

geneity at about the same RPM of 350. However, beyond this speed the chromium pick-up would as before tend to decrease with increasing RPM, so also the inhomogeneity would tend to increase with increasing RPM. It must also be mentioned that this rate of decrease of chromium pick-up and the rate of increase of inhomogeneity are slower at higher R' values. This is illustrated in Fig.34 for an arbitrary choice of 10^7 revolutions as predicted trends. At the lower levels of R' , the progressive decrease in chromium pick-up and increase in inhomogeneity for RPMs beyond the optimum is faster.

We can therefore summarise the joint influence of RPM and R' on the effectiveness of alloying as follows:

- i) There is a minimum in the inhomogeneity versus RPM curve for a given R' . The position of this minimum is independent of R' .
- ii) The RPM value at which a minimum occurs in the inhomogeneity coincides with the RPM at which maximum chromium pick-up occurs.
- iii) The minimum inhomogeneity level increases with decreasing R' .
- iv) The maximum in chromium pick-up is also a function of R' , increasing with increasing R' , although this dependence is smaller than dependence of the minimum in inhomogeneity on R' .

The above characteristic features of Fig.34 can be explained as follows. Consider any constant R' curve. At very low RPMs (lower than the optimum), the milling times are prolonged with decreasing RPM. Nevertheless, alloying

is poor because of inadequate kinetic energy input leading to insufficient localised attrition heat for alloying. For speeds greater than the optimum, effectiveness of alloying is again increasingly poorer probably because of the progressive decrease in the time available for diffusion of alloying elements, and the diminishing 'convective' ball currents at very high speeds. (The energy requirements and the 'convective' currents of agitation in mechanical alloying are described in more detail in Chapter VII. The optimum RPM may therefore be seen as a speed which provides the best combination of the kinetic energy supplied, the time available for diffusion and an optimum level of 'convective' ball currents - leading to maximum effectiveness of alloying. The value of the optimum speed for the attritor size as used here is seen to be approximately 350 RPM. It may be pointed out that this value of the RPM is optimum only in conjunction with the other attritor parameters remaining same as applied (i.e., 6mm diameter balls in 18/1 balls-to-powder weight ratio, round impellers, nickel and chromium powders of 8 and 45 microns average particle size respectively).

Milling time for maximum effectiveness of alloying

The experimental results also suggest the possibility that there is a minimum attritor milling time for attaining maximum effectiveness of alloying at any given RPM. In actual experiment the minimum alloying time has been determined for four speeds namely, 154, 260, 450 and 850 RPM by following the EPMA line scans from the samples at different milling times until the

line scans showed nearly maximum chromium pick-up and near-zero inhomogeneity. These nearly homogeneous line scans are illustrated in Fig.58 for the four different speeds with the corresponding milling times which approximately represent the minimum times for maximum effectiveness of alloying. The plot of this minimum milling time as a function of RPM shown in Fig.59 indicates that, upto certain value of the speed, the milling time decreases. The dotted portion of the curve shows the predicted trend that is likely to be observed beyond the experimental points which are available only upto 850 RPM. This conjecture of a slow increase in the required minimum milling time at very high RPMs beyond the minimum in the curve is based on the observed tendency of slowly increasing inhomogeneity and slowly decreasing chromium pick-up at very high RPMs in the constant R' curves (Fig.34). Speed and design limitations of the available attritor has precluded any experimental verification of the actual values of the very high speeds at which increase in minimum milling time (dotted line of the curve in Fig.59) would begin to emerge.

For the observed optimum speed of 350 RPM, Fig.59 indicates that a milling time of approximately 32 hours would give maximum effectiveness of alloying, whereas, the lowest point in milling time as seen from Fig.59 corresponds to RPM value in the neighbourhood of 2400. This does not mean that 2400 RPM, merely because it requires the least milling time, is the optimum RPM, since the corresponding value of total number of revolutions, R' , required at this speed works out to be larger than that of 350 RPM which is the experimentally observed optimum RPM from Fig.34. At this juncture, it may be

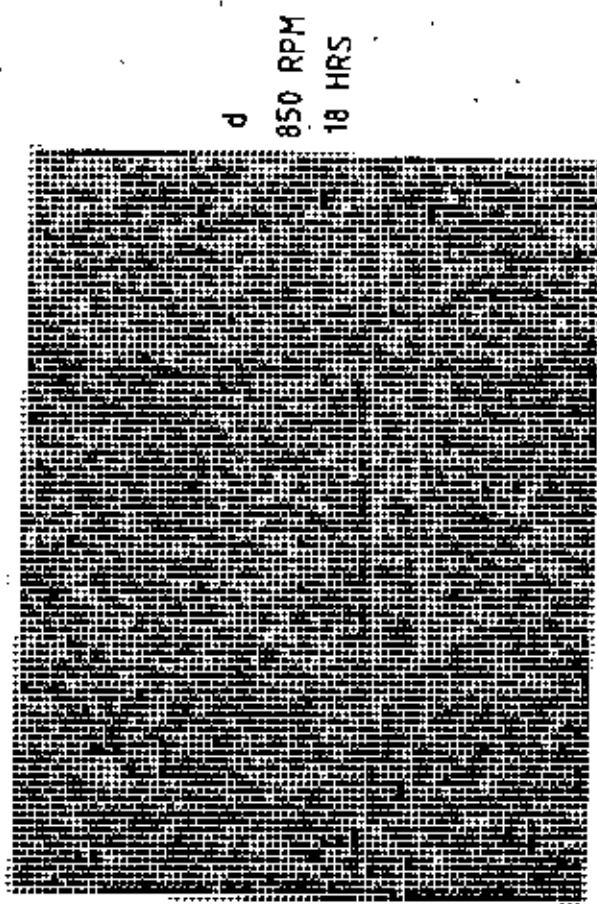
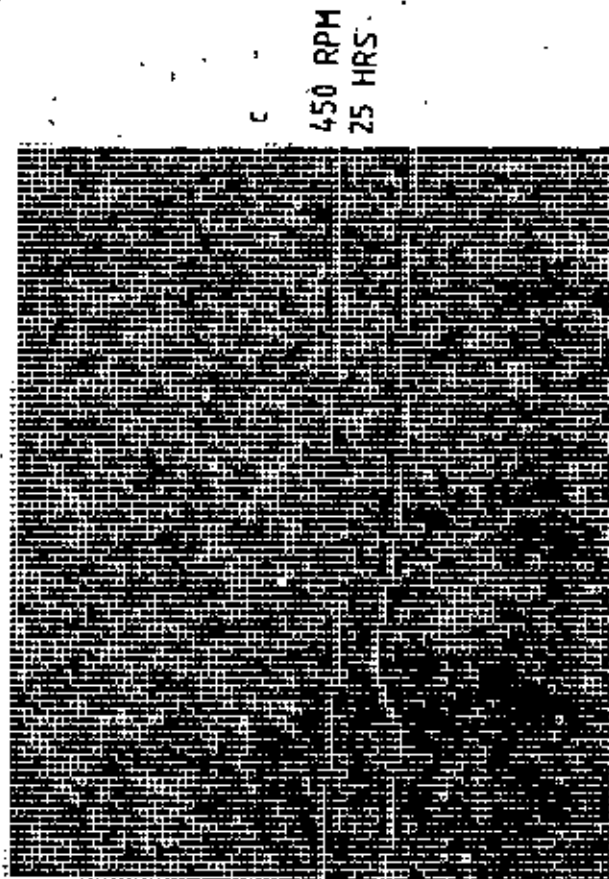
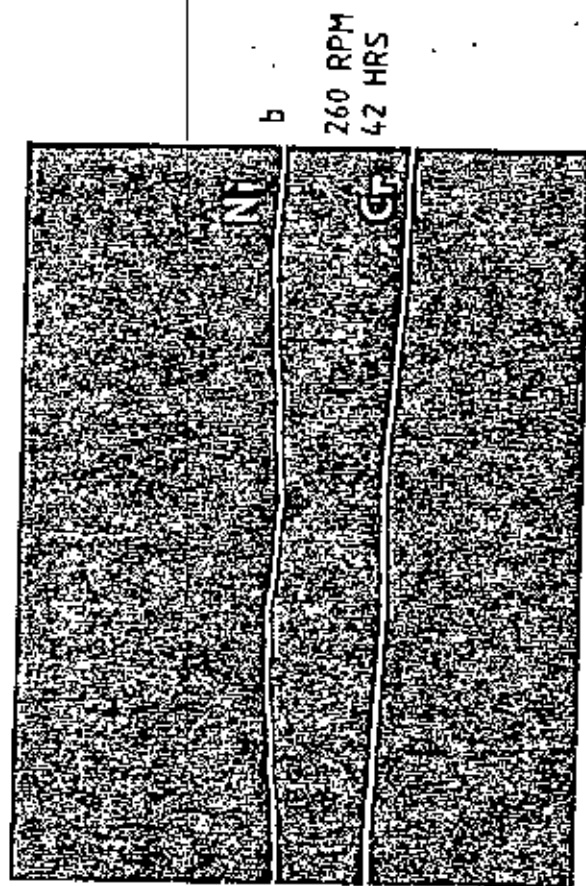
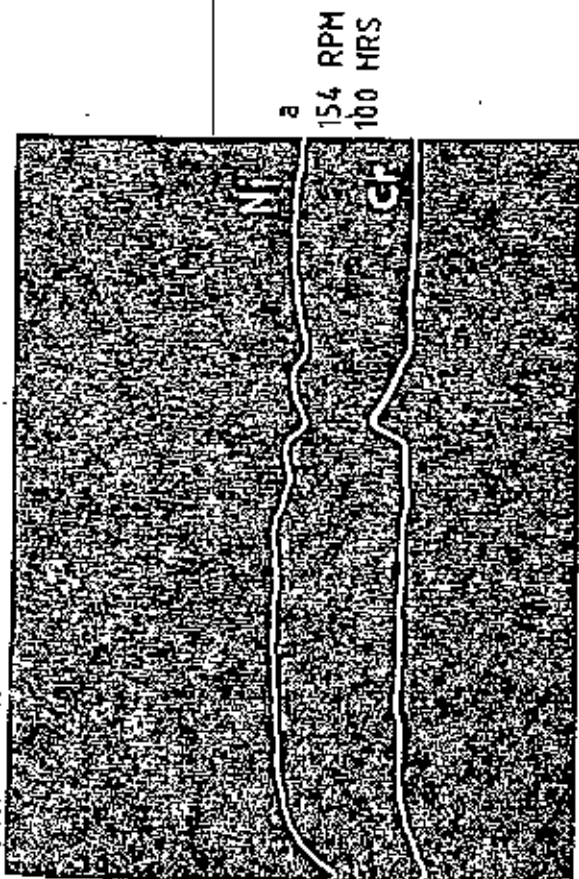


FIG 58 EPMA LINE SCANS AT DIFFERENT ATTRITOR SPEEDS

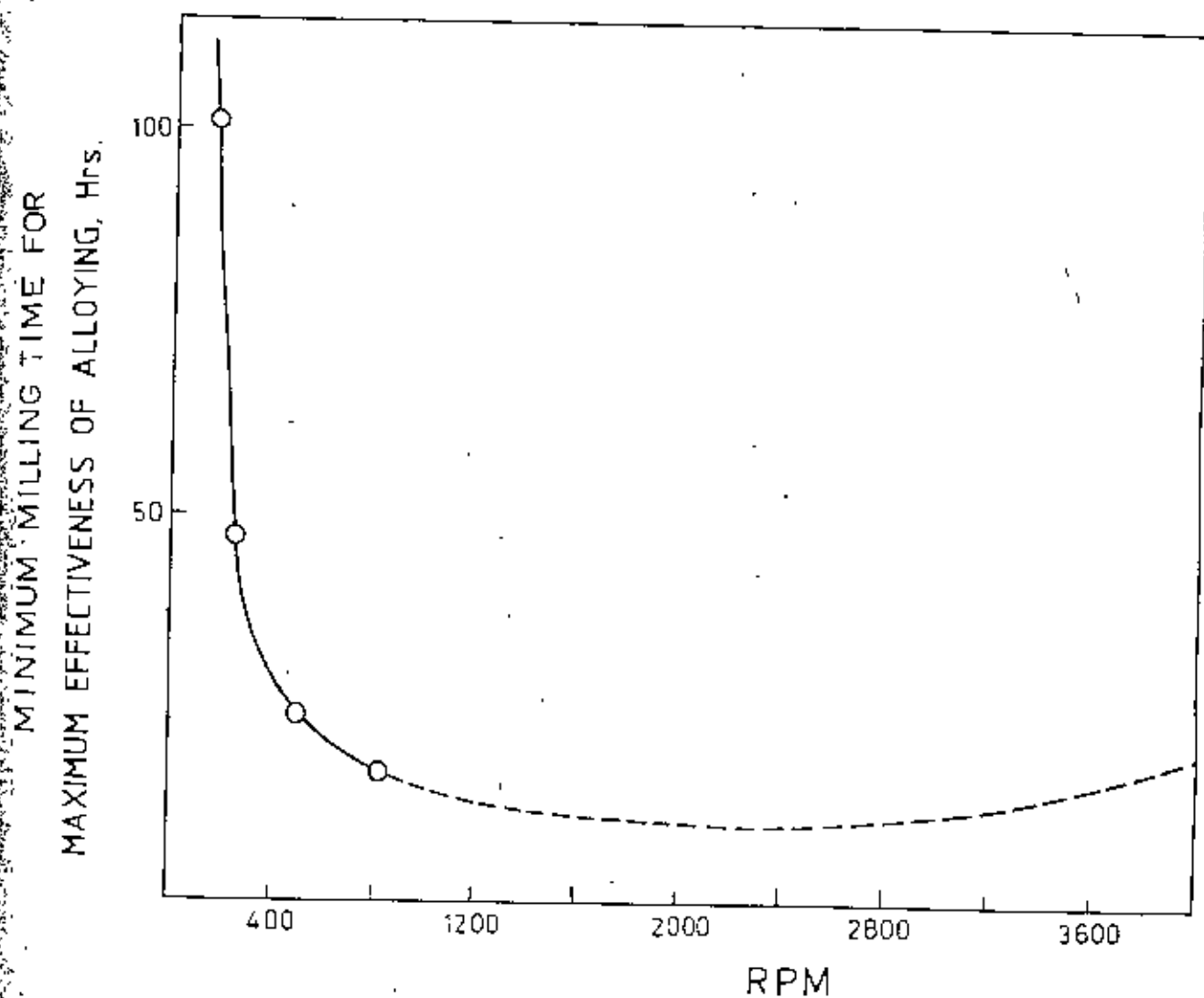


FIG 59 MINIMUM MILLING TIME WITH ATTRITOR RPM

instructive to see how the total number of revolutions associated with each of the points of minimum milling time in Fig.59 varies with the corresponding RPM. Values of this number calculated from the experimental points of Fig.59 are plotted in Fig.60 as a function of the corresponding values of RPM. Fig.60 reveals that the total number of revolutions for maximum effectiveness of alloying initially decreases and subsequently increases. The lowest value of the number of revolutions is associated with 335 RPM. This result vindicates the attritor speed previously optimised at about 350 RPM. Despite the benefit of shorter milling time, other practical disadvantages dominate at high RPMs such as the iron contamination from the balls into the milled powder. For instance, in the 850 RPM run it was found that as much as 3.0% Fe was picked up in 24 hours, compared to 0.4% Fe in the 260 RPM for 42 hours. Another serious drawback with high RPM runs is that the yield of the alloyed powder decreases with higher RPM because of the increasing tendency of powder welding to the balls. An additional problem is the premature wear of the seals in the shaft requiring frequent replacement. From a design point of view, attritors requiring to be operated at high speeds are liable to become more complicated and expensive. Thus, the use of an optimum RPM is desirable not only from the viewpoint of optimising the efficacy of mechanical alloying but also from the viewpoint of practical considerations of contamination, equipment design, yield and production economics.

5.4.2 Balls-to-powder weight ratio

Referring to Fig.38, it is seen that the minimum ball ratio necessary

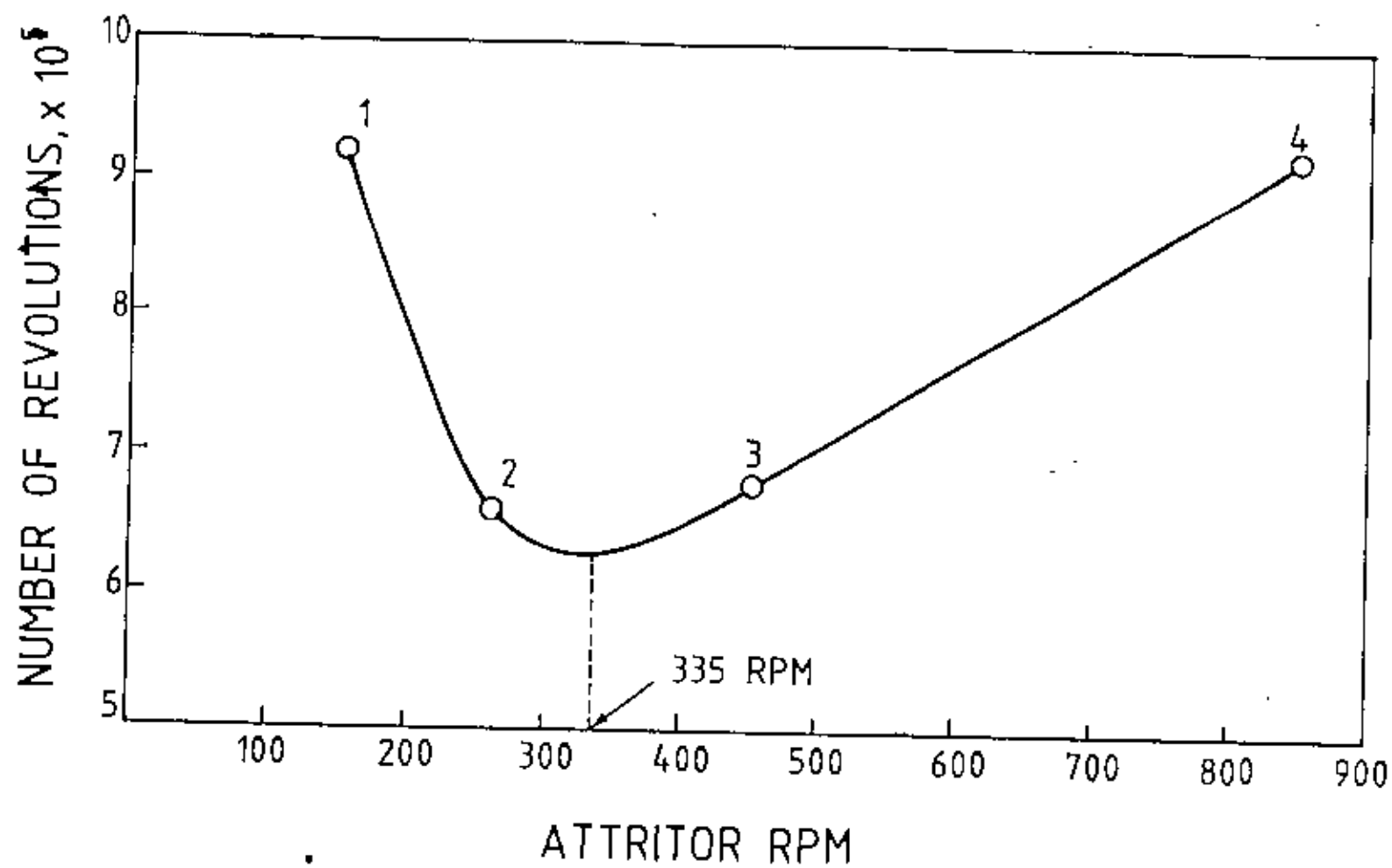


FIG 60 RPM AS A FUNCTION OF No. OF REVOLUTIONS CORRESPONDING TO MAXIMUM EFFECTIVENESS OF ALLOYING

for attaining maximum chromium pick up decreases as the milling time increases, but the chromium pick-up levels plummet to low values at a ball ratio of about 12/1. Fig.38 also depicts the predicted trends of chromium pick-up as a function of ball ratio for two arbitrarily chosen constant milling times of 50 hours and 100 hours and these trends also suggest that even with 50 hours and 100 hours milling, ball ratios upto 12/1 are likely to be ineffective under the applied milling conditions. Similarly, the inhomogeneity curves for the constant milling times (including the predicted curves) suggest poor levels of homogeneity of alloying upto ball ratios of 12/1. It is therefore reasonable to conclude that ball ratios upto 12/1 are ineffective for mechanical alloying at 154 RPM with 6mm balls. On the other hand, if the aim is to obtain zero inhomogeneity level with a maximum in chromium pick-up in relatively short milling times, a ball ratio of 100/1 appears to be necessary (see Fig.38). However, for a milling time of 42 hours, a lower ball ratio of 40/1 is able to bring about nearly maximum chromium pick-up level concomitant with a level of inhomogeneity which is close to zero. The predicted trend for 50 hours constant milling time suggests that all ball ratios ranging from 40/1 to 100/1 can bring about maximum effectiveness of alloying.

For milling periods of 24 and 42 hours, the minimum ball ratio for attaining least inhomogeneity tends to be more than the minimum ball ratio for attaining maximum chromium pick-up (see Fig.38). It can thus be inferred that at a given RPM and for relatively small milling times, elimination of inhomogeneity requires a higher ball ratio than that required to attain the

maximum in chromium pick-up. Sharp peaks are thus noticed in the inhomogeneity curves in respect of 42 hours and 24 hours constant milling times. It is also seen that as the inhomogeneity level rises to peak, chromium pick-up corresponding to these peaks in inhomogeneity also rises sharply and further rise in chromium pick-up is only gradual, approaching the maximum value, with a corresponding trend of approach towards near-zero level in inhomogeneity. The peaks in inhomogeneity therefore imply a sudden increase in chromium pick-up at these ball ratios without having the necessary time for homogenisation of chromium in nickel. This interpretation is further strengthened when one examines the apparently conflicting result of a lower level of inhomogeneity for the shorter milling time of 24 hours than that observed for the longer time of 42 hours, at a ball ratio of 18/1. Here, although the inhomogeneity is lower for 24 hrs it is also associated with a much lower level of chromium pick-up than the level of chromium pick-up in the 42 hr isochronal curve at the same 18/1 ball ratio line. Increasing the ball ratio seems to iron out such inhomogeneity peaks, as can be seen for the 42 hr isochronal curves.

In Fig.38 a noticeable trend that is evident is a decreasing effectiveness of alloying both in terms of chromium pick-up and inhomogeneity as the ball ratio is increased from 100/1 to 150/1 for the 24 hours and 42 hours isochronal curves. By increasing the milling time to longer periods, say 50 or 100 hours, it should be possible to improve this decrease in the effectiveness of alloying. Such improvement is already evident in the 42 hrs milling time curve, in comparison with the 24 hours milling curve.

Since the question of an optimum ball ratio is tied up with the attritor milling time as discussed above, is there a way of 'normalising' the ball ratio-milling time combination? Such a normalised factor could be the 'NtW' described earlier. Although this factor may not have a physical meaning as direct as R , the number of revolutions (given by Nt), it serves to make a distinction in the effectiveness of one ball ratio from another when they belong to same NtW value. Thus two different ball ratios having same NtW, arising from an appropriate difference in the milling times may be taken to be different in their effectiveness for mechanical alloying. The plots of effectiveness of alloying-versus -ball ratio for two values of constant NtW, namely, 1.1×10^7 or 1.7×10^7 in Fig.41, follow a somewhat similar pattern as that of the plots of constant milling time (Fig.38). The significant difference between Fig.38 & Fig.41 however is that the constant NtW plots reveal an approximate coincidence at the same ball ratio of about 35/1 which gives maximum effectiveness of alloying at both the NtW values. For either of the NtW curves, although the chromium pick-up at 35/1 ratio is not the absolute maximum*, it is close to it and is consistent with the least value of inhomogeneity and is therefore to be taken as the most effective ratio. At any other ball ratio, either the inhomogeneity is too high or the chromium pick-up is too low. Thus it is reasonable to conclude that a ball ratio of about 35/1 is the optimum value for

* Absolute maximum value of chromium pick-up, here, should be taken to mean approximately 105% of the 'standard' chromium line at which it equals the 20% chromium aimed in the composition.

maximum effectiveness of alloying. It is also seen that although more or less the same ball ratio is valid for maximum chromium pick-up with minimum inhomogeneity, the value of the chromium pick-up is closer to the absolute maximum value and the minimum in inhomogeneity is lower, as the NtW increases from 1.1×10^7 to 1.7×10^7 . At NtW of 1.7×10^7 , a ball ratio of 100/1 is also seen to give maximum effectiveness of alloying. It is likely that at a still higher value of NtW , the already subdued inhomogeneity at 50/1 ball ratio in the 1.7×10^7 NtW curve may be fully eliminated, and even intermediate ball ratios between 35/1 and 100/1 can also bring about maximum effectiveness of alloying. Following these observations, the predicted curves of chromium pick-up and inhomogeneity for a still higher value of constant NtW (arbitrarily chosen as 10^8) are included in dotted lines in Fig.41. Thus, just as the optimum ball ratio for maximum effectiveness of alloying can vary over a considerable span of ball ratios for longer milling times (Fig.38), the optimum ball ratio can again spread over a range of ratios for large values of NtW (Fig.41).

As mentioned before (in this section), for a given RPM, the minimum milling time for maximum effectiveness of alloying can be reduced by increasing the ball ratio, but not indefinitely. By extrapolating the observed trends in Fig.38, one can expect the minimum milling time required for maximum effectiveness of alloying to increase at low ball ratios as well as at very high ball ratios. Based on the EPMA line scans pertaining to 18/1, 40/1, 50/1, 100/1, 150/1 ratios, the appropriate milling times that nearly maximised the effectiveness of alloying — as deduced from the nearly straight line scans in EPMA —

are treated as the minimum milling times. These line scans are already included in Figs 40a and 40b. The line scan analysis of these samples are shown in Table 17 which shows that the milling times of these samples are fairly close to maximum effectiveness of alloying. Using these data, a plot shown in Fig. 61 has been made between minimum alloying time and ball ratio. A rapid decrease in the minimum milling time upto about 40/1 ratio followed by a gradual decrease upto about 85/1 followed by an increase in the milling time beyond 100/1 are evident in Fig. 61. These features are somewhat similar to the features observed in the plot of minimum milling time with increasing RPM (Fig. 59). Fig. 61 indicates that the least milling time for maximum effectiveness of alloying is associated with a ball ratio of about 90/1. From the experimental points in Fig. 61 of the minimum milling times, the corresponding NtW values are computed and included in Table 17. These NtW values are plotted as a function of the ball ratio in Fig. 62 which shows initially a slight decrease in the NtW followed by an increase. The lowest value of NtW is seen to correspond to a ball ratio of approximately 32/1 and the associated milling time is about 49 hours. Since it is associated with the least value of NtW, a ball ratio of about 32/1 can be deemed to be the optimum ball ratio and it agrees well with the optimum ball ratio of about 35/1 determined from constant NtW curves (Fig. 41). It must of course be remembered that this optimisation is valid only for the milling conditions adopted in this study, namely, 154 RPM as the attritor speed, 6mm diameter steel balls, with 8μ and 45μ average particle size values for nickel and chromium respectively.

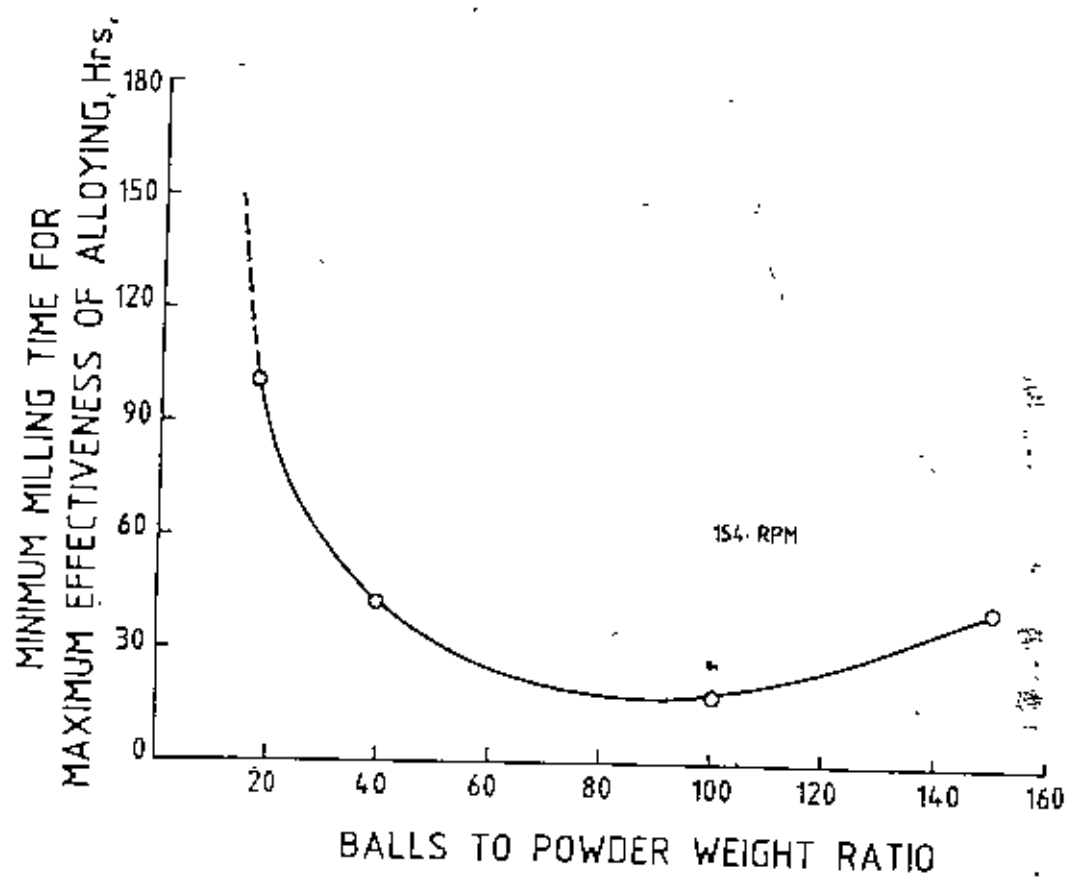


FIG 61 MINIMUM MILLING TIME WITH BALLS-TO-POWDER WEIGHT RATIO

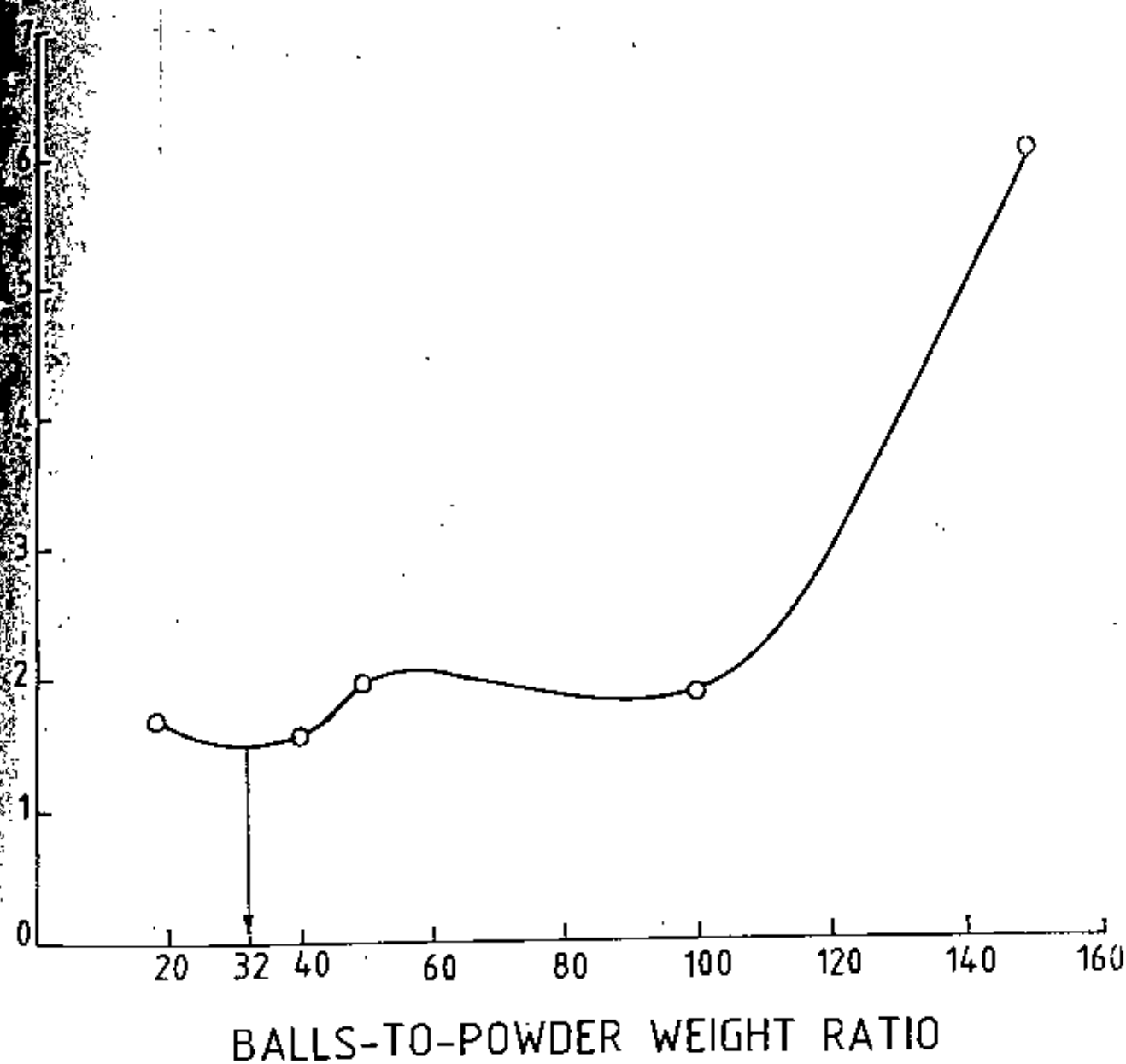


FIG. 62. NTW VALUES OF MINIMUM MILLING TIME WITH BALLS-TO-POWDER WEIGHT RATIO.

While ball ratios higher than the optimum may appear to be advantageous because of reduced milling times, the desired distribution of the dispersoid may not have been attained in the reduced milling times. Furthermore, higher ball ratios call for bigger capacity attritors for processing the same batch size of the powder or reduced quantity of the powder charge for the same capacity of the attritor.

5.4.3 Ball characteristics

The effect of varying the ball diameter on the degree of alloying is reflected in Fig.44. It brings out an optimum value for a ball diameter of approximately 8mm at which the observed degree of alloying is more effective than with the other ball diameters studied. For ball diameters lower than 8mm, the drop in chromium pick-up and increase in inhomogeneity are drastic. As evident from Fig.44, for ball diameters larger than 8mm, while there is no significant difference in chromium pick-up level, the inhomogeneity increases. In general, one can expect a lowering of the inhomogeneity levels and an increase in chromium pick-up levels over a range of ball diameters by increasing the milling time from the 42 hours milling which is the basis for Fig.44. Although not verified experimentally, with very prolonged milling, it is ^{*}predictable^{*} that the optimum ball diameter is likely to spread over a small range of values centred around 8mm. Since there can be no alloying with zero ball diameter

* For instance, for 100 hours milling in a run of 6mm diameter balls in 18/1 ball ratio, the EPMA line scan in Fig.60a shows inhomogeneity level close zero alongside a maximum in chromium pick-up

regardless of milling time, it is reasonable to imagine a minimum value for ball diameter above which only there can be effective alloying for all milling times. It is difficult to assign a fixed value for it, because what occurs at a single value at relatively small milling times, spreads out to a range of ball diameters for prolonged milling times. This situation is depicted in the form of schematic trends of chromium pick-up and inhomogeneity curves for two arbitrary choices of a prolonged (100 hours) and a short (12 hours) milling time shown in Fig.44 itself.

The observed trend of increasing effectiveness of alloying with increasing ball diameter upto a certain optimum value may be understood as an effect of increasing intensity of attrition and collision events, resulting from an increase in the surface area of the ball. The reason for the decreasing effectiveness of alloying beyond the optimum value of ball diameter is not very clear; however, it is very likely that with too large a ball diameter the weight of the ball increases to a point where the effective agitational velocities of the balls for a given RPM of the attritor may begin to decrease.

The same reason as above may be valid for the very poor alloying observed with tungsten carbide balls whose density makes the ball more than twice as heavy as the steel ball. A point to be noted in the case of tungsten carbide balls is that they are much harder (~ 1800 VHN) than the hardened steel balls (~ 800 VHN). The hardened surface of a tungsten carbide ball should make it more difficult for powder to weld to it thus retarding the process of mechanical alloying. Visual observation does indicate the same: there was

hardly any powder seen welded to the balls at the end of attritor milling with tungsten carbide balls, whereas 'projections' of welded powder particles to steel balls after milling are always visible to the naked eye. This may be an additional reason for the poor alloying with WC balls.

In the experiments on the effect of variation of shape of the balls (Section 5.3.3.), it was shown that cylindrical grinding elements were ineffective for alloying despite the surface area associated with a cylindrical shape being larger than that of a sphere. The sharp angularities of a cylinder at its edges, in contrast to the smooth surface of sphere, makes relative motion between the cylindrical elements difficult. This results in retarding the intensity of the collisions as well as agitational velocities, which is the likely reason for the observed poor alloying of the constituent powders. This experimental result is a pointer to a generalised conclusion that sphere is the best shape of the grinding elements for mechanical alloying.

5.4.4 Effect of impellers and baffles

Triangle-shaped impellers have been found to be better than round or flat shapes in bringing about a greater degree of alloying. The reason for this could not be clearly established but it is presumed to arise out of the possibility of greater number of attrition events resulting from the greater 'convective' ball currents that triangular shape impellers are likely to generate among the balls. A detailed description of 'convective' currents is included in Chapter VII dealing with the mechanism of mechanical alloying.

Apart from the shape of the impellers, the results also reveal that the number of impellers also have a bearing on the efficacy of alloying. Too small a number of the impellers cannot be effective because that is likely to leave several layers of the balls inactive. Too many impellers also may be counter-productive because they may actually tend to reduce the individual average velocities of the balls in agitation and therefore reduce the kinetic energy for mechanical alloying. The poor alloying observed with 22 impellers in the attritor (Fig.51) exemplifies this effect. A similar reasoning may apply to the effect of baffles in the attritor which have led to poor alloying compared to the unbaffled attritor. The presence of baffles in the vessel wall must be causing a significant reduction in the velocities of the balls in their immediate vicinity, although it might be helpful in eliminating a vortex formation. The reduction in ball velocities means reduction in kinetic energy for promoting mechanical alloying and hence the result of poor alloying (Fig.53).

5.4.5 Initial particle size of powder

Results of experiments on effect of starting particle size of Ni and Cr on the efficacy of alloying have brought out the strong trend that, for any given average particle size of nickel powder, the use of fine chromium gives better alloying than coarse chromium powder in terms of chromium pick-up as well as inhomogeneity. The greater effectiveness of alloying with fine chromium powder may be explained in the light of the five stages of mechanical alloying (Section 3.8.4). During the course of mechanical alloying, deformation and fragmentation of coarse chromium particles into progressively finer lamellae

lead to diffusion of chromium into the nickel matrix. Thus part of the mechanical energy input of the attritor is consumed in the fragmentation process itself. With fine chromium powder a greater fraction of the energy input is thus likely to be available for alloying per se.

On the other hand, when we turn our attention to the effect of variation in the average particle size of nickel, the results described in Section 5.3.8 suggest that the coarse nickel powder (25μ) is more effective in alloying than the fine nickel powder (8μ). Although the reason for this trend is not very clear, a possible explanation may be the fact that with coarse nickel powder the chromium particles may readily be embedded with less need for welding among nickel particles and thereby enabling the mechanical energy input to be more effectively utilised in alloying of chromium into nickel.

5.5 THE COERCIVITY PROFILE

Coercivity as a means of studying the effects of different operating parameters in attritor milling on mechanical alloying kinetics in respect of Ni-Cr-ThO₂ has proved to be useful in qualitatively distinguishing between a poorly alloyed condition and a well-alloyed condition.

Having seen that the milling time dependent progression of the constituent powders of nickel, chromium (and thorium) to a state of homogeneous alloying is generally predictable from the observation of an initial rise in coerci-

ity to a peak, followed by a drop in coercivity, one can imagine that coercivity drops down as alloying occurs because alloying with chromium from about 6% onwards decreases the Curie temperature of nickel to room temperature, thus rendering the alloyed matrix nonmagnetic. A somewhat similar observation was recorded by Horn, Spyra and Schmidt (141) who measured changes in magnetic susceptibility in attritor milled powder of nickel and chromium along with some other solutes also. They found a rapid decrease in the magnetic susceptibility after milling, and attributed it to alloying of chromium in nickel. However, in the present investigations, there is still a need to understand the reason for the initial rise in coercivity to a peak position. A high coercive force is essentially a manifestation of the hindrance offered by the internal structure of the material to domain boundary motion towards randomization of the aligned, magnetic domains. Coercivity of particles can increase by contributions from four anisotropy factors, namely, crystal anisotropy, strain anisotropy, shape anisotropy and exchange anisotropy (136). The coercivity of nickel has been shown to increase when it is cold worked (136). This is verified in the present work by attritor milling pre-alloyed nickel-18.5% chromium powder upto 70 hours which induced severe cold work in the powder particles, as evidenced by the increase in their average microhardness from 200 VHN to 700 VHN. At the same time it was seen that the coercivity also rose from about 30 Oe to about 110 Oe.

Another possible reason could be the effect of second phase particles on coercivity. Dispersion hardening in a magnetic material is known to increase coercivity as demonstrated in Fe-Mo system with ϵ phase particles (137)



as in Sm-Co system having Sm_2O_3 phase at grain boundaries (142). There is a possibility that in the earlier part of milling, chromium particles themselves — besides the thoria particles — act as a kind of dispersoid in nickel matrix during the course of their fragmentation to finer sizes and thereby contribute to the initial rise in coercivity.

Thus, although the initial rise in coercivity to a peak value can be largely attributed to the effects of cold work, other factors like particle size, particle shape anisotropy, dispersoid effects, annealing effects by the local rise in temperature by attrition, the onset of alloying etc. which can have varying degrees of influence on the property of coercivity, may affect the peak value as well as the subsequent drop in coercivity. Because of the complex effects of such factors, the coercivity value at the end of mechanical alloying need not exactly correspond to a fully non-magnetic condition or to the coercivity of a Ni-20Cr alloy powder. It is, nevertheless, reasonable to conclude that the rise in coercivity to a peak signifies an early approach to solid solution alloying of chromium in nickel, while, the subsequent drop in coercivity to low levels can be interpreted as a consequence of the actual realisation of alloying of all the chromium.

5. THORIA DISTRIBUTION- -

In the previous sections, the various attritor milling parameters have been optimised on the basis of the criterion of homogeneous alloying of chro-

mium in nickel. In the process of mechanical alloying, as described in Section 3.8.3, the oxide particles attain uniform distribution during the course of the weld-fracture cycles of the constituent metallic particles.

Because of their extremely fine size, the oxide particles tend to occur initially as aggregates of relatively coarse cluster particles (Fig.24) which break up into finer particles as milling continues. A uniform distribution of very fine particles is desirable to ensure the expected mechanical properties. It is therefore appropriate to examine whether in the present investigations the thorium particles attained the desired distribution, simultaneous with the homogeneous alloying of chromium in nickel when optimum milling parameters are applied.

For the purpose of studying the thorium distribution, a few illustrative experiments of attritor milling of Ni-Cr-ThO₂ have been selected out of the several that have been conducted in optimizing the milling parameters (described in Section 5.1 to 5.4) and these are listed below:

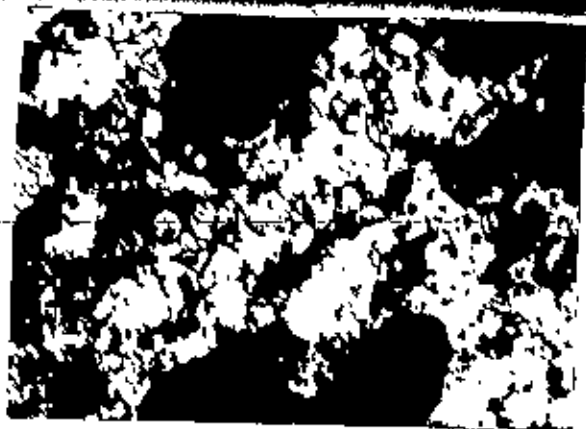
- i) Sample A: A sample of powder milled for 48 hours at 154 RPM using 6mm diameter steel balls in 18:1 ratio and which has 8 μ and 45 μ as the starting average particle sizes of nickel and chromium respectively.
- ii) Sample B: A sample of powder milled for 42 hours at 260 RPM, other parameters remaining as in Sample A.

- iii) Sample C: A sample of powder milled for 42 hours using 8mm diameter steel balls in 18:1 ratio, other parameters remaining as in Sample A.
- iv) Sample D: A sample of powder milled for 48 hours using 8μ and 12μ as the starting average particle sizes of nickel and chromium respectively, other parameters remaining as in Sample A.

The samples have been HIPed to full density and specimens for TEM examination have been prepared, as described in Sections 4.2.3 and 4.4. The typical electron micrographs obtained from these samples are illustrated in Figs. 63a to 63d. The average thoria particle size calculated from these micrographs are shown in Table 18 and the corresponding EPMA line scan analysis of chromium line of the samples A, B, C & D are in Fig. 51b, Fig. 19, Fig. 43 & Fig. 55b respectively.

It can be inferred from Table 18 that under milling conditions where the alloying of chromium in nickel is poor, the thoria particle size remains relatively coarse. This is illustrated by comparing Sample A which is a case of comparatively poor alloying (as indicated in Fig. 28 for 42 hours milling time), with samples B, C, and D wherein the chosen attritor milling parameters were such that they were effective in bringing about better alloying of chromium in nickel; thoria particle size is seen to be finer in Sample B (a case of higher RPM), in Sample C (higher ball diameter) and Sample D (finer chromium).

We may therefore conclude from these results that satisfactory oxide distribution will generally be obtained when the attritor milling parameters are optimised with respect to alloying of the solutes.



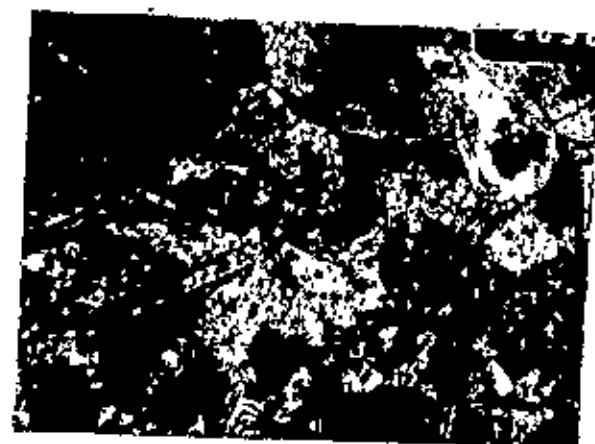
a SAMPLE 'A' (LOW RPM), 50000 x



b SAMPLE 'B' (HIGH RPM), 50000 x



c SAMPLE 'C' (HIGHER BALL DIA), 68100 x



d SAMPLE 'D' (FINER CHROMIUM), 40000 x

FIG 63 THORIA DISTRIBUTION IN DIFFERENT ATTRITOR MILLED SAMPLES

CHAPTER VI

IS MECHANICAL ALLOYING TRUE ALLOYING?

CHAPTER VI

IS MECHANICAL ALLOYING TRUE ALLOYING?

6.1 INTRODUCTION

In Chapter V, we have seen extensive use of EPMA of attritor milled powder particles to characterise the degree and homogeneity of alloying of chromium in nickel. This technique proved to be valuable in arriving at a quantitative assessment of the optimum conditions of milling for mechanical alloying. Whereas EPMA provides evidence for homogeneity on micron scale, its resolution is not adequate to confirm homogeneity on atomic scale, for, the electron probe in EPMA analyses an irradiated sample volume of about 2μ diameter. EPMA may not thus reveal submicron segregation of the alloying elements, if any.

An important question therefore remains: does mechanical alloying lead to true alloying of the solute elements in the matrix? A well-established technique for resolving this question, is x-ray diffraction. However, interpretation of diffraction line profiles is inextricably complicated by several factors such as the effects of cold work in mechanically alloyed powders, as will be explained in Section 6.2.

It is seen in the literature that this problem received only limited attention. Horn et al (141) using magnetic susceptibility conclude that nearly true

solid solution formed in mechanical alloying of Ni-Cr-Mo-ThO₂ but their conclusion does not appear to be unambiguous. White and Nix (131) have examined the possibility of Nb₃Sn compound formation by mechanical alloying of the elemental blend. From x-ray diffraction results, they concluded that the milled powder was only an intimate mechanical mixture of the two elements. A detailed investigation that dealt with this question is that carried out by Wassel and Himmel (130) who have used x-ray diffraction analysis to determine whether mechanical alloying leads to the formation of true solid solutions. They have examined the solid solution formation in the isomorphous Cr-Mo system at 50:50 w/o composition which has its (110) reflection between the Bragg peaks of Cr and Mo with a peak shift of nearly 3° (in 2θ) both from the chromium side and from the molybdenum side. Such a large peak shift can be unambiguously determined, the authors argue, if true solid solution of 50 Cr:50 Mo can be formed by mechanical alloying of the elemental mixture. Their investigations lead to the conclusion that Cr and Mo do get interdispersed on atomic scale but they found the resulting solid solutions to be structurally and chemically inhomogeneous.

The observed lack of homogeneous solid solution formation in this study on Cr-Mo alloy is most probably a combined result of some factors of the design of their experiments. One visible factor is that both chromium and molybdenum are comparatively limited in ductility, while, in attritor milling for mechanical alloying, it is desirable that a ductile component be present to ensure a good degree of cold welding among the particles. Another factor is related to the

choice of milling parameters; in their investigations, Wassel and Himmel were obliged to change the attritor RPM from 150 to 300 RPM when they found 150 RPM milling was inadequate to cause any significant alloying of Cr and Mo. It is also seen that 4mm diameter balls in 17/1 ratio were used for milling. It is possible that with a choice of a somewhat higher RPM, or alternatively, bigger balls in a higher ball-to-powder ratio could have eliminated the observed inhomogeneities of alloying Cr-Mo.

To examine the exact nature of alloying in the subject alloy system of Ni-Cr, x-ray diffraction and Scanning Auger Microprobe (SAM) analysis have been carried out on mechanically alloyed powder samples. These results are supplemented by the results of EPMA and coercivity already described in Chapter V. This chapter describes these investigations.

6.2 X-RAY DIFFRACTION ANALYSIS

Precision lattice parameter determined by x-ray diffraction or line breadth analysis of the diffraction lines of an alloy powder sample could give some information regarding the chemical inhomogeneity of the sample. Both these techniques cannot however be readily applied to mechanically alloyed powder because of excessive x-ray line broadening due to cold work in the attritor milled powders. This also makes the determination of lattice parameter difficult and inaccurate. Further, the measured lattice parameter itself may be merely the averaged value of several layers of internally inhomogeneous particles that participated in the Ewald sphere of diffraction. X-ray line profiles are broadened not only due to chemical inhomogeneity but also due to lattice strains and the 'particle size' effect (143).

Eliminating cold work by annealing treatment is likely to eliminate the inhomogeneities as well. In the case of oxide dispersion strengthened alloys, the stress relieving temperatures are very high and cold work is not easily removed. We therefore resorted to Ni-Cr composition for mechanical alloying experiments rather than Ni-Cr-ThO₂, as our primary interest here is to investigate only the nature of alloying of chromium in nickel.

Despite the complications of line broadening described above, a qualitative judgement of the state of alloying in the powder is still possible through x-ray diffraction by making comparisons between the attritor-milled nickel and chromium powders, and a prealloyed, homogeneous 'standard' powder of about the same composition attritor milled for about the same time as the elemental blend sample. The method of preparation of the 'standard' powder has already been given in Section 4.3.2. The 'standard' powder of -200 mesh size was vacuum annealed at 980°C for 8 hours*, and this annealed powder was subjected to slow-scan recording of (111) x-ray diffraction line profiles. The recording was done according to the experimental conditions described in Section 4.3.3, which are maintained to be same for all the samples discussed here. The 'standard' powder was then attritor milled for 72 hours. The average microhardness of this powder was found to increase from 260 HV in the annealed condition to 700 HV after attritor milling due to cold work induced in it. (111) line profiles were recorded on -200 mesh fraction of the attritor milled standard specimen.

* This treatment was found to be optimum in annealing the powder without agglomeration.

Ni and Cr powders in 80:20 weight proportion were attritor milled at 154 RPM for 72 hours with 6mm balls in .24/1 balls-to-powder weight ratio resulting in mechanically alloyed Ni-Cr powder having an average microhardness of 800 HV. Its EPMA line scan shows well-alloyed condition (Fig.64). X-ray line profile was similarly recorded on -200 mesh fraction of this powder as well. A sample of this powder was then vacuum annealed at 980°C/8hr and its (111) profile was also recorded. This 980°C/8 hr annealing treatment reduced the hardness to 390 HV.

The (111) profile recordings of the 980°C/8 hr annealed, 'standard' powder sample (designated as A), the 72 hour attritor milled 'standard' powder sample (designated as B), the 72 hour attritor milled, mechanically alloyed powder sample (designated as C), the 980°C/8 hr annealed sample of the 72 hr attritor milled, mechanically alloyed powder (designated as D) are shown in Figs.65-68. Integral line-breadths of the recorded peaks of (111) were analysed using a procedure given by Anantharaman and Christian (144). To get the integral breadths, the areas under the peaks were measured with a planimeter. Results of this analysis are shown in Table 19. As these results are strictly of comparative nature, the instrumental broadening correction has been omitted.

The results show that the line broadening of the mechanically alloyed Ni-Cr powder, even with its higher hardness of 800 HV, is nearly the same as that of the attritor-milled 'standard' powder with its somewhat lower hardness

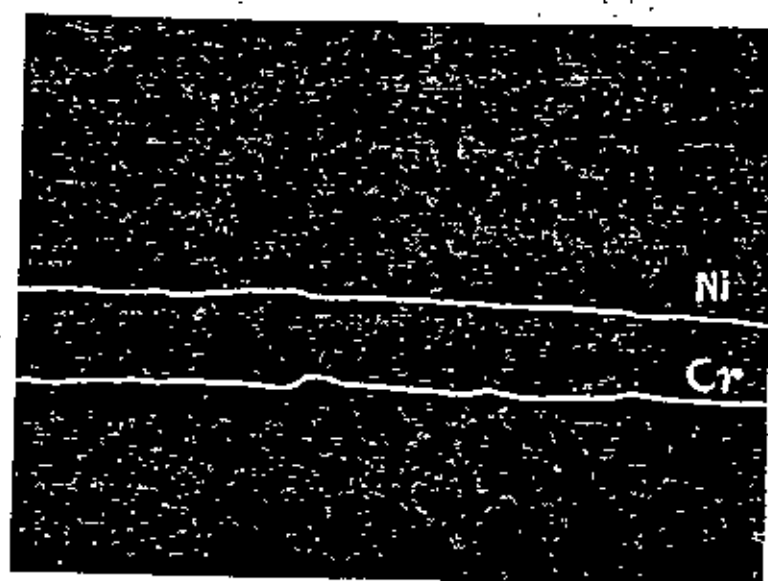


FIG 64 EPMA LINE SCAN OF SAMPLE OF NICKEL AND CHROMIUM ATTRITOR MILLED FOR 72 HRS

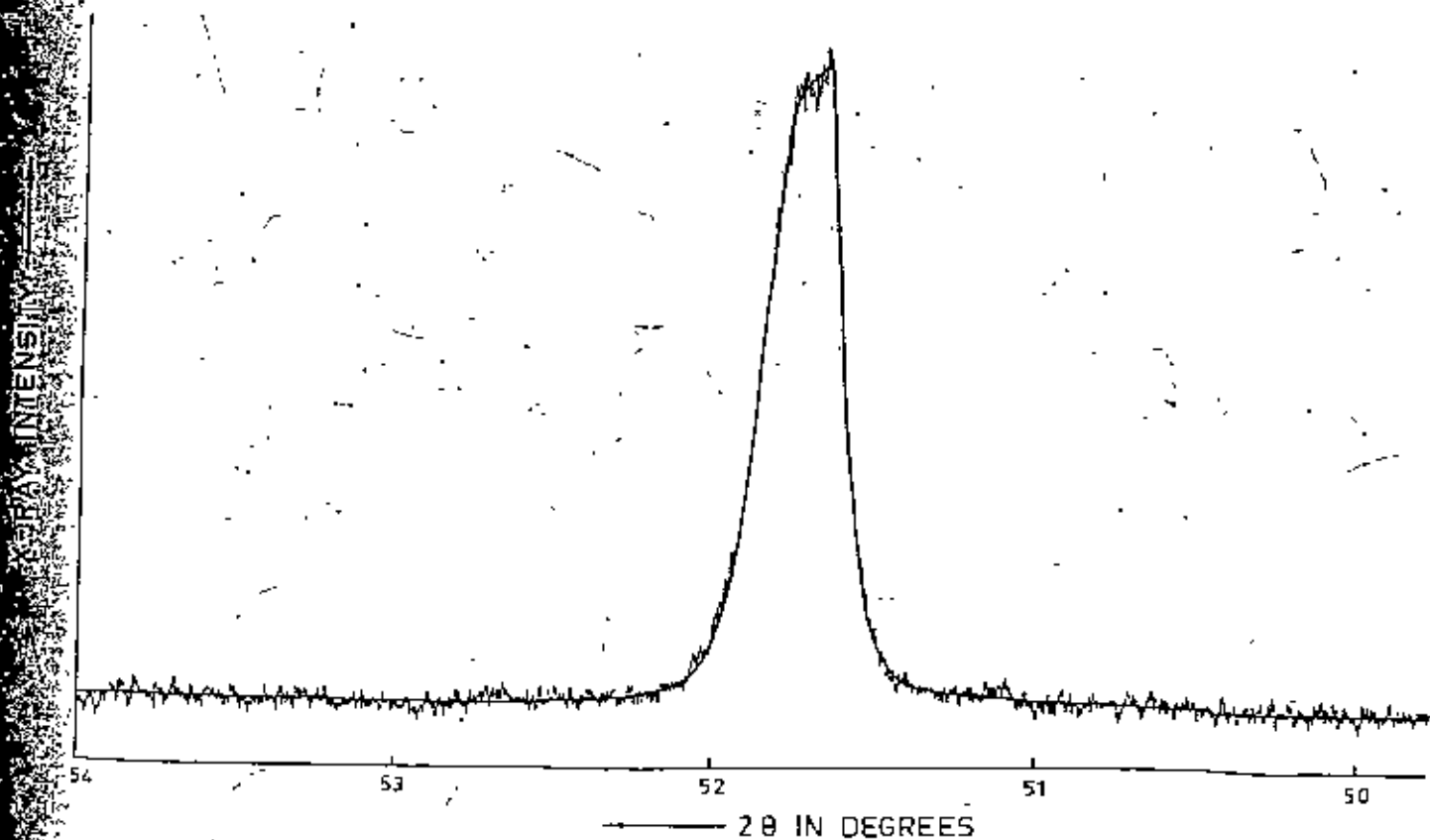


FIG 65 X-RAY LINE PROFILE OF ANNEALED, 'STANDARD' SAMPLE(SAMPLE A)

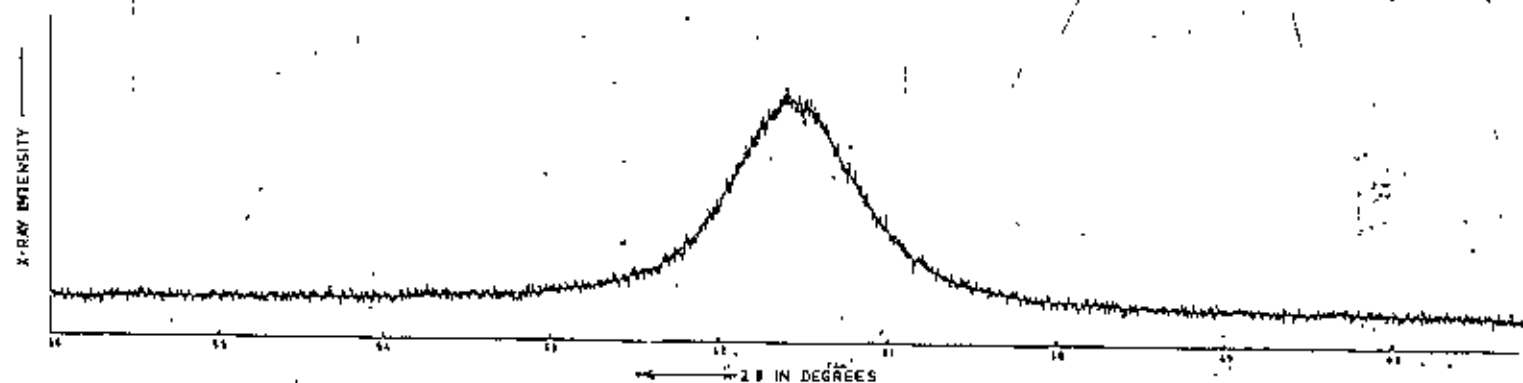


FIG 66 X - RAY LINE PROFILE OF 'STANDARD' SAMPLE
ATTRITOR MILLED FOR 72 HRS (SAMPLE B)

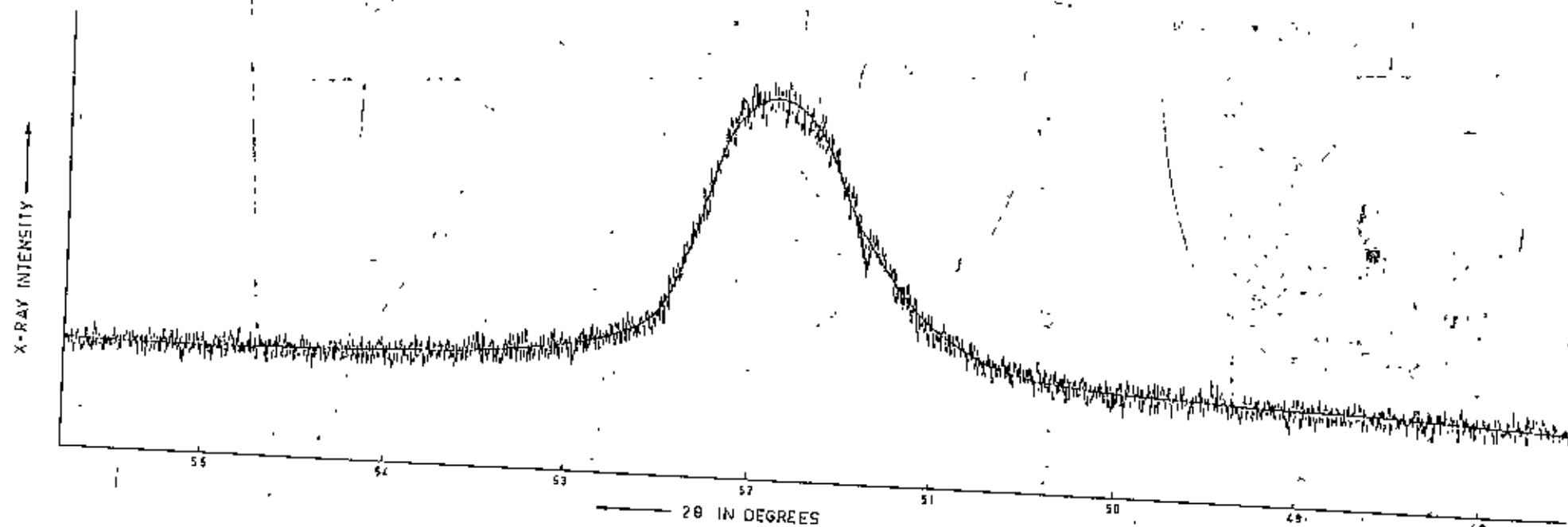


FIG 67. X-RAY LINE PROFILE OF SAMPLE OF NICKEL
AND CHROMIUM ATTRITOR MILLED FOR 72 HRS
(SAMPLE C)

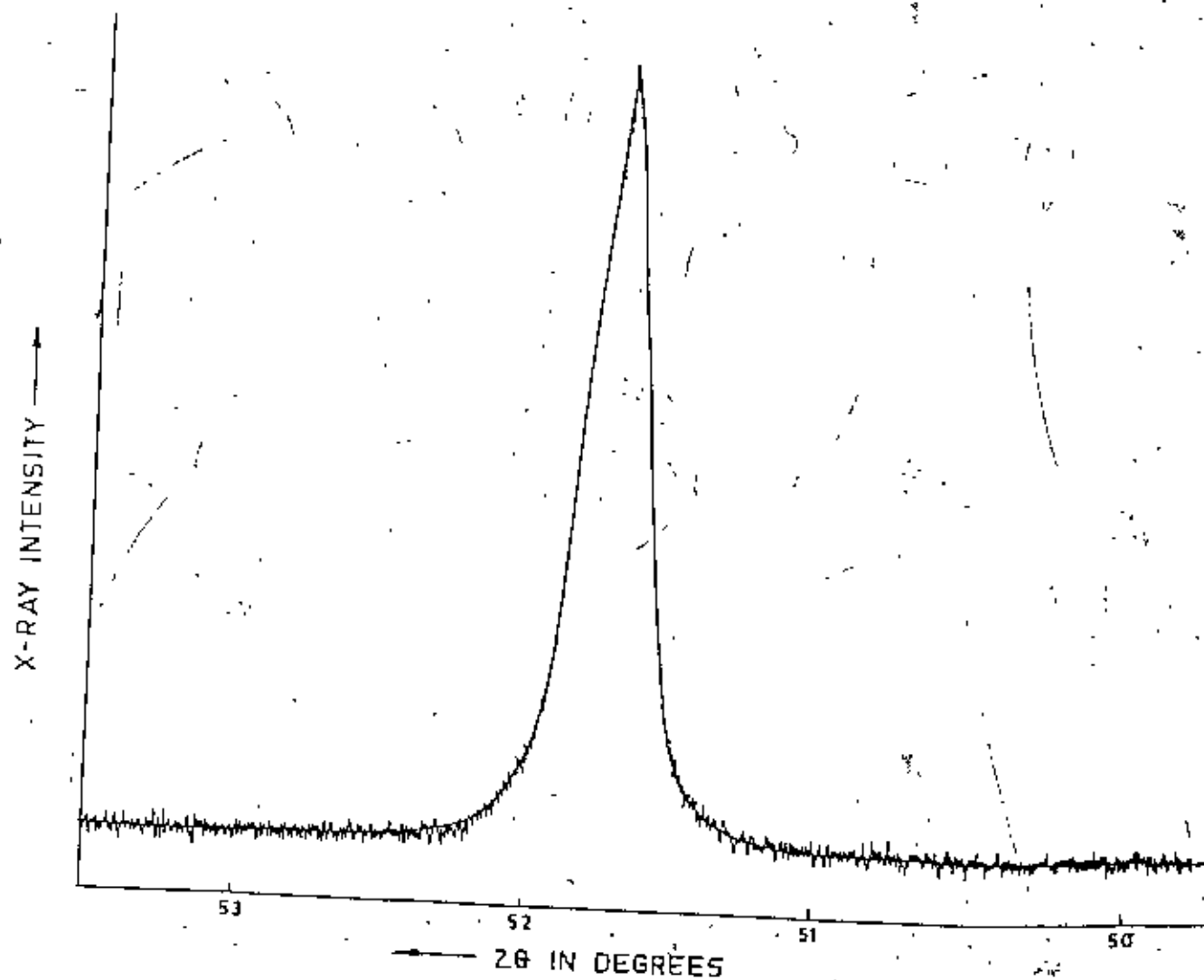


FIG 68 X - RAY LINE PROFILE OF SAMPLE C AFTER ANNEALING (SAMPLE D)

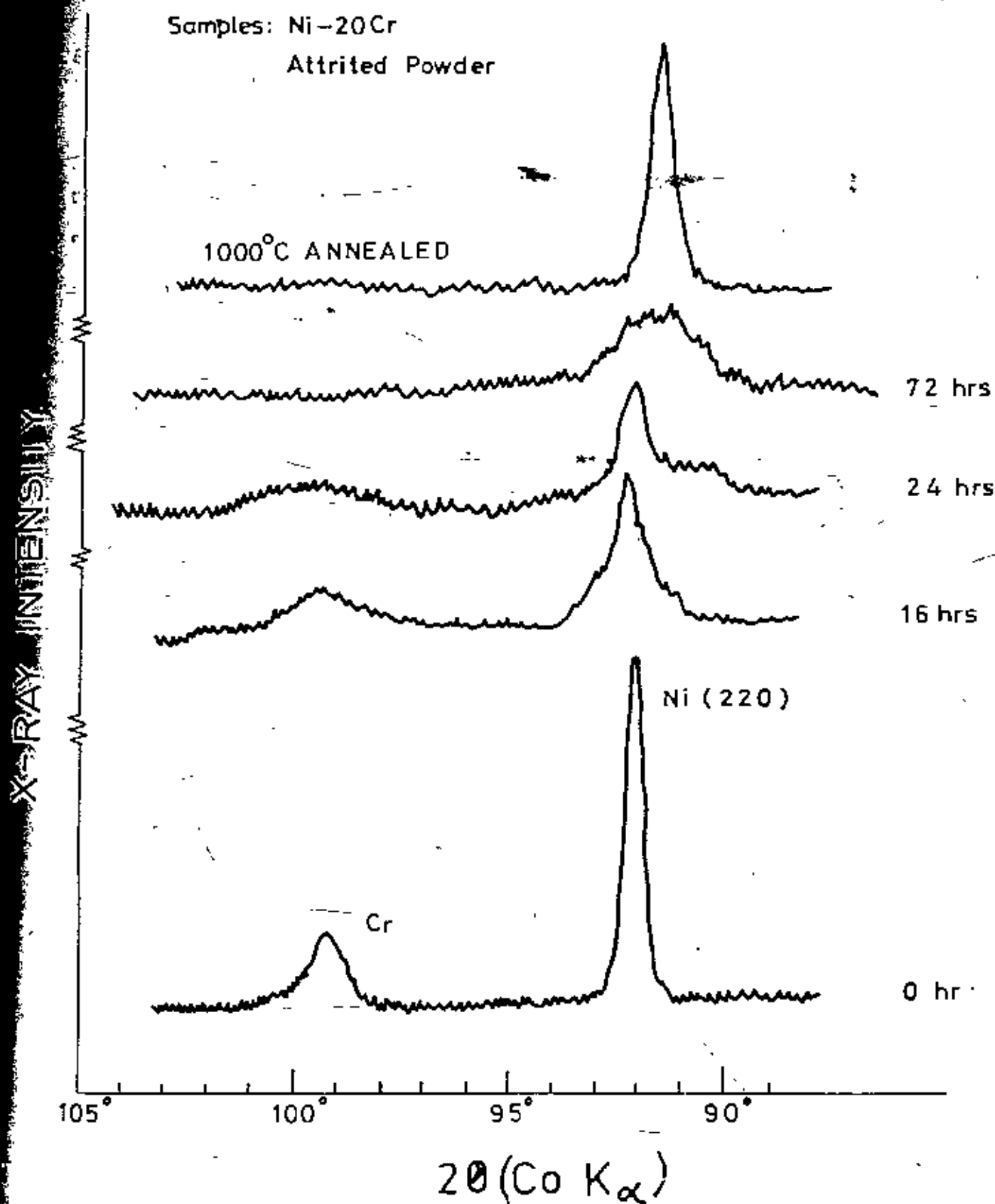


FIG 69 EXTINCTION OF CHROMIUM LINE WITH PROGRESSIVE ATTRITOR MILLING

(700 HV). This result suggests that the contribution of line broadening from chemical inhomogeneity to the cold worked 'standard' powder is somewhat more than that of the attritor milled nickel-chromium elemental blend. Furthermore, the line breadth of the annealed, mechanically alloyed powder is somewhat less than the line breadth of the annealed 'standard' powder. This result suggests that the scale of segregation, if any, in the 'mechanically alloyed' Ni-Cr may be even less than the segregation — to the extent that may be present — in the standard powder that has been produced from atomised liquid alloy. This leads to the conclusion that attritor milled powder of Ni and Cr under the right conditions of milling is at least as well-alloyed as pre-alloyed powder itself.

Another set of X-ray diffraction experiments were conducted on samples drawn at 0, 16, 24 and 72 hours of attritor milling of Ni and Cr powders in 80:20 proportion. The (110) reflections of chromium along with the (111) reflections of Ni-Cr alloy peak have been recorded as shown in Fig.69. The diffraction profile of 1000°C/2hr annealed sample of the 72 hr attritor milled powder is also included in Fig.69. The progressively diminishing peak of chromium and its near-total absence at 72 hours milling time is an indication of the absence of free chromium in the attritor milled sample. This however does not confirm the homogeneity of the dissolved chromium in view of the complications in line broadening. The sharp peak of the annealed sample in Fig.69 is merely an indication of the elimination of cold work and inhomogeneity if any.

6.3 THE SCANNING AUGER MICROPROBE ANALYSIS

The Scanning Auger Microprobe (SAM) is a powerful tool for surface chemical analysis which can be confined to a surface depth as small as a few atomic layers. By bombardment with argon ions, the surface of a sample can be etched away virtually atomic layer by atomic layer and, as etching continues, the exposed surface can be continuously analysed for the chosen elements (Depth Profile Analysis). The unique advantage of Auger Electron Spectroscopy is that while it provides the analysis of as small a depth as a few atomic layers of the sample, the technique — being a process of chemical analysis — is not in any way influenced by the cold worked condition of the sample. This technique thus becomes suitable for detecting homogeneity of alloying very nearly in the atomic scale.

Randomly selected, four particles of a sample in a well alloyed condition as indicated by line scan EPMA were subjected to : depth profile analysis in SAM. They were sputter-etched continuously to a depth of about 1000Å, simultaneously analysing for Ni and Cr. In addition, the Auger spectra of Ni and Cr at a depth of 135Å and subsequently at a depth of 950Å were also recorded for all the four particles of the sample, and these are shown in Fig.70 and Fig.71 respectively. The ratio of peak-to-peak amplitudes of Ni to Cr for the four different particles of sample at the sputter etch depths of 135Å and 950Å were computed from Figs.70 and 71 and presented in Table 20. The peak-to-peak amplitudes of the Auger electron energy derivative $\frac{dN}{dE}$ of nickel and chromium, which are directly proportional to the concentra-

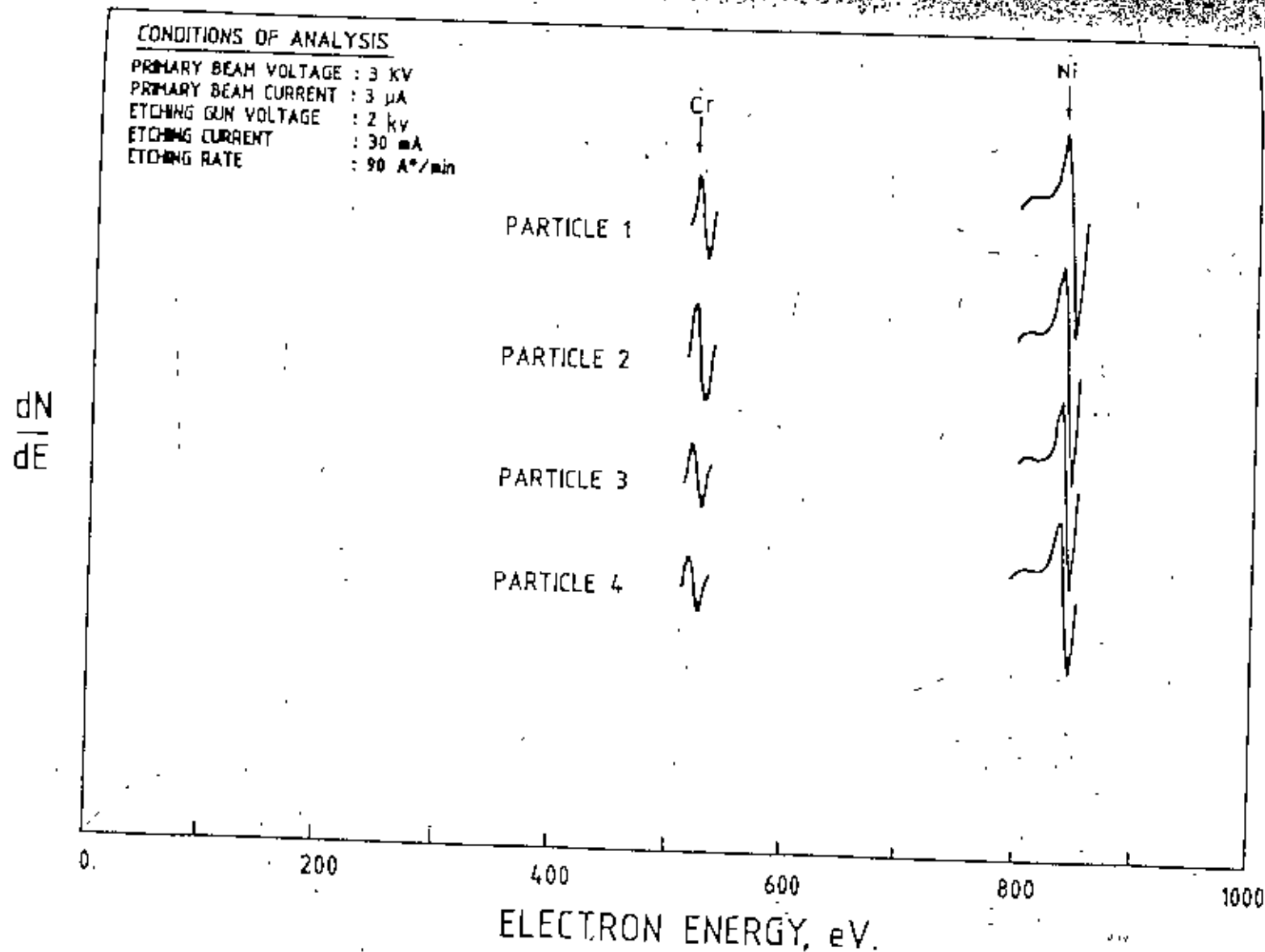


FIG 70 AUGER SPECTRUM OF Ni AND Cr OF FOUR MECHANICALLY ALLOYED PARTICLES AT 135 $\text{\AA}$ DEPTH

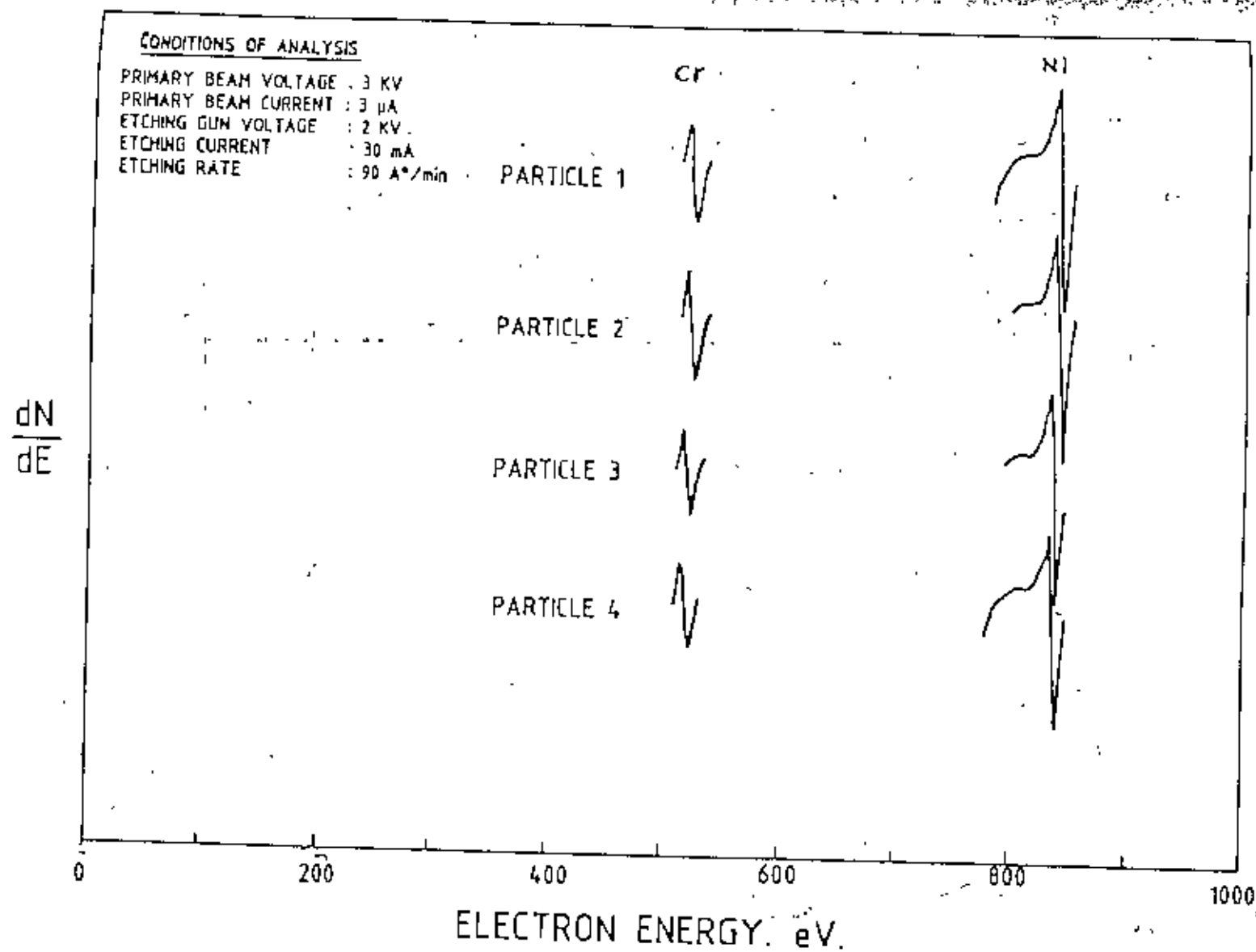


FIG 71 AUGER SPECTRUM OF Ni AND Cr OF THE FOUR MECHANICALLY ALLOYED PARTICLES IN SAMPLE A AT 950 $\text{\AA}$ DEPTH

tions of the respective elements, were continuously recorded as a function of the sputter etched depth. This record is presented in Fig.72.

Fig.72 which is the continuous depth profile analysis of Ni and Cr clearly suggests a chemically homogeneous state of chromium in nickel in the attritor-milled powder, indicated by the uniform levels of nickel and chromium throughout the sputter etched depth in the particle after the superficial oxygen-rich layer (upto $\sim 300\text{\AA}$) is removed. This is further reinforced by the results (Table 20) of $\frac{\text{Ni}}{\text{Cr}}$ ratio of peak-to-peak amplitude of $\frac{dN}{dE}$ which remains essentially same at $135\text{\AA}$ depth of the particle and $950\text{\AA}$ depth of the same particle, and also from particle to particle among the four particles analysed.

6.4 CONCLUDING REMARKS

As seen in Chapter V, magnetic coercivity behaviour of mechanically alloyed Ni-Cr- ThO_2 powders suggests the formation of a solid solution of Ni-Cr alloy by mechanical alloying. From the EPMA results described in Chapter V, it can be inferred that mechanical alloying can give chemically homogeneous alloying of the solute on a fine scale. X-ray diffraction line breadth analysis presented here strongly suggests that mechanical alloying leads to homogeneity on atomic scale as well, which is at least comparable to what is obtained in pre-alloyed powder. Scanning Auger Microprobe analysis provides a more direct evidence of atomic scale homogeneity. It is therefore reasonable to conclude that mechanical alloying by attritor milling is capable of producing

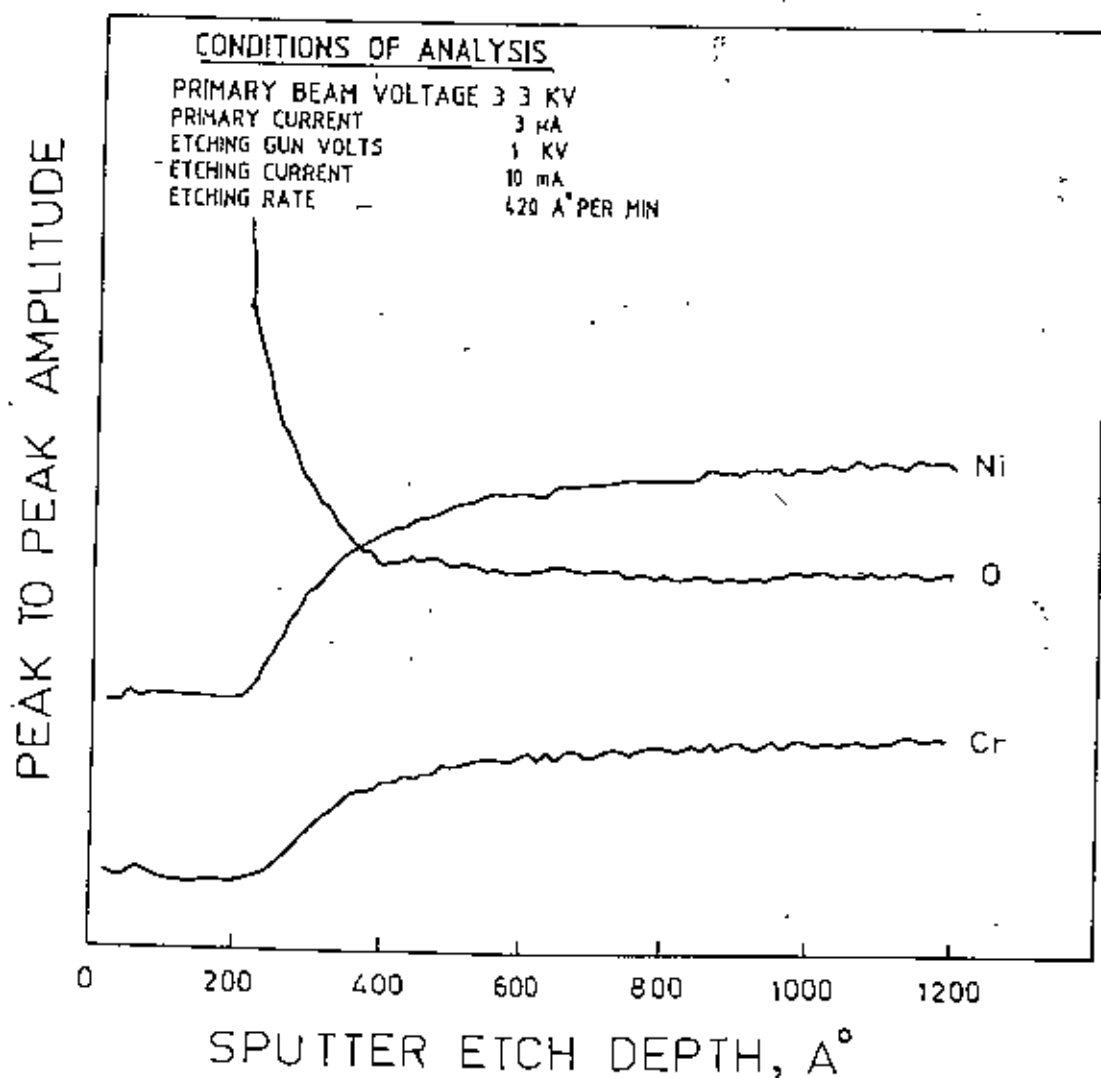


FIG 72 DEPTH PROFILE ANALYSIS OF AUGER-ELECTRON ENERGY OF THE MECHANICALLY ALLOYED POWDER

a homogeneously alloyed state that cannot be distinguished from that of a true solid solution provided that optimum milling conditions are chosen for maximum effectiveness of alloying.

CHAPTER VII

A MODEL FOR MECHANICAL ALLOYING

CHAPTER VII

A MODEL FOR MECHANICAL ALLOYING

7.1 INTRODUCTION

While mechanical alloying is essentially a process for incorporating oxide particles in uniform dispersion, it also enables alloying of solute additions into the matrix. How does this alloying take place in an attritor? What is the underlying mechanism responsible for causing the observed degree of alloying of the constituents in relatively short periods? How is the alloying influenced by the presence of the oxide dispersoid which is the principal ingredient of the composition to be produced by the process? How can we relate the mechanical energy input of the attritor to the physical process of alloying of the constituents? This chapter is addressed to these questions. Some special experiments have been carried out with a view to gain some clues to the mechanism of alloying in the attritor. These experiments and results are described here and, in the light of these and other experimental observations, a likely mechanism is proposed. This is followed by presentation of an energy-based model which is able to predict some of the milling parameters for mechanical alloying.

7.2 EXPERIMENTAL RESULTS

7.2.1 Studies on the ball motion

An attempt has been made to observe the motion of the balls in the

attritor by replacing the top lid of the attritor vessel with a transparent acrylic sheet. A vortex formation was noticed which became deeper at higher RPMs. The appearance of the balls in motion as photographed from the top is shown in Fig.73. With the balls still in motion, molten wax was poured into the attritor vessel through a hole in the transparent sheet. The attritor was switched off as soon as the wax started solidifying. The positions of the balls 'frozen' in the solidified wax should nearly correspond to instantaneous positions of the balls in motion. The wax assembly of balls was carefully detached from the impellers. The outward appearance of the wax-frozen ball assembly is shown in Fig.74. The ball positions of the outermost layer of balls in the cylindrical surface were marked onto a tracing paper. The outermost layer of balls was removed carefully from the assembly exposing the second layer whose ball positions were again traced; this was done for the cylindrical surface as well as the bottom surface. A third layer of only the cylindrical surface was similarly exposed and marked. The ball traces of the three layers of the cylindrical surface and two layers of the bottom surface are shown in Fig.75 and Fig.76 respectively. The increased randomisation and the enlarged gaps between the balls as one proceeds from the outermost to the third layer can be seen in these figures.

Another experiment was conducted wherein the bottom-most layer of the attritor was filled with 8mm diameter balls while the rest of the layers were filled with 6mm diameter balls until all the impellers were well-embedded in balls. The arrival of the balls to the top was studied at different attritor speeds (154, 260 and 450 RPM). It was observed that the 8mm balls from the

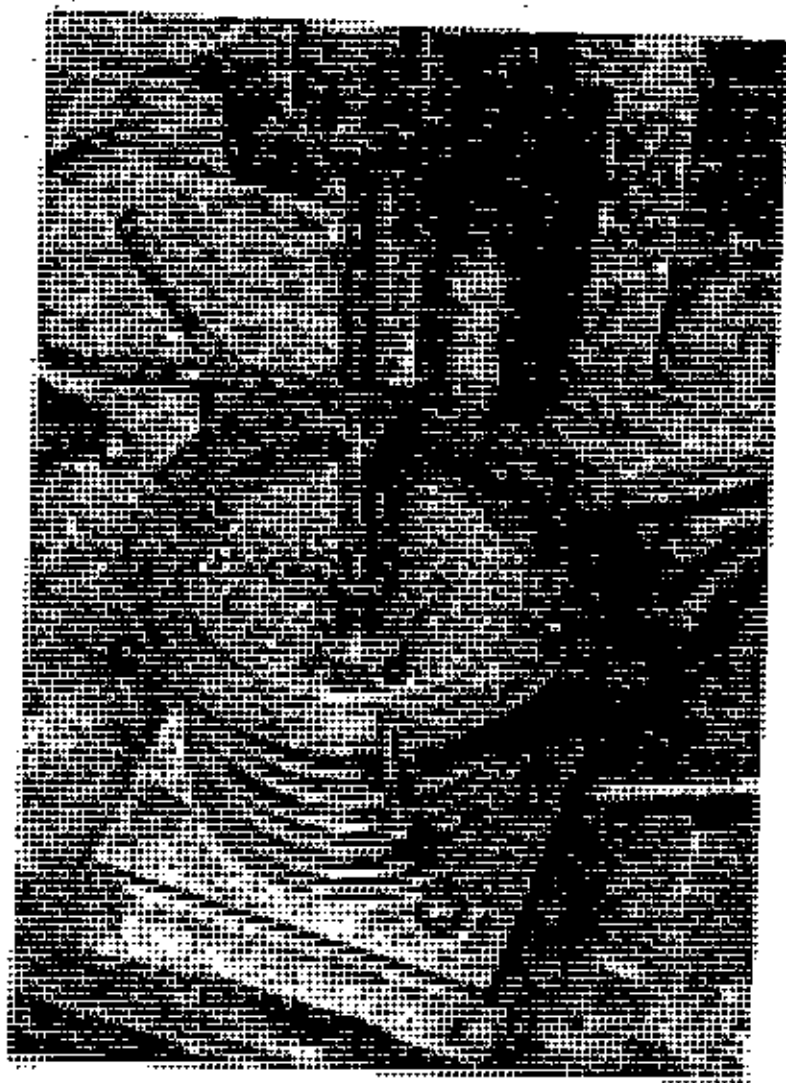
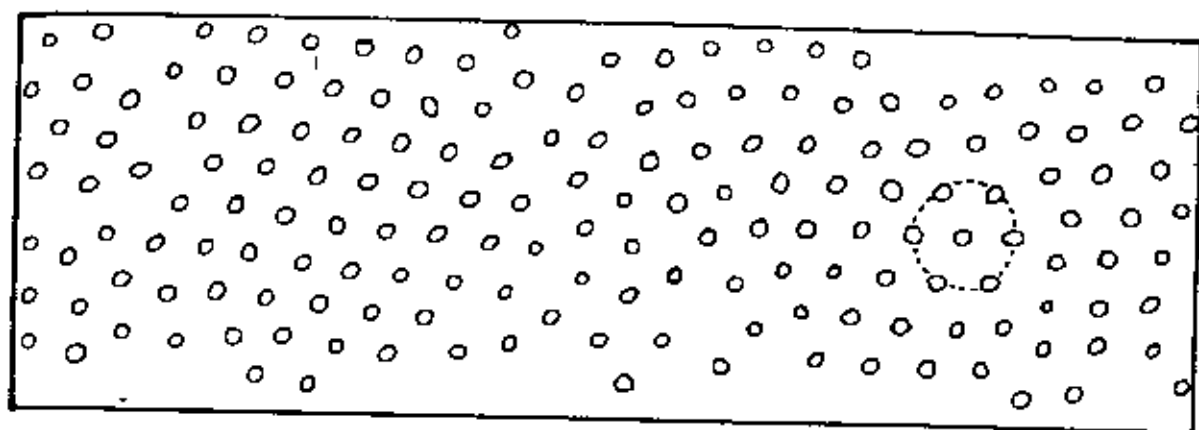


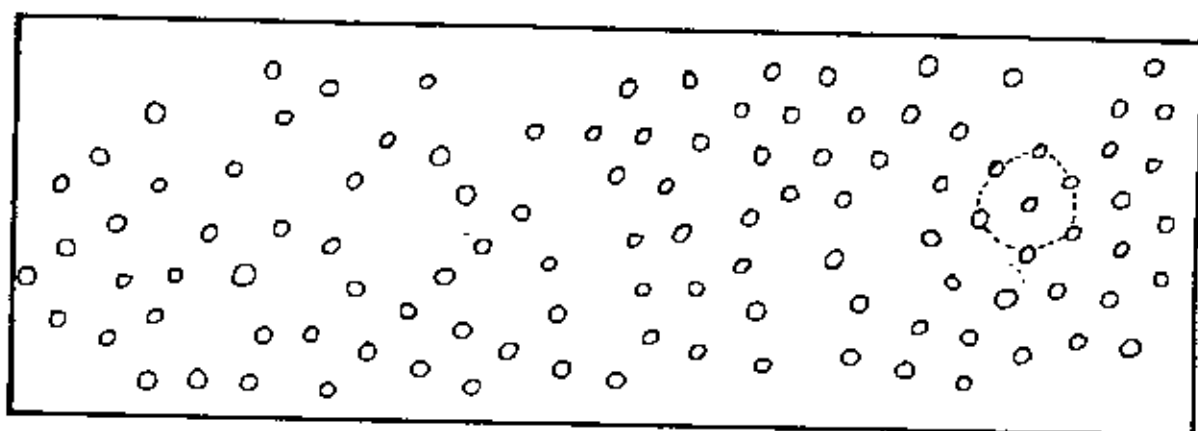
FIG 73 ATTRITOR BALLS IN MOTION-STILL PHOTOGRAPH



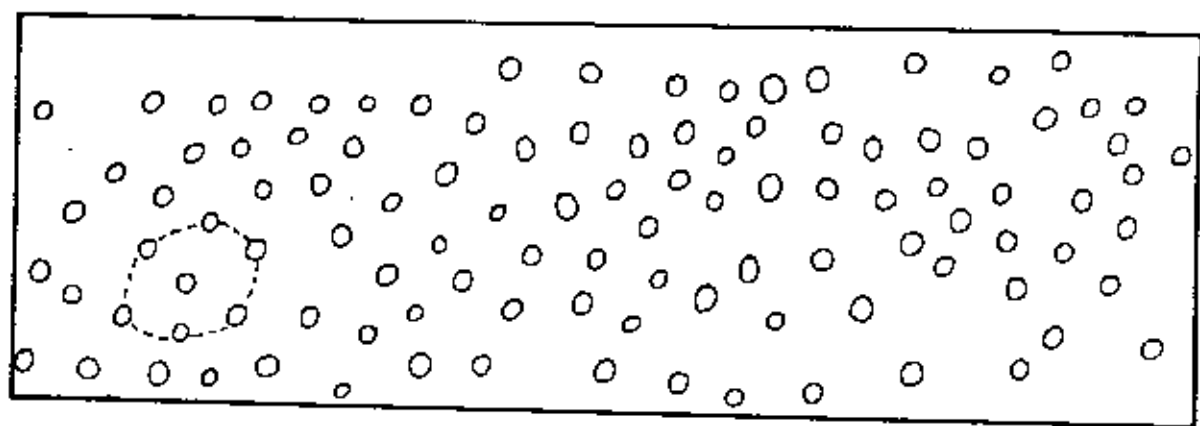
FIG 74 WAX-FROZEN SEGMENT OF BALLS



OUTER MOST LAYER



SECOND LAYER



THIRD LAYER

FIG 75 BALL TRACES OF THE OUTER CYLINDRICAL
SURFACE LAYERS

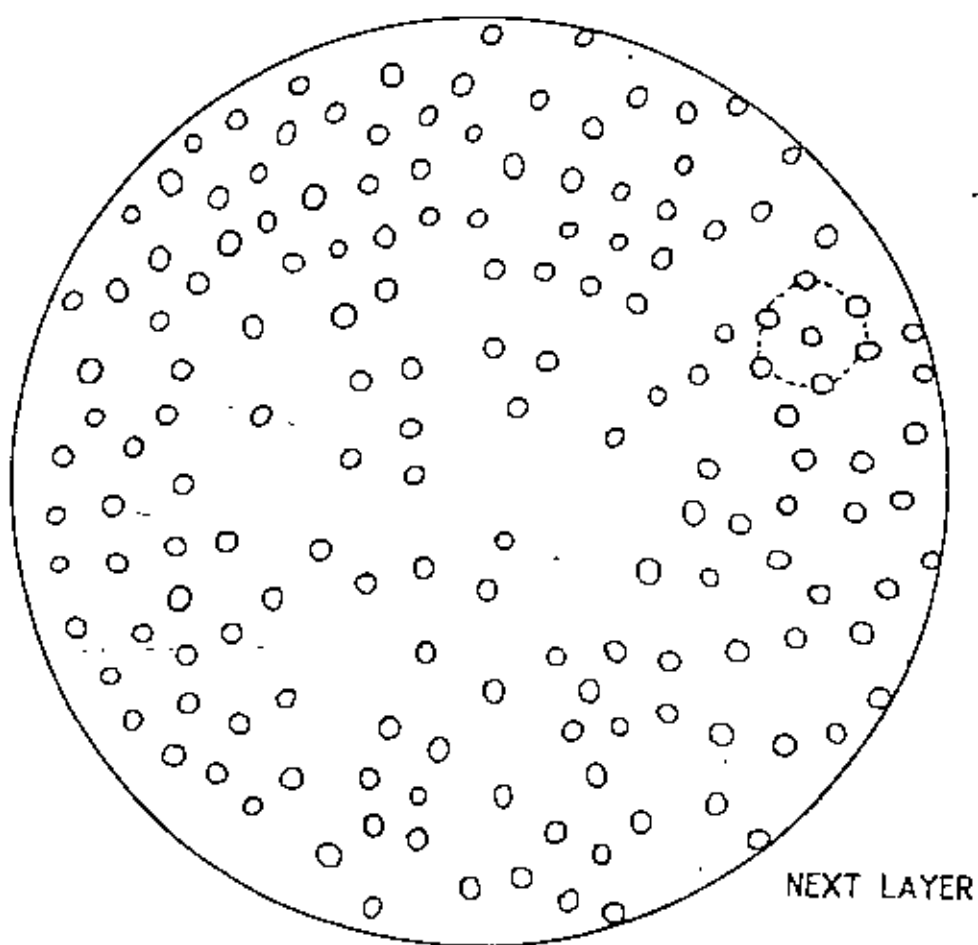
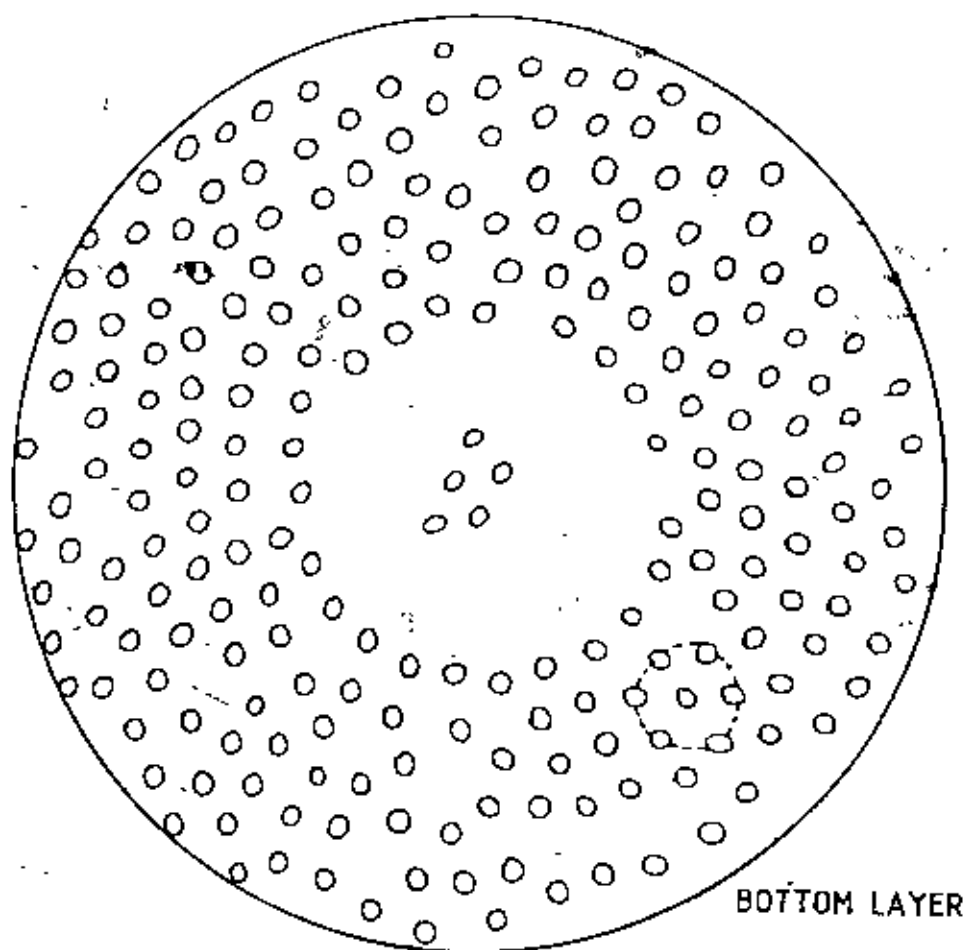


FIG 76 BALL TRACES OF BOTTOM SURFACE LAYERS

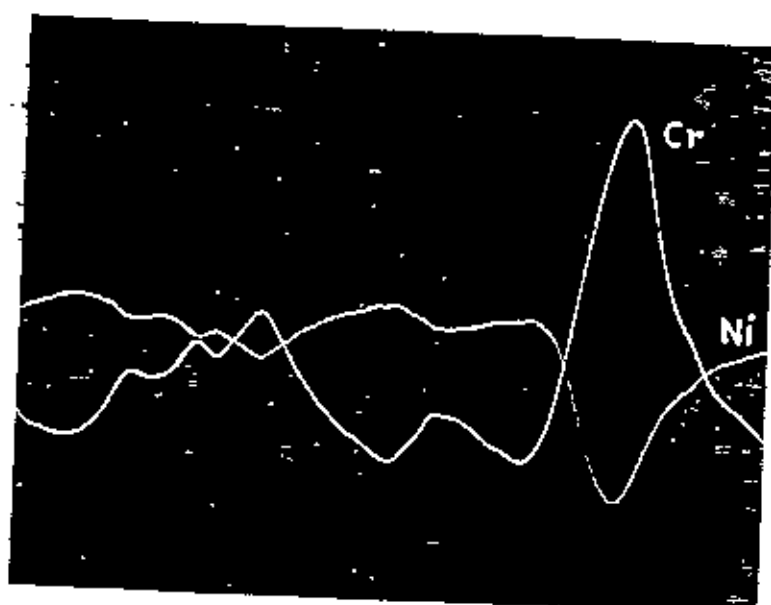
bottom came up to the top layer individually and at random intervals of time. This observation indicates that the balls from bottom layers come up at random to the top layers and go down again. These vertical motions of the balls can be taken as evidence for the presence of 'convective' currents whose significance in mechanical alloying will be discussed in Section 7.4.3.

7.2.2. Thoria-free attritor milling

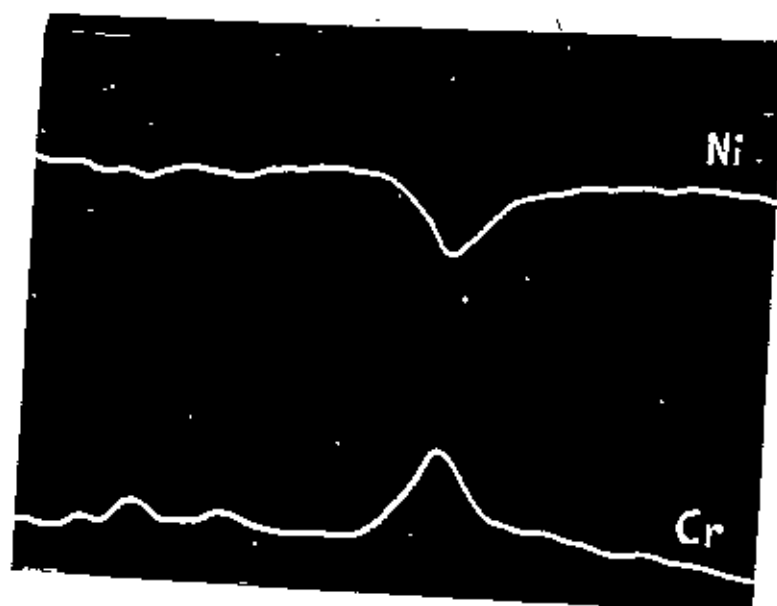
Nickel and chromium powders in 80:20 weight ratio without any thoria were attritor milled at 154 and 260 RPM upto 48 and 24 hours respectively, to be compared with similarly milled powder with 2% thoria. EPMA was carried out on the milled powders. Microhardness values are recorded in Table 21. Fig.77 shows the EPMA line scans of the thoria-free sample milled for 48 hours at 154 RPM, in comparison with a thoria-containing sample attritor milled similarly for 48 hours at the same RPM. Fig.78 shows the EPMA line scans of the thoria-free sample milled for 24 hours at 260 RPM in comparison with the EPMA scan of the thoria-containing sample milled for 24 hours at the same RPM. The analysis of these EPMA line scans are presented in Table 22. These results clearly indicate a better degree of alloying when thoria is absent.

7.2.3 Attritor milling of thoriated nickel and chromium

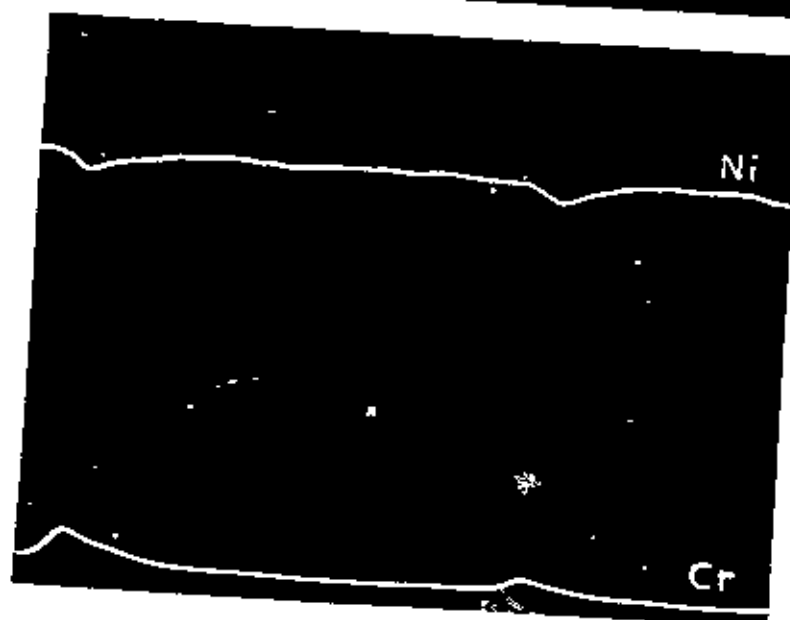
2% thoria-dispersed nickel powder was prepared by the method of chemical coprecipitation and selective reduction (see Appendix 1 for details of the



a
WITHOUT THORIA

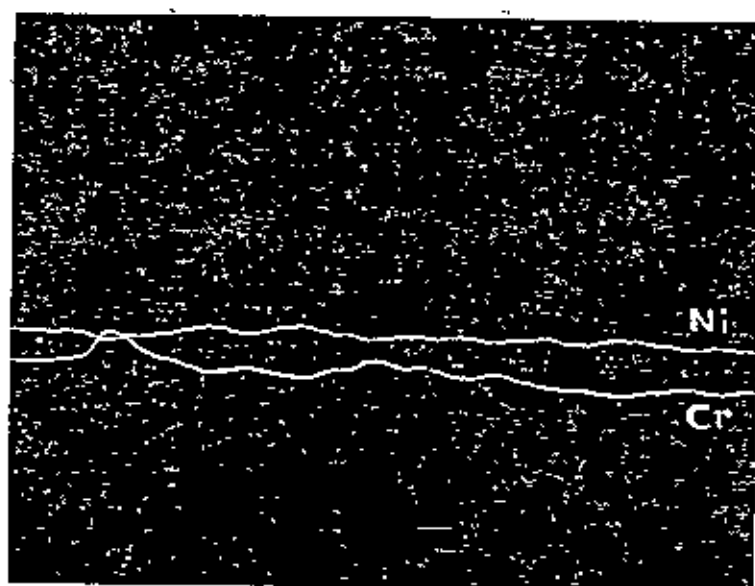


b
WITH THORIA

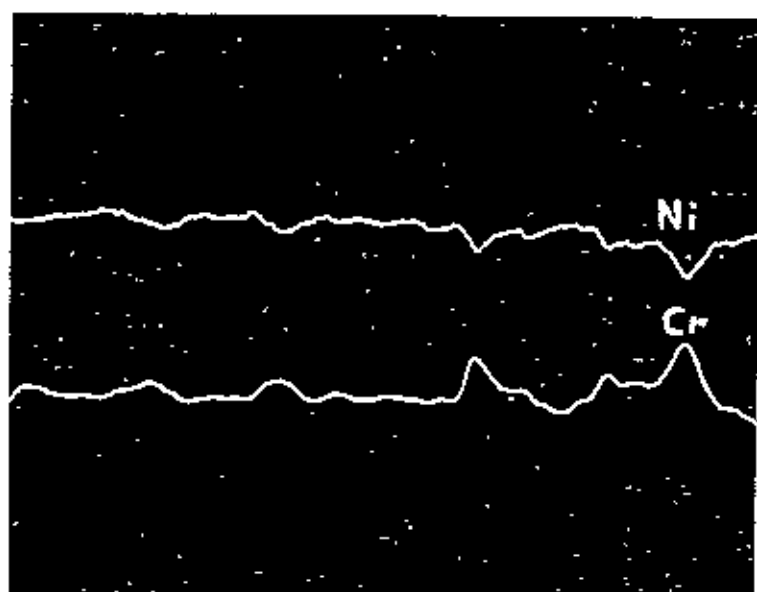


c
WITH THORIA
PRE - DISPERSED IN NICKEL

FIG 77 EPMA LINE SCANS OF SAMPLES MILLED FOR
54 HRS AT 154 RPM



a WITHOUT THORIA



b WITH THORIA

FIG 78 EPMA LINE SCANS OF SAMPLES MILLED
FOR 24 HOURS AT 260 RPM

method used). The powder was found to have an average thorium particle size of about $1000\text{\AA}$ as measured from transmission electron micrographs of the HIP-consolidated sample, illustrated in Fig.79. The thoriated nickel powder so produced was attritor milled at 154 RPM for 54 hours with chromium powder using 6mm balls in 18/1 ball ratio. The milled powder was subjected to EPMA. The line scans and line scan analysis are included in Fig.77 and Table 22 which clearly reveal a very poor alloying of chromium in thoriated nickel.

7.2.4 Attritor milling of nickel powder

Pure nickel powder was attritor milled at 260 RPM for 42 hours. Coercivity variation of this runs as a function of milling time is shown in Fig.80. Pure nickel powder was also attritor milled at 154 RPM and its coercivity variation is included in Fig.80. Microhardness measurements of these runs are presented in Table 21. It is seen that coercivity does not significantly change with milling time for pure nickel and its average microhardness is lower at the higher RPM.

7.2.5 Cooling water temperature

The attritor is water-cooled externally to enable continuous operation of the attritor for many hours and for producing optimum yield of the milled powder.

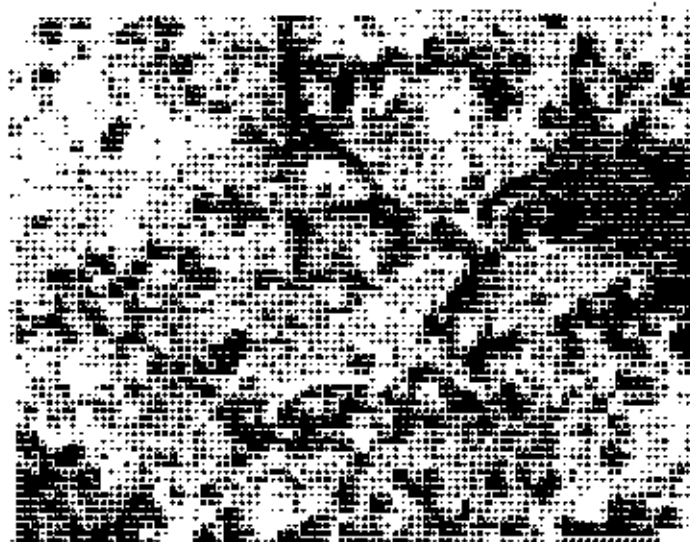


FIG 79 THORIA DISTRIBUTION IN CHEMICALLY PREPARED
Ni - 2 ThO₂, 30000 x

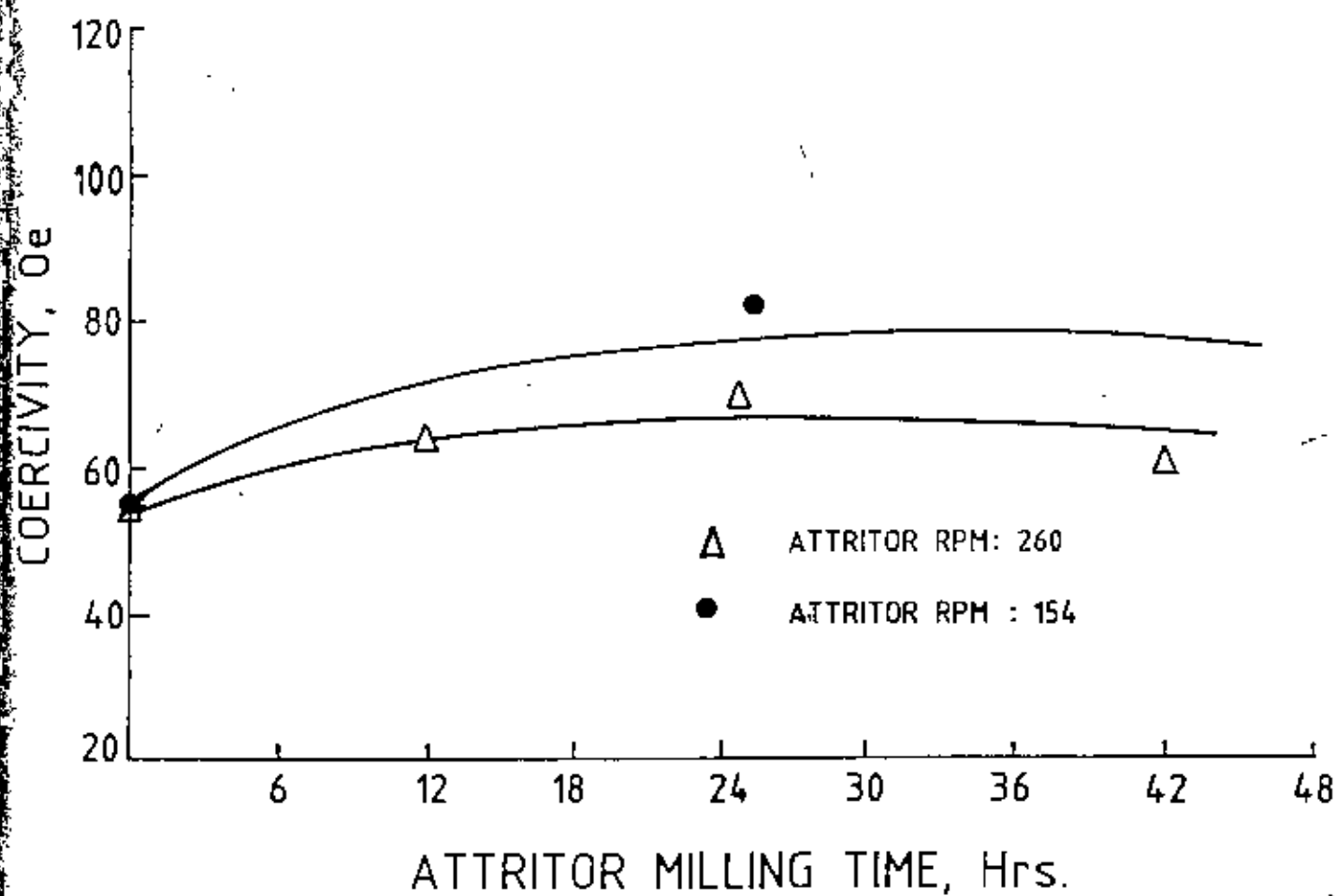


FIG. 80. COERCIVITY VARIATION IN ATTRITOR MILLING OF PURE NICKEL.

The rise in cooling water temperature from inlet to outlet is a measure of the heat generated in the attritor as a result of the agitation and motion of the balls during the course of milling of the powders. With this in view, measurements were made of the inlet and outlet water temperature, in two experiments of attritor run, one at 154 and the other ^{at} 260 RPM each time with a charge of 20% chromium, 2% thoria and rest nickel, using 6mm balls in 18/1 weight proportion; the cooling water flow was maintained at 1 litre per minute. The outlet cooling water temperature as a function of milling time is plotted in Fig. 81. The steady state rise in temperature with respect to the inlet temperature is 3°C for 154 RPM and 5°C for 260 RPM.

7.3 CHARACTERISATION OF MILLED POWDERS

7.3.1 Fisher particle size analysis

As growth in particle size and its comminution play an important role in the mechanical alloying, a study has been made of the average particle size as given by Fisher Sub-sieve Sizer on samples drawn at different time intervals in two experiments of attritor milling of nickel, chromium and thoria — one at 154 RPM and the other at 260 RPM (in both cases, 6mm diameter balls in 18/1 weight proportion were used). Fig. 82 shows the variation of average particle size with milling time. Following features are seen in the 154 RPM run: the particle size increases very slowly and also decreases very slowly and there is only one such cycle of particle growth and comminution in a milling

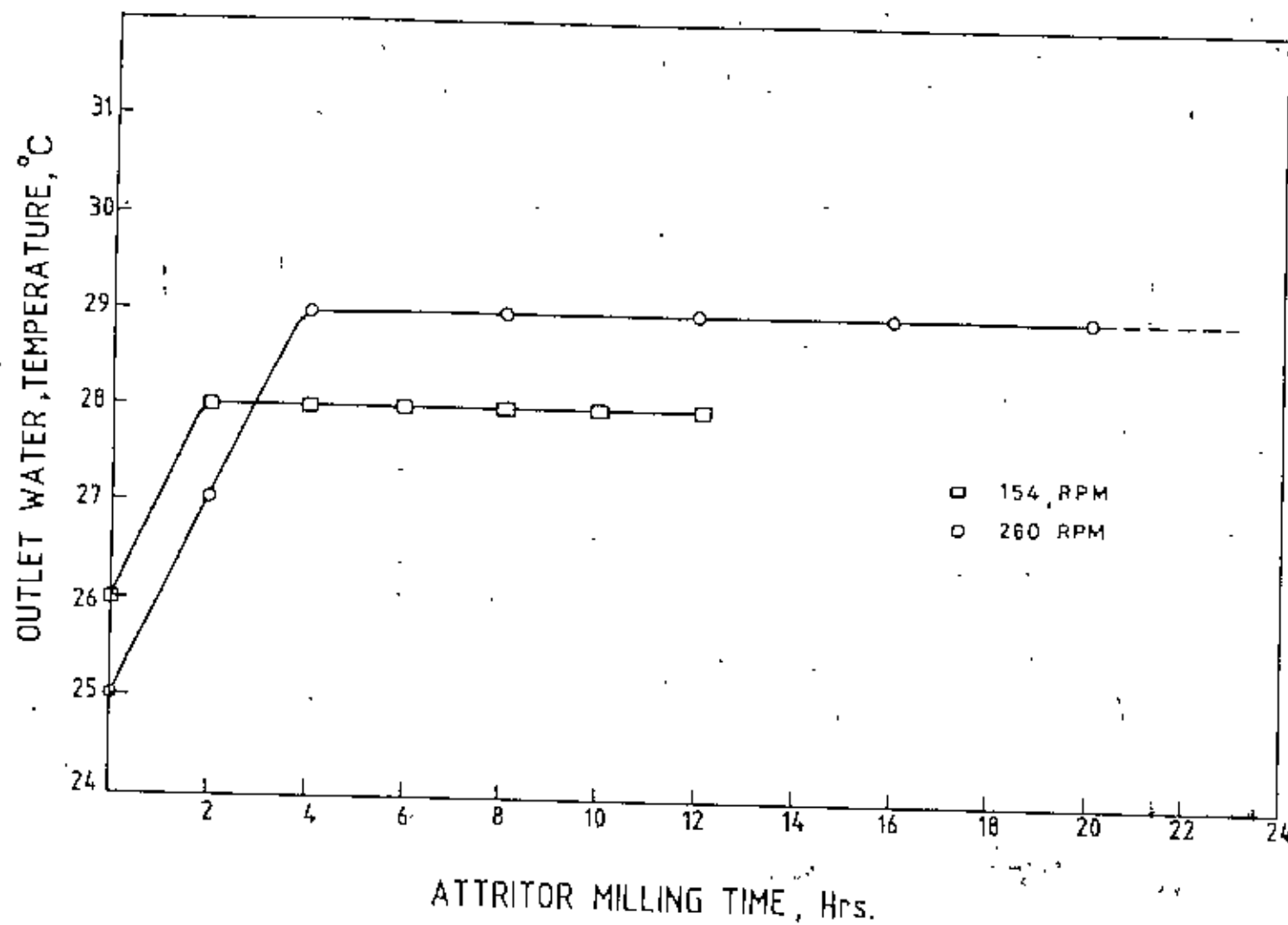


FIG 81 COOLING WATER TEMPERATURE WITH ATTRITOR MILLING TIME

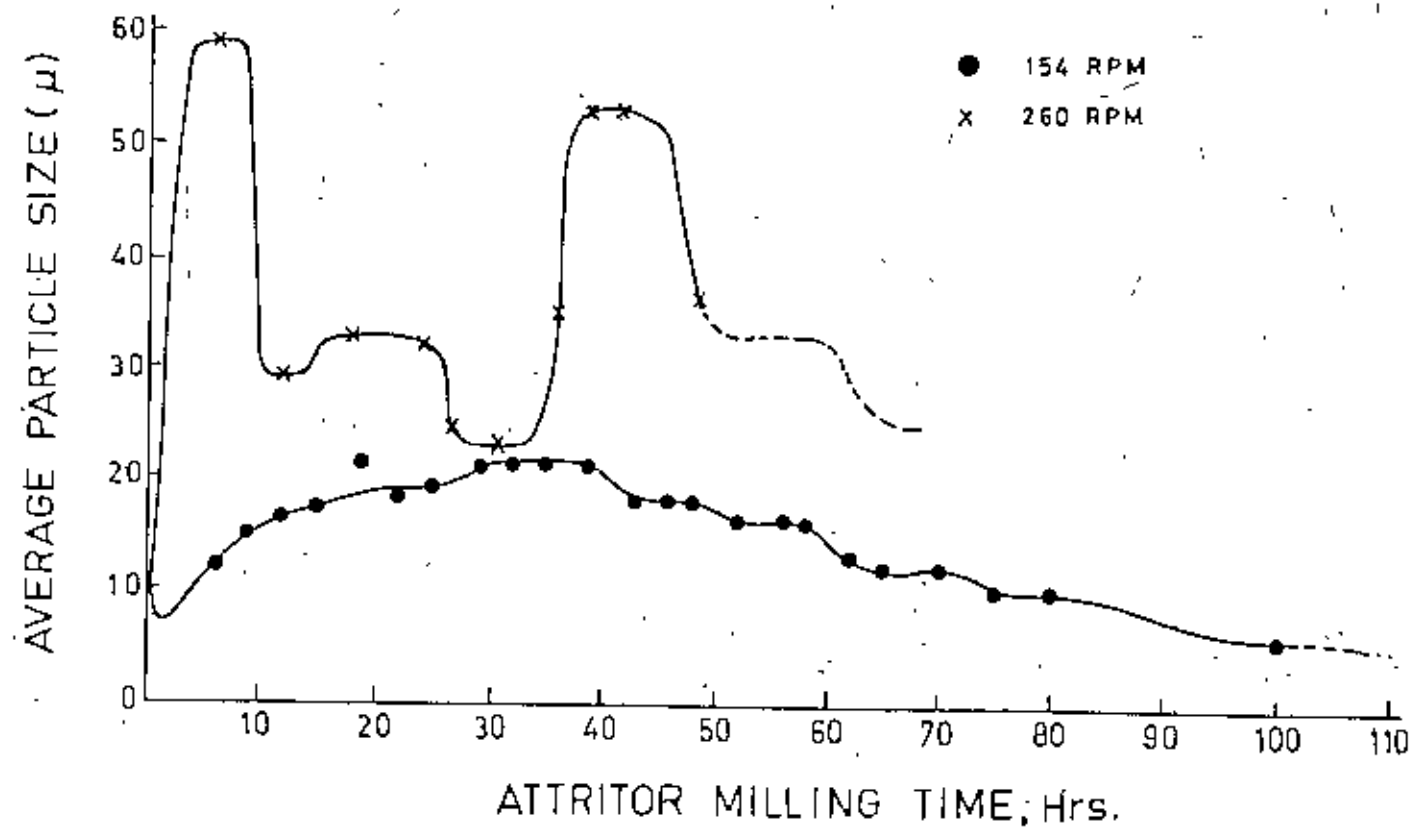


FIG 82 AVERAGE PARTICLE SIZE OF MILLED POWDER (Ni-Cr-ThO₂)
WITH ATTRITOR MILLING TIME

time of 100 hrs; the maximum particle size is only about 2-3 times the initial average size. In contrast, in the 260 RPM run, there is a more rapid rise and decrease in the particle size and two such cycles of growth and comminution are seen in a 48 hr milling time; furthermore, the maximum particle size is about 5-6 times the initial average size.

7.3.2 Microstructure and morphology of milled particles

The samples of attritor milled powder drawn at progressively increasing milling times were examined in the optical microscope. Initially chromium is seen as coarse lamellae (Fig.83a). With increasing milling time they become elongated and thinner and also convoluted in random orientations (Fig.83b). These observations are essentially similar to those reported by Benjamin and Volin (123). Average thickness of these lamellae at 12, 18, 24, 30 and 36 hrs are given in Table 23. These thickness values are used in an order-of-magnitude calculation of the average diffusion coefficient of chromium in nickel and the resulting values of diffusivities are also included in Table 23.

Scanning electron microscopy (SEM) was carried out on the attritor milled particles. While Fig.84a shows a SEM view of fracture of a composite particle during the course of mechanical alloying. Fig.84b shows the scanning electron micrograph of a composite particle revealing the interparticle-welding and layer-wise build-up of the composite particle. The inter-particle welding

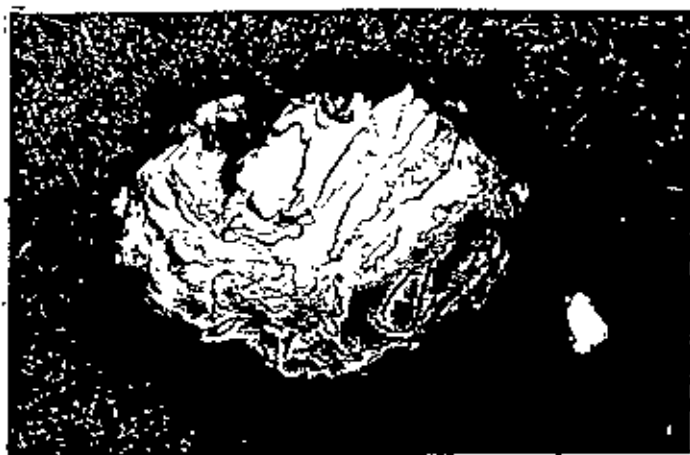


FIG 83 a COARSE CHROMIUM PARTICLES IN NICKEL MATRIX IN THE
EARLY STAGES OF MECHANICAL ALLOYING, 100 x

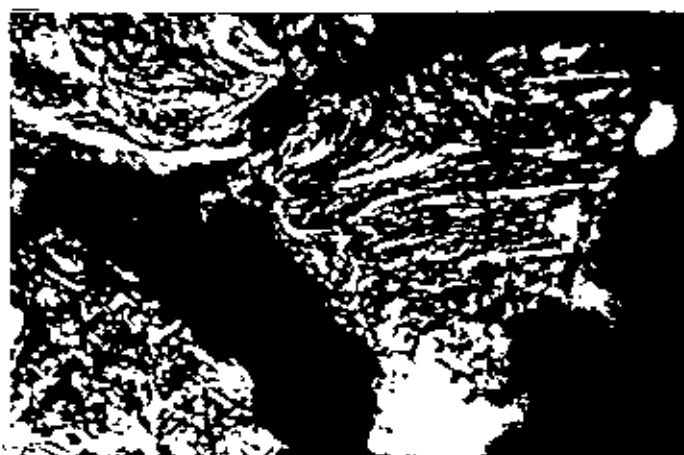


FIG 83 b ELONGATED AND CONVOLUTED CHROMIUM LAMELLAE IN
COMPOSITE PARTICLES TOWARDS THE END OF MECHANICAL
ALLOYING, 500 x

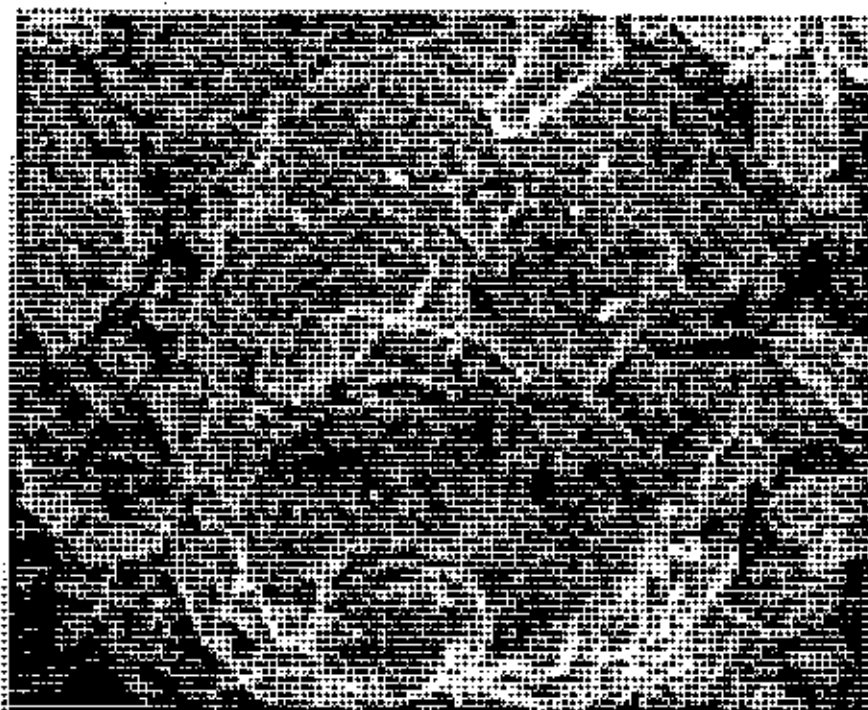


FIG 84 a FRACTURE OF A COMPOSITE PARTICLE (SEM) 2000 x

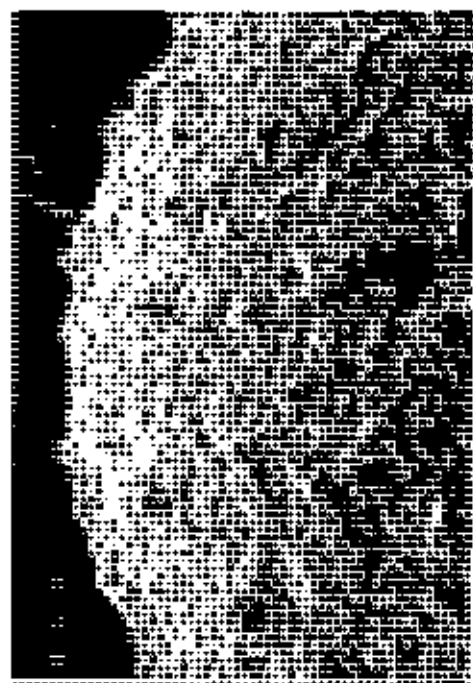


FIG 84 b WELDED LAYERS IN A COMPOSITE PARTICLE (SEM) 3000 x

and build-up of the composite particle occur on the ball surfaces at the site of their collisions. Fig.85a, b, c reveal the welded particle agglomerates on a ball surface as seen through SEM at increasing magnifications and Fig.85d is a scanning electron micrograph of a welded composite particle layer beginning to peel off a ball. When mechanical alloying is complete, the balls are coated with alloyed particles of chromium, nickel and thorium, and such a coating in fact appears as several 'peaks' of the composite particles welded to the balls (Fig.85a), each peak apparently a result of the multiple collision events during attritor milling. The EDAX (Energy Dispersive Analysis by X-ray Spectroscopy) attachment of SEM was used to analyse the chromium concentration build-up in the particles as a function of milling times; both the loose powder sample and the powder welded to balls were analysed by EDAX in the form of $\frac{\text{Cr}}{\text{Ni}}$ ratio of concentrations and the averaged results are given in Table 24. These results of chromium pick-up in the composite particles are plotted in Fig.86 as a function of milling time.

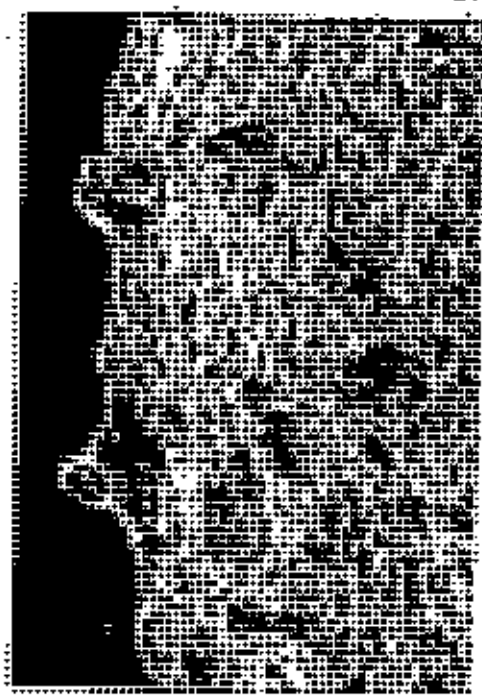
All the experimental results detailed above are used in Section 7.4 to explain the phenomenology of mechanical alloying and also in developing a new mechanism of mechanical alloying (Sections 7.5 and 7.6).

Microhardness measurements were made on several powder particles of samples drawn at different milling times from attritor milling experiments carried out at three different attritor speeds. The values were averaged for each of the samples and plotted as a function of milling time in Fig.87. It



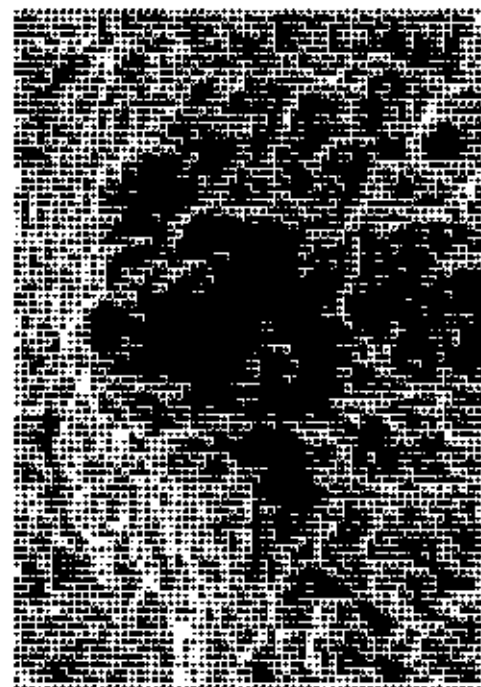
a

16X



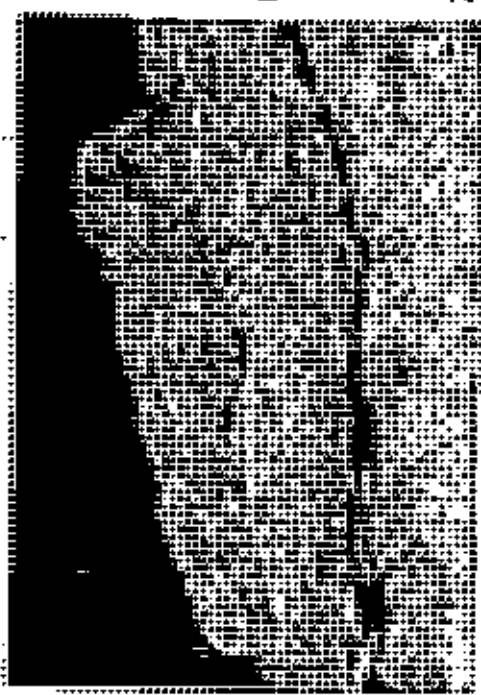
b

50X



c

200X



d

200X

FIG 85a,b,c COMPOSITE PARTICLES OF Ni, Cr, TiO WELDED TO THE BALL SURFACE

FIG 85d WELDED COMPOSITE PARTICLE PEELING OFF THE BALL

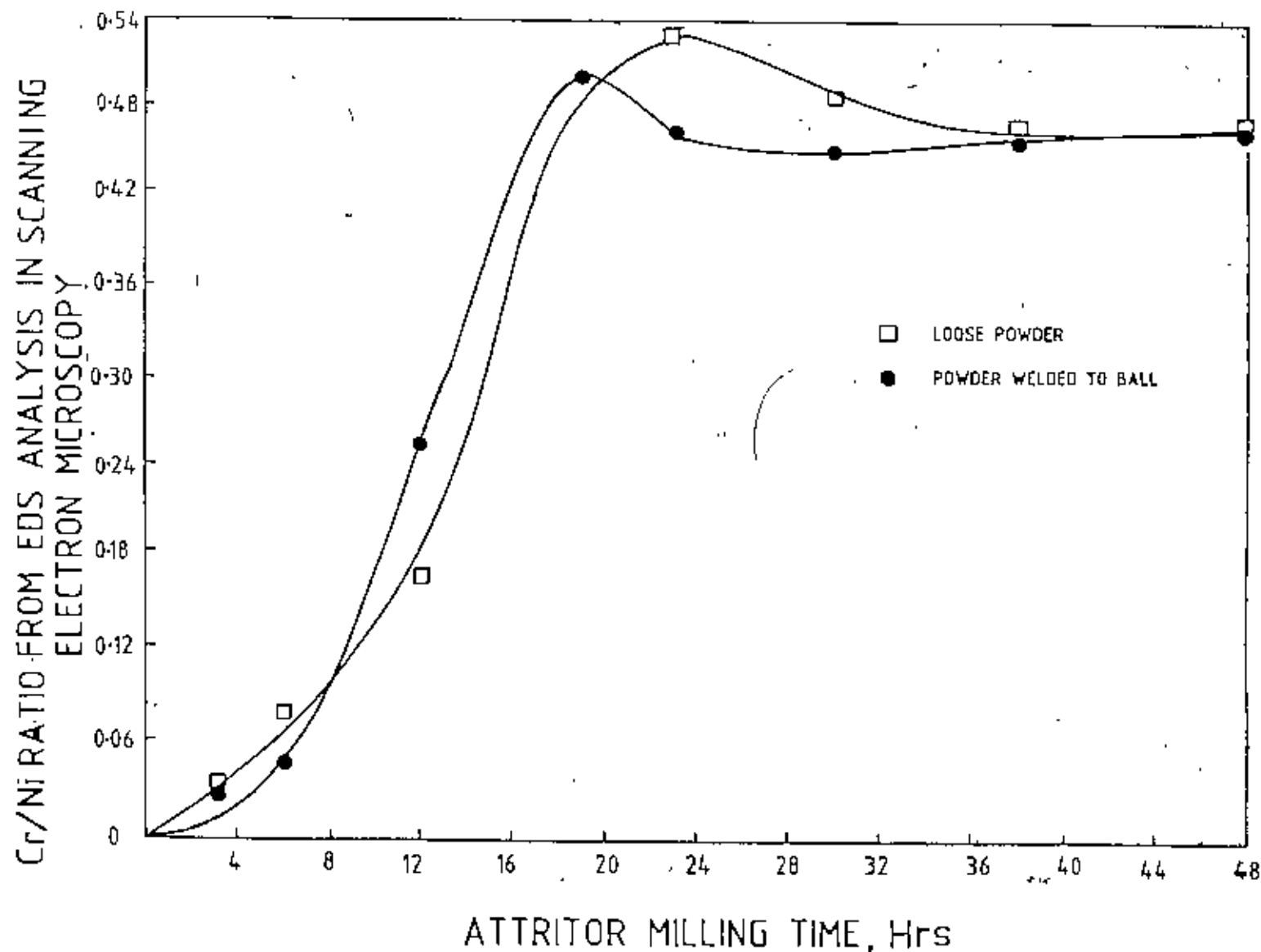


FIG 86 PROGRESSIVE CHROMIUM PICK-UP (EDAX) OF POWDER WELDED TO BALL AND LOOSE POWDER

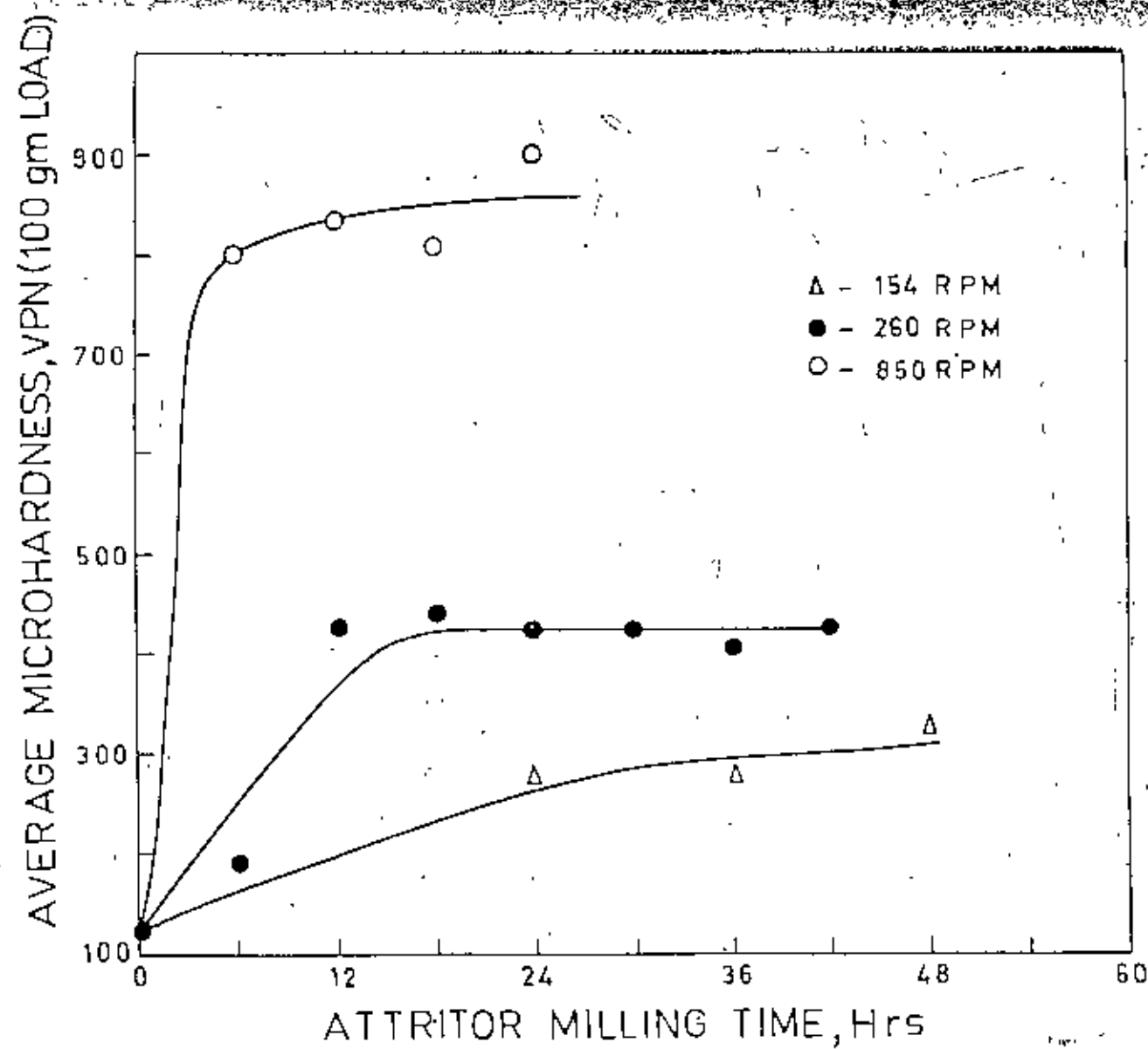
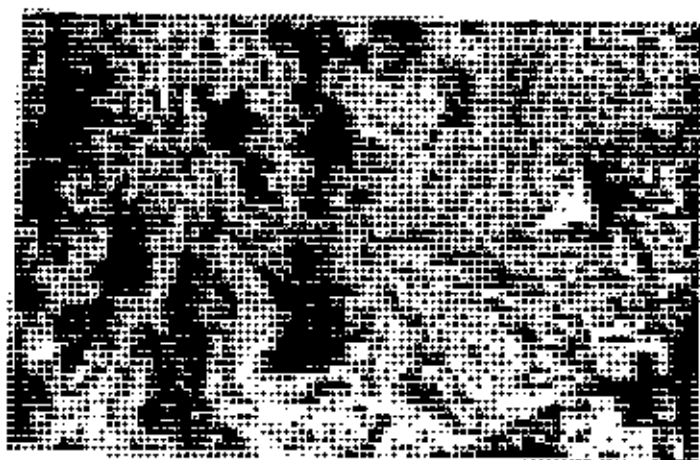


FIG 87 MICROHARDNESS WITH MILLING TIME AT DIFFERENT SPEEDS



200X



1000X

FIG 88 MICROSTRUCTURE OF ATTRITOR MILLED
PURE NICKEL PARTICLE

the one in dark etched area is harder (270 VPN). This microstructure suggests that the light etched, softer region could be a large grain resulting from a localised process of recrystallization and grain growth.

7.4 THE DYNAMICS OF MECHANICAL ALLOYING IN ATTRITOR

7.4.1 Cold work in particles

According to Benjamin (7, 117, 123) the continuous and repetitive process of welding between the particles and comminution of the particles provides the basis for mechanical alloying in an attritor. A prerequisite for mechanical alloying is that a major constituent of the powders must be sufficiently ductile to promote cold welding among the metal particles. Welding of the alloying constituents to the base metal powder particles results in the formation of composite particles whose progressive refinement in the course of the five stages of mechanical alloying (Fig.14) leads to the production of uniformly alloyed particles. Powders caught in the friction between the colliding balls undergo compressive deformation to the extent of their inherent ductility. Deformation strains thus build up within the composite particles to a point at which fracture becomes inevitable. As milling continues, the events of welding and fracturing reach a steady state. This dynamic balance between welding and fracture is indicated by production of composite particles of a narrow size distribution.

In steady state situation there will also be no further rise in the mean hardness of particles indicating saturation in cold work. During these events of welding, deformation and fracture of the metal particles, the dispersoid particles are trapped along the weld seams and distributed uniformly in the matrix (Fig.13).

Experimental observations in the present investigations corroborate the concepts of Benjamin's mechanism and the basic description of the process of mechanical alloying. Figs.84a & b provide good evidence of particle welding and fracture in attritor milling of Ni-Cr-ThO₂. Referring to Fig.82 it may be seen that in the 260 RPM run, there is an initial increase in average particle size corresponding to welding of particles, which is quickly followed by a reduction of particle size corresponding to fracture of particles. This cycle is repeated once more with an increase in milling time upto 48 hours. Furthermore, for the same 260 RPM run, the average microhardness was found to rise substantially and shows a saturation fairly early in the milling time (Fig.87). EPMA for the same run has shown homogeneous alloying in 42 hrs of milling (Fig.28). On the other hand, for the 154 RPM run the average particle size shows only a marginal and slow increase followed by a slow decrease (Fig.82) indicating comparatively poor welding among particles. For the same run, the hardness rise is slow and small, and tends towards saturation much later in the milling time. Correspondingly this run gives poor alloying as evidenced by EPMA (Fig.28). In a similar fashion a milling experiment with still higher attritor

speed of 850 RPM shows attainment of saturation hardness even earlier (Fig.87) than in 260 RPM and the level of this saturation hardness is also much higher. It has already been seen that the alloying is nearly complete in the 850 RPM as early as in 12 hrs milling time (Fig.29). These results thus highlight an important aspect of the mechanism of mechanical alloying: for homogeneous alloying to occur, attritor milling parameters should be sufficient to induce extensive cold welding among particles and also a relatively high degree cold work as indicated by a high saturation hardness. With milling conditions that induce only low saturation hardness levels, alloying is too slow and poor. Alloying is rapid and effective under milling conditions wherein high saturation hardness can be produced in relatively short milling times.

7.4.2 Progress of alloying

As described in Section 3.8.4 Benjamin and Volin (123) observe five stages in mechanical alloying during which a progressive refinement of the lamellae of the alloying elements takes place within the composite particles. In the context of the present investigation, the lumps of chromium (Fig.83a) in the composite particles of nickel, chromium and thorium break up as milling proceeds and the chromium lamellae tend to get elongated and even convoluted under the compressive stresses of attrition (Fig.83b). A point is soon reached when individual chromium particles within the composite particles cannot be resolved in an optical microscope and mechanical alloying is deemed to have been completed.

During milling the balls collide and rub against each other. Powder particles trapped in the collision sites get welded to the contacting balls. This welded layer builds up in thickness (Fig.85c) as the same ball undergoes multiple collision events, but there will be such other collisions too that cause the welded and strain-hardened layer to peel or break off from the ball as illustrated in Fig.85d. When all the composite particles are cold worked to saturation hardness levels, welding of the layers to balls becomes progressively more difficult than fracture. The progress in alloying of the layers welded to balls closely follows that of the dewelded, loose powder in the attritor, as verified by the EDAX analysis in SEM (Fig.86). Fig.86 also reveals that alloying occurs at the ball collision sites. A point to be noticed in Fig.86 is that around mid-time of milling, the chromium concentration goes to a peak before it levels out to a uniform concentration, both in the case of powder welded to the ball and in the case of the loose powder. This suggests that Cr pick-up in the composite particles occurs more rapidly than the rate at which it can be homogenised into the matrix. Furthermore, the rate of alloying of loose powder is seen to slightly lag behind that of the welded layer in the ball in the intermediate milling time, indicating that the loose powder is from earlier ball collisions. Towards the end of milling, these differences vanish and the state of alloying of the welded layer of the ball is same as that of the free powder.

7.4.3 Agitation velocities

The essence of attritor milling lies in the action of balls which are made to collide and rub against each other by the impellers. The wax-frozen

ball traces (Figs.75, 76) clearly suggest that the ball motion in the attritor is randomized. The randomization however is seen to be more in the vicinity of the impeller-ends. The randomised motion of balls implies turbulent flow, which is generally considered to be a necessary condition for producing a 'well-mixed' condition in agitators and for mixing of fluids (132). In turbulent fluid flow, there is an average velocity vector at each point in the agitator, as well as a random fluctuation of the values of this vector about their mean values, which causes an interchange of the fluid between different parts of the vessel, leading to homogenisation of the composition of the fluid mixture. We have already seen in Section 7.2.1 that the balls from the bottom layers tend to come up individually to the topmost layer and go down again. Thus the balls perform a vertical loop motion producing some kind of 'convective' loop currents, in addition to their revolutions around the axis of the attritor. A schematic illustration of the convective currents is shown in Fig.89.

As in the mixing of fluids in agitators, the convective currents in the attritor are a result of the vertical components of the velocity vectors which will also have components in the other two directions, producing radial and tangential motion. We believe that these convective currents in the attritor are vital for effective alloying. Without them, only the bottom layer balls will be participating in the alloying action and the top layers will remain in idle rotation; most of the powder which always tends to settle at the bottom would then have little chance of being subjected to collisions between balls.

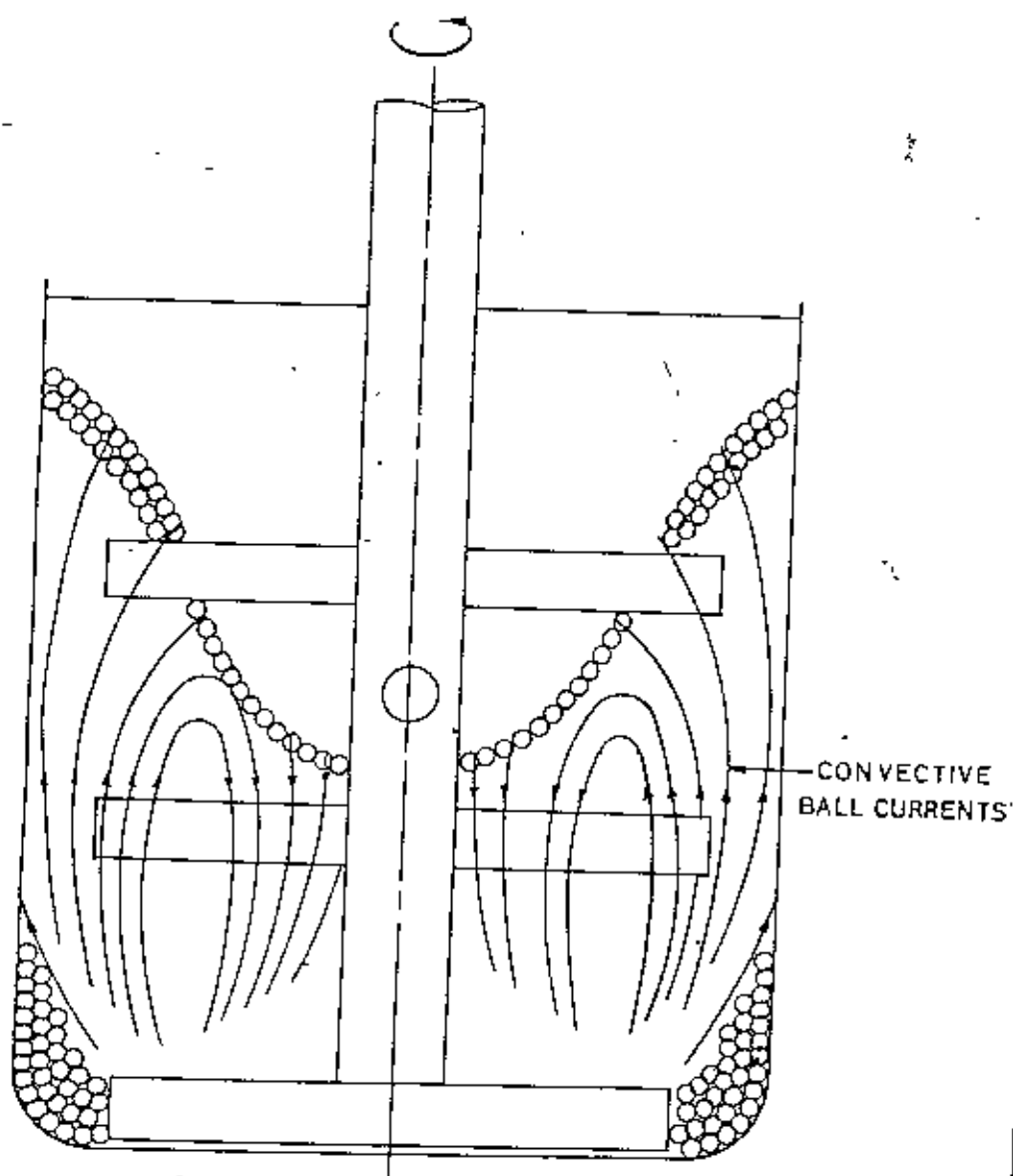


FIG 89 SCHEMATIC VIEW OF CONVECTIVE BALL CURRENTS
IN ATTRITOR

7.4.4 Mixing versus mechanical alloying

At this juncture, it is interesting to note some difference between mechanical alloying occurring in an attritor and mixing in an agitator, despite the above mentioned basic similarities between agitators as used for mixing and attritors which are a special type of agitators. The balls in motion in attritors closely simulate flow of fluids. For instance, vortex formation by the balls has been observed in the attritor (see Section 7.2.1). Vortex formation is generally considered to be undesirable in achieving good mixing of fluids in agitators and baffles are generally used to eliminate vortex formation (although, even unbaffled agitators have sometimes been used with good results of mass transfer). In contrast, the use of baffled attritor has been shown in the present work to retard mechanical alloying (Fig.53) in comparison with milling in an unbaffled attritor. Apparently, the baffles in the attritor have only served to diminish the kinetic energy of the balls in motion, and this in turn diminishes the energy involved in the attritive collisions between the balls that is necessary for mechanical alloying. The baffles also subdue the vertical convective currents. The result thus points to a generalized conclusion that not all factors that are useful for good mixing are necessarily useful for mechanical alloying despite the similarities involved. One of the main reasons for this difference could be the fact that in mixing applications, the impellers in the agitators directly drive the fluids to be mixed without any intermediate medium, whereas for mechanical alloying the attritors use grinding balls without which alloying of the powders is not feasible.

7.5 ESTIMATION OF MEAN, LOCAL TEMPERATURE RISE

It was shown in Chapter VI that there will be true alloying of chromium in nickel attritor milling under the right operational conditions. Since alloying requires diffusion of the species, and since diffusion is predominantly a temperature dependent phenomenon, one can not but postulate local rise in temperature during the attrition of the powder trapped between two colliding balls to account for alloying in attritor. Obviously the friction and collisions during attrition can cause local and momentary temperature rises. Many questions now arise: what kind of average temperature rise must be occurring that can account for the observed alloying? How can one account for the very poor or very slow alloying observed under one set of conditions of attrition as against the excellent alloying under another set of operational parameters? Can we incorporate the various operational parameters into one unifying equation for mechanical alloying? In this section we propose a model for mechanical alloying to answer these questions.

First let us consider the average extent of diffusion of chromium in nickel that occurs in a known time interval in a typical mechanical alloying experiment. From the microstructures of the milled particles at 6, 12, 18 and 24 hours of milling time, several measurements of the thicknesses of chromium lamellae have been made and their averaged values are given in Table 23 which also shows the corresponding diffusion coefficients based on the very approximate relation:

$$x \approx \sqrt{Dt}$$

(eqn. 13)

where x = Distance of diffusion, which, here is the reduction of thickness of Cr lamellae,

D = Average diffusion coefficient for the diffusion of chromium by distance x

t = time of milling involved

It can be inferred from Table 16 that the average rate of diffusion of chromium in nickel works out to be about $2 \times 10^{-13} \text{ cm}^2/\text{sec}$. Search of literature has revealed that the diffusivity data of Cr in Ni are available only in the range of 950-1200°C which are given to be (145):

$$Q_c = 54.7 \text{ kcal/mole}$$

$$D_0 = .037 \text{ cm}^2/\text{sec}$$

These are to be used in the Arrhenius relation,

$$D = D_0 \exp(-Q_c/RT)$$

(eqn. 14)

Where D = Diffusivity at temperature, T (Kelvin)

Q_c = Activation energy for diffusion

D_0 = Pre-exponential frequency factor

Assuming these values to be applicable for our estimated value of D , it is calculated that a D value of $9 \times 10^{-13} \text{ cm}^2/\text{sec}$ is applicable for a temperature of about 800°C.

The above calculation therefore suggests that the mean, effective temperature during attrition should be of the order of 800°C for the observed diffusion by mechanical alloying of Cr in Ni. Since local temperature rise occurs in transient spurts during attritive collision events, the individual thermal spikes would be of higher magnitude. However, no noticeable microstructural change was seen in the perimetric edge of the attritor milled steel balls to account for such a high temperature rise, although the temperature rise in the steel balls can be expected to be lower than that in the particles in view of the formation of a coating of the Ni-Cr alloy on the ball surface. If, therefore, one presumes conservatively that such high temperatures of the order of 800°C are not generated in mechanical alloying, then there must be some other means by which such fast diffusivities may be attained.

An order of magnitude calculation can now be done to estimate the overall mean temperature in the attritor as a whole, by balancing the heat quantity absorbed by the cooling water with the heat that may be transferred by the attritor during mechanical alloying. This may be expressed as:

$$q_v \rho_w C_{p_w} (T_2 - T_1) = M C_{p_A} \Delta T \quad (\text{eqn. 15})$$

where:

- q_v = measured volume flow rate of the cooling water
- ρ_w = density of cooling water
- C_{p_w} = specific heat capacity of water

- T_1 = water temperature at inlet
 T_2 = water temperature at outlet
 t = time in minutes during which steady state T_2 has been attained
 M = total mass of the attritor plus powder and ball charge
 C_{pA} = specific heat capacity of the attritor as a whole which is taken to be equivalent to a typical value of steel, since the vessel and the balls are all made of steel
 ΔT = Overall, mean temperature rise inside the attritor that can account for the heat liberated to the cooling water

From the cooling water temperature measurements described in Section 7.2.5, we have, for the case of the well-alloyed, attritor run at 260 RPM:

- q_v = 500 cc/min
 ρ_w = 1 gm/cc
 t = 4 x 60 minutes (Fig.82 shows steady temperature of 29°C attained in about 4 hours of milling time from an initial temperature of 25°C).
 $T_2 - T_1$ = 4°C
 $C_{pW} \approx 42 \times 10^3 \text{ joules/gm}^\circ\text{C}$ for water
 M = 13 kg (about 7 kg for the attritor and about 6 kg for the balls and powder)

$$C_{PA} \approx 4.7 \times 10^2 \text{ joules/gm/}^\circ\text{C for steel}$$

These data, introduced into eqn. 15 give a value of 330°C for ΔT as an approximate estimate of the overall temperature rise inside the attritor. The local, mean temperature rise at collision sites will of course be somewhat higher than this value.

If one now considers that the mean temperature rise in attritor milling lies in the vicinity of 300°C , the normal diffusion rates (of Cr in Ni) applicable at these temperatures would be inadequate to cause homogeneous alloying. If we assume the bulk diffusion data available only for $950\text{--}1200^\circ\text{C}$ range for chromium in nickel to be valid even at about 300°C , then D , the diffusion coefficient works out to be in the order of magnitude of $10^{-15} \text{ cm}^2/\text{sec}$. On the other hand, the minimum value of D that may be applicable for the observed rate of alloying as already shown previously in this section works out to be in the order of magnitude of $10^{-13} \text{ cm}^2/\text{sec}$. Apparently attritor milling involves some process(es) that enhance(s) the diffusivities by some two orders of magnitude.

7.6 MECHANISMS OF ENHANCED DIFFUSIVITY

7.6.1 The possibilities

Possible causes of enhanced diffusion of chromium in nickel in attritor milling will now be examined. It is seen from the microhardness and coercivity

measurements that the initial period of milling is characterised by increasing cold work. For instance, the microhardness exhibits an increase with time ultimately leading to a saturation level (Fig.87). It is during the saturation stage that alloying tends to become homogeneous. It appears therefore that heavy cold work of the particles is a necessary precursor for homogeneous alloying. Cold work can enhance diffusivities in the following ways:

- i. by an increase in vacancy concentration
- ii. by causing pipe diffusion i.e. diffusion along dislocation lines

The latter possibility appears attractive since very high dislocation densities are generated in a mechanically alloyed particle due to severe cold work. Furthermore, pipe diffusion needs a lower activation energy than bulk diffusion thereby resulting in enhanced diffusivities even at such low temperatures as 300°C. (Pipe diffusion has been indicated as a possible creep mechanism in metals at not too high a temperature (54)).

There is yet another possibility for enhancement of diffusion in mechanical alloying, and that is, recrystallization of the cold worked particles. The mean temperature rise inside the attritor, calculated to be around 300°C, may be enough to induce recrystallization of severely cold worked metal since it is known that cold worked metals generally recrystallize at about 0.3 to 0.4 T_m and further that the recrystallization temperature decreases with increasing cold work. It has been shown (146) that diffusivities are enhanced

ii) Relatively weak alloying is observed for the case of attritor milling of nickel, chromium and thorium wherein thorium is added separately as compared to the milling of nickel and chromium alone (Figs. 77, 78 and Table 22). It is also seen that the degree of alloying of chromium in nickel is comparatively better when thorium is added individually than when it is added as pre-alloyed with nickel. This result reinforces the case for a recrystallization mechanism in the following manner. In the initial stage of milling, thorium when added separately is not initially dispersed as fine particles in the nickel matrix but attains the desired dispersion only progressively with milling. Thus ThO_2 does not initially offer resistance to recrystallization of nickel and hence does not hinder alloying as much as when ThO_2 is predispersed in nickel wherein it resists recrystallization right from the beginning of milling with chromium.

iii) Another support for the recrystallization model comes from the results of attritor milling of pure nickel. It was seen that pure nickel milled at 260 RPM induced an average hardness of 350 VPN in the particles, and when milled at 154 RPM the average hardness in the milled particles was about 500 VPN. Apparently the higher RPM generated higher local temperatures of attrition which can cause localised recrystallization and therefore a lowering of the average hardness. Admittedly, the average particle hardness of 350 VPN is higher than the normal value of annealed nickel (about 200 VPN). The reason for this difference could be the variety of collisions in the attritor. All collisions do not have the same kinetic energy. Collisions near the upper regions or near the shaft have lower energy than collisions near the periphery

and towards the bottom. Some collisions occur close to the impellers by direct hit and have high energy while some take place when balls attempt to fall into the open spaces by gravity and hence have lower energy. Thus there is a wide distribution of energy of collisions. Only the critical, high energy collisions may be inducing recrystallization while many others merely serve to induce only cold work.

iv). Presence of 'soft' spots in individual particles, even after mechanical alloying is completed, could be an indication of localised recrystallization areas within the particles. Several microhardness measurements were carried out on individual particles (at the end of milling) and, as shown underlined in Table 25, some of these values within each of the particles are far lower than the others. Such soft spots were seen in numerous particles. It is most likely that such soft regions are recrystallized. An example of a coarsened grain showing a lower hardness, apparently a result of recrystallization and grain growth is given in the photomicrograph in Fig. 88*.

From the foregoing discussion it is not unreasonable to postulate that the mean local temperature rise during attritor milling for effecting mechanical alloying need not be higher than the recrystallization temperature of the matrix

* Difficulties of etching the severely cold worked particles aborted the several attempts of obtaining a more clear-cut evidence for recrystallization in the particles. Sample preparation for TEM of individual particles (to delineate recrystallized areas) did not prove to be successful.

element in cold worked state, although recrystallization may not solely be responsible for the enhanced diffusivity.

With this background, an attempt will now be made to derive an order-of-magnitude expression for the minimum heat energy required for mechanical alloying, and to compare it with an expression for mechanical energy input of an attritor.

7.7 THE ENERGY BALANCE MODEL

7.7.1 The heat energy density

We have seen in the previous section that mechanical alloying by diffusion is facilitated in an attritor if the local temperature rise in the attritive collisions is sufficient to cause recrystallization of the cold worked powder. Let us assume that all the powder is uniformly distributed throughout the ball charge inside the attritor. Consider a unit volume of the ball charge of the attritor wherein mechanical alloying is taking place. The minimum heat energy developed in the power contained in a unit volume of the attritor — which we may call the heat energy density — can be expressed in terms of the average heat capacity of the powder material as follows:

$$HE_v = \rho'_b C_p (T_R - T_A) \quad (\text{eqn. 16})$$

where

HE_v = heat energy density, or the minimum heat energy required for mechanical alloying in unit volume of the attritor

ρ'_b = weight of the powder participating in unit volume of the attritor

C_p = specific heat capacity of the powder

T_R = recrystallization temperature of the cold worked matrix (Kelvin)

T_A = ambient temperature (Kelvin)

We shall now find an expression for ρ'_b in terms of known parameters.

By definition,

$$\begin{aligned}\rho'_b &= \frac{\text{total weight of the powder in the attritor}}{\text{total volume occupied by ball-powder charge}^*} \\ &= \frac{\text{total weight of the powder}}{\text{Total volume of balls/packing factor of balls}} \\ &= \frac{\text{total weight of the powder} \times \text{packing factor of balls}}{\text{total weight of balls/density of ball material}} \\ &= \frac{\text{total weight of the powder}}{\text{total weight of balls}} \times \text{packing factor} \times \text{density of ball material}\end{aligned}$$

By definition,

$$W = \text{balls-to-powder weight ratio} = \frac{\text{total weight of balls}}{\text{total weight of powder}}$$

* approximately taken to be the volume occupied by ball charge only

Thus

$$\rho'_b = \frac{\delta \rho_b}{W}$$

where δ = packing factor of balls of a uniform diameter

ρ_b = density of the ball material

Therefore,

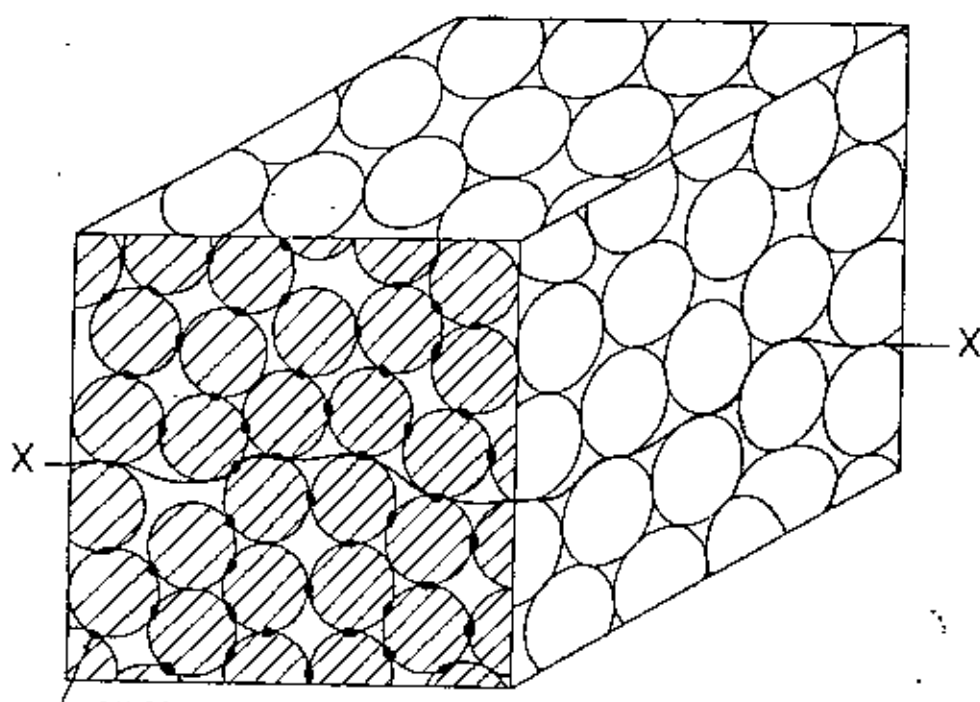
$$HE_v = \frac{\delta \rho_b}{W} C_p (T_R - T_A) \quad (\text{eqn. 17})$$

Spheres of uniform diameter in densest, static packing have a packing factor of about 0.7. The packing factor in reality in the case of balls moving in an attritor will of course be less than this value. The wax-frozen ball assembly, described in Section 7.2.1, has been examined in different portions and the average packing density of the balls has been calculated which also works out to be approximately 0.6 of the ball density. We can therefore assume an approximate value of 0.6 for δ .

7.7.2 The kinetic energy density

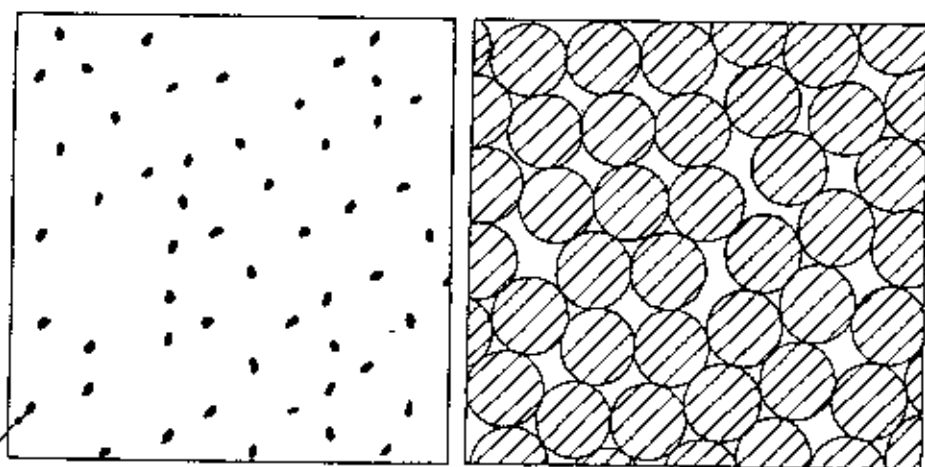
The heat energy density for alloying, as given above must be supplied by the mechanical energy input given to the balls in motion. The mechanical energy responsible for heat generation in the attrition milling is a complex function of the several variables involved in the kinetics of ball motion. We can now interpret in simple terms, the kinetic energy density in the following manner.

1. The attritor consists of an energetic medium of balls communicating



POWDER TRAPPED IN CONTACT POINTS OF COLLIDING BALLS

A UNIT VOLUME OF THE BALL MEDIUM



CONTACT AREA BETWEEN COLLIDING BALLS

A_{CONTACT}

IN PLANE X-X

A_{AVERAGE}

IN PLANE X-X

FIG 90 SCHEMATIC DEPICTION OF LOCAL DENSITY OF ATTRITOR BALL MEDIUM AND CONTACT AREAS OF ALLOYING

with each other at points of contact. The points of contact experience intense pressures and the powder particles trapped therein get deformed and alloyed. The energy of the ball medium is primarily kinetic and is derived by the passage of the rotating impellers through them. The energy density — which is the kinetic energy available in a unit volume of the medium — can be written as $\frac{1}{2} \rho_b v^2$ where

v = average linear speed of the ball medium

This energy density can also be considered equivalent to average kinematic pressure. At contact points, this average pressure is transmitted across the individual ball contact areas which are relatively very small in comparison with the surface area of the balls transmitting the average pressure (see Fig.90). This situation leads to locally enhanced pressures at ball contacts. A simple force balance can be visualised through the following equation:

$$P_{\text{contact}} \times A_{\text{contact}} = P_{\text{average}} \times A_{\text{average}}$$

$$\text{or, } P_{\text{contact}} = P_{\text{average}} \times \frac{A_{\text{average}}}{A_{\text{contact}}} \quad (\text{eqn. 18})$$

$$\text{where, } P_{\text{contact}} = \text{local, contact pressure}$$

$$A_{\text{contact}} = \text{area in contact}$$

$$P_{\text{average}} = \text{average kinematic pressure of ball medium}$$

$$A_{\text{average}} = \text{average area over which the } P_{\text{average}} \text{ is transmitted}$$

Since kinematic pressures are equivalent to energy densities, we may write the above equation as:

$$\frac{1}{2} \rho'_b v^2 = \left(\frac{1}{2} \rho'_b v^2 \right)_{\text{average}} \times \frac{A_{\text{average}}}{A_{\text{contact}}} \quad (\text{eqn. 19})$$

where the LHS represents the local energy density arising from contact pressures.

$$\text{Since } \frac{A_{\text{average}}}{A_{\text{contact}}} = \frac{D'^2}{d^2}$$

where D' = ball diameter

and d = average length of contact, which is here approximated to the typical, average diameter of the composite particle undergoing alloying at the contact area

We may thus express the average kinetic energy density, KE_v , which is the local energy density of the ball medium as:

$$\frac{1}{2} \rho'_b v^2 = \frac{D'^2}{d^2} \left(\frac{1}{2} \rho'_b v^2 \right)_{\text{average}} \quad (\text{eqn. 20})$$

Mechanical alloying is seen to be a gradual phenomenon, the degree of alloying progressively improving with milling time. This is because of the statistical nature of 'fruitful' collisions of balls (— that is, collisions having the right conditions to cause alloying —) in addition to the fact that diffusion is time-dependent. The kinetics of the ball motion largely determines the extent of alloying and the time required for it. The linear velocity imparted

to a ball by the impeller of length 'L' rotating at a shaft RPM of N is given by $2 \pi N L$, $2 \pi N$ being the angular velocity. All the balls do not receive the same velocity under the action of the rotating impellers because (i) the velocity imparted tends to be minimum at the root of the impeller ($L=0$) and maximum at the tip of the impeller ($L=L$) and (ii) the velocity diminishes as we go along the direction of rotation from the balls located in immediate contact at the impeller to the balls located just behind the next impeller. Furthermore, depending on the location of the ball with respect to the perimeter of the impeller cross section the direction of velocity varies, giving rise to 'convective' motion of the balls.

If it is assumed for simplicity that all collisions cause alloying and that the maximum linear velocity of a ball is available to all the balls, and in view of

$$\rho'_b = \delta \rho_b$$

then the average kinetic energy density of the ball medium is given by

$$\frac{1}{2} (\delta \rho_b) \left(\frac{2 \pi N L}{60} \right)^2$$

From this, the local kinetic energy density intensified by contact pressures, given in eqn. 20 can be expressed as follows:

$$KE_v = \left(\frac{D}{d} \right)^2 \frac{1}{2} (\delta \rho_b) \left(\frac{2 \pi N L}{60} \right)^2 \quad (\text{eqn. 21})$$

7.7.3 The energy criterion for mechanical alloying

For alloying to occur, it is logical to postulate that the local kinetic energy density given by eqn. 21 must exceed the minimum heat energy required for alloying as given by eqn. 17, and thus this criterion may be written as:

$$\left(\frac{D'}{d}\right)^2 \frac{1}{2} (\delta P_b) \left(\frac{2\pi NL}{30}\right)^2 > \frac{\delta P_b}{W} C_p (T_R - T_A) \quad (\text{eqn. 22})$$

This reduces to:

$$\frac{W}{2} \left[\left(\frac{D'}{d}\right) \left(\frac{\pi NL}{30}\right) \right]^2 > C_p (T_R - T_A) \quad (\text{eqn. 23})$$

Eqn. 23 thus relates the mechanical energy input expressed in terms of the operational parameters of attritor milling to the heat energy requirement for alloying and can be used to predict the minimum values of the parameters of milling for mechanical alloying.

The RHS of eqn. 23 assumes a fixed value since C_p and T_R are constants for a given system. For most metals C_p is about 0.1 cal/gm/K and T_R is approximately 0.4 T_m where T_m is the melting point of the matrix. For the system under investigation, then, we get:

$$T_R - T_A \approx 390 \text{ K}$$

Thus the value of $C_p (T_R - T_A)$ will be* :

$$0.1 \times 390 \times 4.2 \times 10^7 = 1.64 \times 10^9 \text{ ergs/gm}$$

The use of eqn. 21 in predicting attritor milling parameters is now exemplified below for a few cases.

a) Attritor speed

In Section 5.3.1 dealing with the question of optimum attritor speed, the RPM was varied keeping other variables fixed. We will now examine how the alloying criterion will be met from eqn. 23 for the same values of the attritor parameters.

Since it has been observed that in most of the cases of attritor milling, the final average particle size at the end of mechanical alloying is in the neighbourhood of 50μ , we can reasonably assume this value for d in eqn. 23. The other parameters fixed in the experiments of RPM variation are:

$$N = 154 \text{ RPM}$$

$$L = 7 \text{ cm (from the centre of attritor shaft)}$$

$$D = 6 \text{ mm}$$

*Because of the deletion of ρ_b on either side of eqn. 23, $C_p (T_R - T_A)$ has units of ergs/gm instead of ergs/cc which is the correct units for heat energy density. However, $C_p (T_R - T_A)$ is hereafter loosely referred to as the heat energy density for convenience. Similarly the LHS of eqn. 23 is referred to as the mechanical energy density.

Substituting the above values in eqn. 23 we get

$$\frac{W}{2} \left(\frac{D}{d} \right)^2 \left(\frac{\pi N L}{30} \right)^2 = 1.65 \times 10^9 \text{ ergs/gm}$$

It is thus seen that the kinetic energy density at 154 RPM is barely adequate to meet the heat energy requirement. It thus explains the result of EPMA which showed poor alloying at this RPM even upto 66 hours of milling (Fig.30) and required 100 hours of milling for satisfactory alloying (Fig.58a). If we now consider a higher RPM of 260 as was used in the experiments described in Section 5.3.1 and other parameters remaining as above, we will get a value of $\sim 4.7 \times 10^9$ for the kinetic energy term, which is substantially higher than the heat energy requirement, a condition favourable for alloying. This is borne out experimentally as seen in Fig.28.

It is easily seen from the above kinetic energy value for 154 RPM that the energy input will be even lower at a lower RPM and will therefore be unable to match the heat energy requirement. Similarly it can also be seen that higher RPMs will boost the kinetic energy above the heat energy values. We may therefore conclude that attritor speeds below about 150 RPM will not be adequate for mechanical alloying and speeds above 150 RPM will be necessary for effective alloying, when 6 mm balls in 18:1 ratio are used.

b) Balls-to-powder weight ratio

We have observed (Section 5.3.2) effective alloying when ball ratios at and above 40:1 are used in conjunction with the same speed of 154 RPM. Applying this value for W and other parameters as before in eqn. 23, we get:

$$\frac{W}{2} \left(\frac{D'}{d} \right)^2 \left(\frac{\pi N L}{30} \right)^2 \approx 3.67 \times 10^9 \text{ ergs/gm}$$

which is substantially higher than the heat energy value of 1.64×10^9 ergs/gm and therefore should lead to effective alloying. This is indeed the case as seen in Fig. 36b.

c) Ball diameter

We can interpret the result illustrated in case (a) wherein we obtained 1.65×10^9 ergs/gm for the mechanical energy at 154 RPM as also the mechanical energy input valid for a 6mm ball diameter run, other parameters remaining same. As before, this is only barely matching with the heat energy requirement and therefore not effective for alloying. Obviously lesser ball diameters will fail to meet the heat energy requirement. By increasing the ball diameter to 8 mm, we get from eqn. 23,

$$\frac{W}{2} \left(\frac{D'}{d} \right)^2 \left(\frac{\pi N L}{30} \right)^2 \approx 2.94 \times 10^9 \text{ ergs/gm}$$

which well exceeds the heat energy requirement, and therefore should lead

to effective alloying as verified by EPMA in the actual experiment (Fig.43).

The above examples illustrate the basic validity of eqn. 23 as an expression of a criterion for mechanical alloying. It is further seen that - where the kinetic energy term is lower than or barely matches the heat energy value, the mechanical alloying is experimentally found to be poor and where it considerably exceeds the heat energy value, the alloying is likewise found to be effective and comparatively fast. It must however be pointed out that not all the attritor parameters figure in this equation. Furthermore, only threshold values rather than optimum values of the attritor parameters can be predicted. Besides such limitations, this energy balance model ignores the kinetics of the process and hence milling time which is also an important variable cannot be predicted. An additional factor to be noted here is that it is difficult to assign any precise value for 'd' in the eqn. 23. Thus the value of 50μ is only a reasonable estimate of a typical size of the composite particles based on actual observations made in the present investigations.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

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8.1 SUMMARY

This thesis comprises detailed investigations on the process of mechanical alloying in a typical composition, Ni-20Cr-2ThO₂. Starting with powders of nickel, chromium and thoria, mechanical alloying experiments have been conducted in a specially built laboratory attritor mill. The efficacy of mechanical alloying in an attritor compared to a conventional ball mill has been demonstrated using electron probe microanalysis. A performance index has been formulated to quantify the degree of alloying. This index is expressed in terms of the average amount of chromium picked up in a composite particle at any instant of milling and the average degree of inhomogeneity of distribution of chromium in the particle as determined from the results of electron probe microanalysis. Magnetic coercivity change has also been used to monitor the degree of alloying of chromium in nickel. Distribution of the dispersoid (thoria) under different conditions of milling has also been studied by transmission electron microscopy. Using the above - mentioned performance indicators, the parameters of attritor milling that could be optimised for maximum effectiveness of alloying were the attritor speed, diameter of the grinding balls, balls-to-powder weight ratio, impeller geometry and starting particle sizes of nickel and chromium.

An important aspect studied in the present work is the question whether mechanical alloying leads to the formation of true solid solution of chromium in nickel. Besides the evidence of EPMA, X-ray diffraction line breadth analysis has been combined with Scanning Auger Microprobe analysis of the attritor milled powder to bring out the scale on which the homogeneity of alloying has occurred.

Based on the clues provided by some specially chosen experiments of attritor milling of nickel, chromium and thoria, the most likely mechanisms of alloying in the light of available literature have been discussed.

Since the essence of attritor milling lies in its high mechanical energy input, the observed effects of variation of milling parameters on the efficacy of mechanical alloying must be related in some manner to the mechanical energy input to the powders. A model has been attempted in which an expression for the mechanical energy input resulting from the different operational parameters has been derived. This is set against an expression for the heat energy required for alloying based on a likely diffusion mechanism of mechanical alloying. The model is able to predict some of the threshold conditions of attritor milling for mechanical alloying.

8.2 CONCLUSIONS

The results of these studies lead to the following main conclusions:

1. Under optimum conditions of attritor milling, mechanical alloying is capable of producing a homogeneous state of alloying that cannot be distinguished from a true solid solution.
2. Mechanical alloying of Ni-20Cr-2ThO₂ in an attritor of about 200mm inside diameter is found to be most effective when the attritor speed is about 350 RPM in conjunction with 6mm steel balls in 18/1 balls-to-powder weight ratio. It is also seen that the least number of revolutions to be performed for bringing about maximum effectiveness of alloying approximately corresponds to this optimum RPM value. The milling time associated with the optimum RPM is about 32 hours.
3. Mechanical alloying can be made equally effective at speeds lower than the optimum by increasing the balls-to-powder weight ratio.
4. A balls-to-powder weight ratio of about 35/1 is optimum when the ball diameter is 6mm and the attritor RPM is about 150. The milling time associated with this optimum ratio is about 39 hours.
5. A ball diameter of about 8mm is optimum when the attritor has to be run at about 150 RPM and when the balls-to-powder ratio is 18/1.
6. The attritor RPM, the balls-to-powder weight ratio, and the ball diameter cannot be indefinitely increased because values of these parameters

beyond the optimum are seen to produce less effective alloying. This can however be improved in all these cases by increasing the milling time.

7. Satisfactory thoria distributions are obtained when the attritor milling parameters are optimised with respect to alloying of chromium in nickel.
8. Triangular cross section impellers are more effective for mechanical alloying than round or flat section impellers and, 8 impellers are adequate for an attritor height of 180 mm.
9. The average particle sizes of chromium and nickel have considerable influence on the effectiveness of mechanical alloying: finer chromium and/or coarser nickel lead to better alloying.
10. Magnetic coercivity change can make distinctions between a case of less degree of alloying and a case of greater degree of alloying in compositions where a magnetic change occurs with alloying in the constituents. In the present investigations on Ni-20Cr-2ThO_2 , it is found that a peak-crossed drop in coercivity is necessary in order for chromium to alloy into nickel in attritor milling. Absence of a peak indicates poor alloying. The technique however cannot quantify the extent of alloying and the degree of homogeneity of alloying.

11. The peak in magnetic coercivity is attributed mainly to the attainment of a 'saturated' degree of cold work of the particles which the imposed milling parameters have to generate during the course of milling and its subsequent drop is a result of the predominance of dissolution of chromium.
12. A necessary condition for mechanical alloying is that a high level of 'saturated' cold work must be induced in the composite particles. Alloying of the solute is a diffusion process resulting from the localised rise in temperature during the intense, attritive collisions between the balls. It is estimated that the mean, local rise of temperature in the attritor under milling conditions for effective alloying may be of the order of 300°C. Since such magnitudes of temperature are too low to account for the estimated rate of diffusion of chromium in nickel, an enhanced diffusivity mechanism is expected to be operating for mechanical alloying in an attritor.
13. Metallographic and EPMA results suggest that instantaneous recrystallization of the cold worked matrix by the local rise in temperature in high intensity collisions between the balls may be the process that provides a powerful means of evening out concentration gradients of chemical inhomogeneity, even at such relatively low temperatures as 300°C.

14. The criterion for mechanical alloying in an attritor can be expressed in the form of the following equations:

$$KE_v > HE_v$$

where KE_v is the effective kinetic energy input per unit volume of the attritor, and HE_v is the minimum heat energy required to cause the desired alloying in unit volume of the attritor.

With some simplifying assumptions, it is shown that:

$$KE_v = \frac{1}{2} \left(\frac{D'}{d} \right)^2 (\delta P_b) \left(\frac{\pi N L}{30} \right)^2$$

and

$$HE = \frac{\delta P_b}{W} C_p (T_R - T_A)$$

Assuming T_R to be ~ 690 K for nickel, the heat energy requirement for mechanical alloying of nickel and chromium has been calculated and the threshold values for the attritor milling parameters are thereby estimated. Such estimates have been found to corroborate the experimental results on alloying of chromium in nickel.

8.3 SUGGESTIONS FOR FUTURE WORK

It is hoped that this dissertation has provided some answers to questions that arise when one looks at the process of mechanical alloying from

a theoretical as well as practical angle. However, there is considerable scope for further research in this area. It is still arguable whether recrystallization is definitely the exclusive or even predominant mechanism of enhanced diffusivity in mechanical alloying. It would therefore be of value to probe into this question further specially by an extensive use of transmission electron microscopy. While the results shown here did help in making certain order-of-magnitude estimates of the mean, local rise in temperature, more specific and ingenious experiments and theoretical calculations are desirable to provide firm estimates of this parameter.

The energy balance approach to the model needs to be refined further to predict not only the lower bound values for the attritor parameters but also the upper bound values above which alloying is seen to be of decreasing effectiveness. Having established the optimisation of the main attritor milling parameters, it would be of interest to study the mechanical properties of the resultant material and how these properties would be affected by subsequent consolidation and thermo-mechanical treatments.

A peculiar feature that came up in the present investigation is the appearance of the light-etching phase in the consolidated powder of Ni-20Cr-2ThO₂. Although it could be eliminated by a process modification, the exact process by which its formation is taking place needs to be fully established.

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TABLE 1
MECHANICALLY ALLOYED ODS ALLOYS

<u>Alloy Designation</u>	<u>Composition</u>	<u>Author & Affiliation</u>		<u>Year</u>
MA-753	Ni-20Cr, 1.5Al, 2.5Ti 1.3 v/o Y_2O_3	Benjamin	INCO	1970
DS Fe-Cr	Fe, 16Cr, 2.6 Y_2O_3	Wright	Battelle	1974
Co	Co, 20Ni, 18Cr, 1 Y_2O_3	Klarstrom	Cabot	1974
DS-Ti	Ti, 6Al, 4V	Wilcox	Battelle	1974
DS-Fe	Fe, 2Al ₂ O ₃	Lawn	Fulmer	1975
ODS-B-1900	Ni, 0.05C, 8Cr, 10Co, 6Mo, 7Al, 1Ti, 4Ta, 0.1Zr, 0.01B, 0.6 Y_2O_3	Glasgow	NASA	1975
Ni-Cr-Al	Ni, 18Cr, 4.75Al, 2 Y_2O_3	Klarstrom	Cabot	1975
Fe-Cr-Al	Fe, 25Cr, 6Al, 2Y, 5 v/o Al ₂ O ₃	Wilson	Fulmer	1976
MA-956	Fe, 20Cr, 4.5Al ₂ O ₃ , 0.5Ti 0.5 Y_2O_3	Fischer	INCO	1976
WAZ-D	Ni, 16.6W, 7.3Al, 4.3Fe, 0.8Y	Glasgow	NASA	1976
Ni	Ni-1.8 v/o ThO ₂	Arias	NASA	1976
MA-754	Ni-20Cr, 0.3Al, 0.5Ti, 0.6 v/o Y_2O_3	Benjamin	INCO	1976
DS-IN-738	Ni, 8.5Co, 16Cr, 1.75Mo, 2.6W, 1.75Ta, 3.4Ti, 3.4Al, 1.5 Y_2O_3	Gessinger	BBC	1976
MA-755A	Ni, 0.1C, 19Cr, 19Co, 4Mo 3Cb, 2.9Al, 4Fe, 3Ti, Y_2O_3	Shultz	INCO	1976
Al-Al ₂ O ₃	Al+2.4 v/o Al ₂ O ₃	Benjamin	INCO	1977
Al-Al ₂ O ₃	Al, 0.6Si, 1Mg, 1-4C	Jangg	Vienna	1977
Udimet 700 +2.5 Y_2O_3	Ni, 0.1C, 15W, 19Co, 5Mo,	Kramer	Krupp	1977
Cu-Ru	Cu, 15Ru	Green et al	Ref. 120	1984

TABLE 2

DESCRIPTION OF PARTS SHOWN IN FIG.15a

PART No.	DESCRIPTION	MATERIAL	PART No.	DESCRIPTION	MATERIAL
1.	ATTRITOR SHAFT	S.S.304	16.	FIN	S.S.304
2.	SHAFT	-do-	17.	SCRAPER	-do-
3.	COVER BUSH	-do-	18.	PLATE	-do-
4.	HOUSING	-do-	19.	CHANNEL	MILD STEEL
5.	THRUST BUSH	-do-	20.	BOLT SQUARE HEAD	-do-
6.	SPACER	-do-	21.	"O" RING	NEOPRENE
7.	WASHER	-do-	22.	EYE BOLT	MILD STEEL
8.	COVER PLATE	-do-	23.	"O" RING	NEOPRENE
9.	COVER SQUARE HEAD	-do-	24.	WASHER	-do-
10.	BUSH	-do-	25.	BALL BEARING	
11.	TOP LID COVER	-do-	26.	OIL SEAL	
12.	NIPPLE	-do-	27.	BALL BEARING	
13.	COLLAR	-do-	28.	SCREW	
14.	NUT HEXAGONAL	-do-	29.	"O" RING	NEOPRENE
15.	PLUG	-do-	30.	NUT HEXAGONAL	S.S.304

TABLE - 3

CHEMICAL ANALYSIS OF NICKEL AND CHROMIUM POWDERS

Trace Element	In nickel powder %	In chromium powder %
C	0.06	0.05
O	0.09	0.15
Fe	0.006	0.33
S	0.005	0.005

TABLE 4

THORIA PARTICLE SIZE FROM INTEGRAL BREADTH ANALYSIS
OF X-RAY DIFFRACTION LINE PROFILE

Silicon standard				$\bar{b}_{\text{ThO}_2}$					
Reflection	Degrees θ	Area under peak (cm^2)	Integral breadth b_{Si} (rad)	Reflection	Degrees θ	Area under peak (cm^2)	Integral breadth b_{ThO_2} (rad)	b_{ThO_2} (rad)	Thoria particle size ($\text{\AA}$)
111	14.2	11.45	0.00345	111	13.8	25.60	0.00777	0.00432	346.7
200*	16.0	-	0.00340*	200	16.5	8.10	0.00742	0.00402	368.1
220	23.7	9.35	0.00327	220	23.0	25.95	0.00755	0.00428	331.9
311	28.1	13.85	0.00423	311	27.2	32.35	0.00873	0.00449	305.1

• Diffraction conditions: Ni-filter, Cu K_α , 20 Kv, 12mA

• * b_{Si} for (200) was not recorded due to low intensity, hence obtained by interpolation from b -vs- θ

• A is obtained by planimeter measurement

• b is obtained by Anantharaman's method of Integral Breadth Calculation (ref. 144)

$$\bar{b}_{\text{ThO}_2} = b_{\text{ThO}_2} - b_{\text{Si}}$$

TABLE 5

EPMA LINE SCAN ANALYSIS OF SAMPLES FROM DIFFERENT RPM RUNS
AT 24th AND 42nd HOUR OF MILLING TIME

R P M	Milling time of the sample (hr)	Area* under curve (mm ²)	AVERAGE CHROMIUM % PICK-UP			% INHOMOGENEITY**			
			Relative Mean % Cr**			Positive Mean Deviation (mm)	Negative Mean Deviation (mm)	Total Mean Deviation (mm)	Total Mean Deviation (Cr%) from: 26mm ht. of standard line=18.5%
			Mean height of line (mm)	From: 26mm ht. of standard line=18.5%	From: 26mm ht. of standard line=100%				
154	24	250	2.6	1.9	10.0	5.3	1.0	6.3	4.5
	42	1040	11	7.8	42.3	8.2	3.8	12.0	8.6
260	24	2390	25.2	17.9	96.9	2.6	1.6	4.2	3.0
	42	2720	28.6	20.3	110.0	1.0	0.6	1.6	1.1
450	24	2530	26.6	18.9	102.3	1.2	0.9	2.1	1.5
	42	----- RUN TERMINATED AT 24th HOUR -----							
850	24	2610	27.5	19.6	105.8	NIL	NIL	NIL	NIL
	42	----- RUN TERMINATED AT 24 th HOUR -----							

*Measured by planimeter

** As per method described in Chapter IV and Appendix 2

TABLE 6

NUMBER OF REVOLUTIONS WITH INCREASING MILLING TIMES FOR DIFFERENT RPM

RPM	Attritor Milling time in hours											
	3½	6	12	14	18	24	30	36	42	48	66	
154	--	0.554	1.109	--	1.663	2.218	2.772	3.326	$\frac{3.88}{(A)}$	4.435	$\frac{6.1}{(F)}$	X10 ⁵
260	--	0.922	1.843	--	2.765	$\frac{3.686}{(B)}$	4.608	5.53	$\frac{6.451}{(G)}$	7.373	--	X10 ⁵
450	--	1.620	3.240	$\frac{3.78}{(C)}$	4.860	$\frac{6.480}{(H)}$	--	--	--	--	--	X10 ⁵
850	--	$\frac{3.06}{(D)}$	$\frac{6.12}{(J)}$	--	9.180	12.240	--	--	--	--	--	X10 ⁵
1880	$\frac{3.950}{(E)}$	--	--	--	--	--	--	--	--	--	--	X10 ⁵

TABLE 7

EPMA LINE SCAN ANALYSIS OF SAMPLES FROM DIFFERENT
RPM RUNS AT ABOUT 3.6×10^5 AND 6.2×10^5 REVOLUTIONS

R P M	Sample Identification (See Table 2)	Milling time of the sample (hr)	No. of Revolutions (rounded off to first decimal value)	AVERAGE CHROMIUM % PICK-UP				% INHOMOGENEITY **			
				Area* under curve (mm ²)	Relative Mean % Cr**			Positive Mean Deviation(mm)	Negative Mean Deviation(mm)	Total Mean Deviation(mm)	Total Mean Deviation(Cr%) from: 26mm ht. of standard line=18.5%
					Mean height of line(mm)	From: 26mm ht. of standard line=18.5%	From: 26mm ht. of standard line=100%				
154	A	42	3.9×10^5	1040	11	7.8	42.3	8.2	3.8	12.0	8.6
154	F	66	6.1×10^5	2430	25.6	18.2	98.5	4.3	6.6	10.9	7.9
260	B	24	3.7×10^5	2390	25.2	17.9	96.9	2.6	1.6	4.2	3.0
260	G	42	6.5×10^5	2720	28.6	20.3	110.0	1.0	0.6	1.6	9.1
450	C	24	3.8×10^5	2160	22.7	16.2	87.3	1.2	2.4	3.6	2.6
	H	24	6.5×10^5	2530	26.6	18.9	102.3	1.2	0.9	2.1	1.5
850	D	6	3.1×10^5	2110	22.2	15.8	85.4	3.2	2.3	5.5	3.9
	J	12	6.1×10^5	2430	25.6	18.2	98.5	0.4	0.6	1.0	0.7
1880	E	3.5	4.0×10^5	2005	21.1	15.0	81.2	5.8	7.8	13.6	9.7

*Measured by planimeter

** As per method described in Chapter IV and Appendix 2

TABLE 8

EPMA LINE SCAN ANALYSIS OF SAMPLES FROM DIFFERENT BALLS-
TO-POWDER WEIGHT RATIO RUNS AT THE 42nd HOUR MILLING TIME

Balls-to-powder weight ratio	AVERAGE CHROMIUM % PICK-UP				% INHOMOGENEITY**			
	Area* under curve (mm ²)	Relative Mean % Cr**			Positive Mean Deviation(mm)	Negative Mean Deviation(mm)	Total Mean Deviation(mm)	Total Mean Deviation(%Cr) from:26mm ht. of standard line=18.5%
		Mean height of line(mm)	From:26mm ht. of standard line=18.5%	From:26mm ht. of standard line=100%				
12/1	160	1.7	1.2	6.5	9.8	1.8	11.6	8.3
18/1	2070	21.8	15.5	83.9	3.2	2.1	5.3	3.8
24/1	2410	25.4	18.1	97.7	6.6	2.2	8.8	6.3
40/1	2620	27.6	19.6	106.2	1.5	0	1.5	1.1
50/1	2610	27.5	19.6	105.8	1.1	0.5	1.6	1.2
100/1	2610	27.5	19.6	105.8	NIL	NIL	NIL	NIL
					(Straight line scan)			
150/1	2432	25.6	18.2	98.5	1.3	0.5	1.8	1.3

*Measured by planimeter

** As per method described in Chapter IV and Appendix 2

TABLE 9

EPMA LINE SCAN ANALYSIS OF SAMPLES FROM DIFFERENT BALLS-
TO-POWDER WEIGHT RATIO RUNS AT THE 24th HOUR MILLING TIME

Balls-to-powder weight ratio	AVERAGE CHROMIUM % PICK-UP				% INHOMOGENEITY**			
	Area* under curve (mm ²)	Relative Mean % Cr **			Positive Mean Deviation(mm)	Negative Mean Deviation(mm)	Total Mean Deviation(mm)	Total Mean Deviation(%Cr) from:26mm ht. of standard line=18.5%
		Mean height of line (mm)	From:26mm ht. of standard line=18.5%	From:26mm ht. of standard line=100%				
12/1	220	2.3	1.6	8.8	8.0	1.3	9.3	6.6
18/1	250	2.6	1.9	10.0	5.3	1.0	6.3	4.5
24/1	---- Sample not drawn ----							
40/1	2290	24.1	17.2	92.7	3.0	1.3	4.3	3.1
50/1	2570	27.1	19.3	104.2	6.9	4.2	11.1	7.9
100/1	-	26.4	18.8	101.6	-- straight line --			NIL
150/1	2210	23.3	16.6	89.6	2.1	1.1	3.2	2.3

*Measured by planimeter

** As per method described in Chapter IV and Appendix 2

TABLE 10

VALUES OF NtW^* FOR DIFFERENT BALLS-TO-POWDER WEIGHT
RATIO RUNS WITH INCREASING MILLING TIME

Balls- to- powder weight ratio (R)	Attritor Milling time in hours											
	6	12	18	24	30	36	42	48	66	72	100	
18/1	0.998	1.996	2.994	3.992	4.99	5.988	6.985	7.983	<u>10.977</u> (A)	--	<u>16.632</u> (F)	$\times 10^6$
24/1	1.331	2.661	3.992	5.322	6.653	7.983	9.314	<u>10.645</u> (B)	--	<u>15.967</u> (G)	--	$\times 10^6$
40/1	2.218	4.435	6.653	8.87	<u>11.088</u> (C)	13.306	<u>15.523</u> (H)	17.741	--	--	--	$\times 10^6$
50/1	2.772	5.544	8.832	<u>11.088</u> (D)	13.86	<u>16.632</u> (J)	19.404	22.176	--	--	--	$\times 10^6$
100/1	5.544	<u>11.088</u> (E)	<u>16.632</u> (K)	22.176	27.72	33.264	38.808	44.352	--	--	--	$\times 10^6$
150/1	--	<u>16.632</u> (L)	--	--	--	--	--	--	--	--	--	$\times 10^6$

(* N = 154 Revolutions per minute, t = milling time in minutes, W = balls-to-powder weight ratio)

TABLE 11

EPMA LINE SCAN ANALYSIS OF SAMPLES FROM DIFFERENT BALLS-TO-POWDER
 WEIGHT RATIO RUNS AT NEW OF ABOUT 1.1×10^7

Balls-to-powder weight ratio	Milling time of the sample (hr)	Sample Identifi- cation	AVERAGE CHROMIUM % PICK-UP				% INHOMOGENEITY **			
			Relative Mean % Cr**				Positive Mean Deviation(mm)	Negative Mean Deviation(mm)	Total Mean Deviation(mm)	Total Mean Deviation(Cr%) from: 26mm ht. of standard line=18.5%
			Area* under curve (mm ²)	Mean height of line(mm)	From: 26mm ht. of standard line=18.5%	From: 26mm ht. of standard line=100%				
18/1	66	A	2430	25.6	18.2	98.5	4.3	6.6	10.9	7.8
24/1	48	B	2380	25.1	17.9	96.5	2.6	2.9	5.5	3.9
40/1	30	C	2410	25.4	18.1	97.7	2.5	1.9	4.4	3.1
50/1	24	D	2570	27.1	19.3	104.2	6.9	4.2	11.1	7.9
100/1	12	E	450	4.7	3.3	18.1	1.3	0.5	1.8	1.3

*Measured by planimeter

** As per method described in Chapter IV and Appendix 2

TABLE 12

EPMA LINE SCAN ANALYSIS OF SAMPLES FROM DIFFERENT BALLS-TO-
POWDER WEIGHT RATIO RUNS, AT NEW VALUE OF ABOUT 1.7×10^7

Balls-to-powder weight ratio	Milling time of the sample(hr)	Sample Identifi- fication	AVERAGE CHROMIUM % PICK-UP				% INHOMOGENEITY **			
			Relative Mean % Cr**							
			Area* under curve (mm ²)	Mean height of line(mm)	From:26mm ht. of standard line=18.5%	From:26mm ht. of standard line=100%	Positive Mean Deviation(mm)	Negative Mean Deviation(mm)	Total Mean Deviation(mm)	Total Mean Deviation(% Cr) from:26mm ht. of standard line=18.5%
18/1	100	F	2250	23.7	16.9	91.1	2.1	1.2	3.3	2.4
24/1	72	G	2360	24.8	17.7	95.4	5.1	2.3	7.4	5.3
40/1	42	H	2620	27.6	19.6	106.2	0.9	0.6	1.5	1.1
50/1	36	J	2780	28.4	20.2	109.3	2.6	1.7	4.3	3.1
100/1	18	K	-	26.5	18.9	101.9	-- straight line --			NIL
150/1	12	L	900	9.5	6.8	36.5	1.5	0	1.5	1.1

*Measured by planimeter

** As per method described in Chapter IV and Appendix 2

TABLE 13

EPMA LINE SCAN ANALYSIS OF SAMPLES FROM DIFFERENT
BALL DIAMETER RUNS AT 42nd HOUR MILLING TIME

Ball Diameter (mm)	Milling time of the sample (hr)	AVERAGE CHROMIUM % PICK-UP				% INHOMOGENEITY**			
		Area* under curve (mm ²)	Relative Mean % Cr**			Positive Mean Deviation(mm)	Negative Mean Deviation (mm)	Total Mean Deviation (mm)	Total Mean Deviation(Cr%) from: 26mm ht. of standard line=18.5%
			Mean height of line(mm)	From: 26mm ht. of standard line=18.5%	From: 26mm ht. of standard line=100%				
4	42	660	7	5.0	26.9	15.4	6.4	21.8	15.5
6	42	2070	21.8	15.5	83.9	3.2	2.1	5.3	3.8
8	42	2150	22.6	16.1	87.0	2.6	0.6	3.2	2.3
10	42	2310	24.3	17.3	93.5	3.3	2.4	5.7	4.1
Cylinder 6x6mm	42	400	4.2	3.0	16.2	10.8	2.5	13.3	9.5
Tungsten carbide ball 6mm dia	42	155	1.6	1.1	6.2	5.4	0.9	6.3	4.5

*Measured by planimeter

**As per method described in Chapter IV and Appendix 2

TABLE 14
EPMA LINE SCAN ANALYSIS OF SAMPLES FROM DIFFERENT IMPELLER
SHAPE RUNS AT 42nd HOUR MILLING TIME

Impeller shape	Milling time of the sample (hr)	AVERAGE CHROMIUM % PICK-UP			% INHOMOGENEITY**			
		Area* under curve (mm) ²	Mean height of line (mm)	Relative Mean % Cr**	Positive Mean Deviation (mm)	Negative Mean Deviation (mm)	Total Mean Deviation (mm)	Total Mean Deviation (%Cr) From: 26mm ht. of standard line=18.5%
				From: 26mm ht. of standard line=18.5%	From: 26mm ht. of standard line=100%			
Round	42	1000	10.5	7.5	40.4	3.2	-2.1	5.3
								3.8
Flat	42	140	1.5	1.1	5.8	1.6	0.7	2.3
								1.6
Triangular	42	2340	24.6	17.5	94.6	4.7	1.8	6.5
								4.6

*Measured by planimeter

** As per the method described in Chapter IV and Appendix 2

TABLE 15
COMBINATIONS OF STARTING PARTICLE SIZES OF
NICKEL AND CHROMIUM POWDERS

Run Identification	Average particle size of nickel powder (microns)	Average particle size of chromium powder (microns)
8/45	8	45
8/12	8	12
25/45	25	45
25/12	25	12

TABLE 16

EDTA LINE SCAN ANALYSIS OF SAMPLES FROM RUNS OF DIFFERENT STARTING
PARTICLE SIZES OF NI AND CR AT 48th HOUR MILLING TIME

Run Identification	Starting Average particle size (Fisher)		Milling time of the sample(hr)	AVERAGE CHROMIUM % PICK-UP				% INHOMOGENEITY**			
	Nickel (microns)	Chromium (microns)		Area* under curve 2 (mm ²)	Relative Mean % Cr**			Positive Mean Deviation(mm)	Negative Mean Deviation(mm)	Total Mean Deviation(mm)	Total Mean Deviation (Cr%) from:26mm ht. of standard line=18.5%
					Mean height of line(mm)	From:26mm ht. of standard line=18.5%Cr	From:26mm ht. of standard line=100%std.				
25/45	25	45	48	2130	22.4	15.9	86.2	4.8	8.3	8.1	5.8
25/12	25	12	48	2450	25.8	18.4	99.2	4.0	3.3	7.3	5.2
8/45	8	45	48	560	5.9	4.2	22.7	3.1	2.7	5.8	4.1
8/12	8	12	48	2340	24.6	17.5	94.6	3.0	1.4	4.4	3.1

*Measured by planimeter

**As per method described in Chapter IV and Appendix 2

TABLE 17

DATA OF SAMPLES OF MINIMUM MILLING TIME FOR MAXIMUM* EFFECTIVENESS
OF ALLOYING FOR DIFFERENT BALL RATIOS

Balls-to-powder weight ratio	Minimum milling time	Chromium pick-up as percentage of 'standard' sample	Inhomogeneity percentage	Corresponding N _W value
10/1	100	91.1	2.4	1.66×10^7
40/1	42	106.2	1.1	1.55×10^7
50/1	42	109.3	1.2	1.94×10^7
100/1	18	101.9	0	1.66×10^7
150/1	42	99.0	1.4	5.8×10^7

* The effectiveness of alloying could be improved further for ball ratios of 10/1, 40/1, 50/1 and 150/1 with milling times better than corresponding milling times shown in this table. However for the milling times shown, the effectiveness of alloying is seen to be close to the maximum levels.

TABLE 18

AVERAGE PARTICLE SIZE OF THORIA DISTRIBUTION IN ATTRITOR.
MILLED AND HIP CONSOLIDATED SAMPLES
(Corresponding to Fig.63)

Sample Identification	Brief history of attritor milling conditions	Average particle size μ
A	154 RPM, 6mm balls, 18/1 ball ratio, 8 u Ni, 45 u Cr 48 hours milling	6200
B	260 RPM, 6mm balls, 18/1 ball ratio 8 u Ni, 45 u Cr 42 hours milling	400
C	154 RPM, 8mm balls, 18/1 ball ratio, 8 u Ni, 45 u Cr, 42 hours milling	790
D	154 RPM, 6mm balls, 18/1 ball ratio, 8 u Ni, 12 u Cr, 48 hours milling	430



TABLE 19

X-RAY LINE BREADTH ANALYSIS OF ATTRITOR MILLED POWDERS

Sample Designation	Sample History	Average microhardness HV/100gm	Integral line breadth b(2 θ) (Degrees)
A	Standard powder, vacuum annealed at 980°C/8hr	260	0.259
B	Standard powder after attritor milling for 72 hrs	700	1.226
C	Ni and Cr powders attritor milled for 72 hrs	800	1.223
D	Sample 'C' after vacuum annealing at 980°C/8hr	390	0.208

TABLE 2C

RATIO OF PEAK-TO-PEAK HEIGHT OF $\frac{dN}{dE}$ OF NI AND Cr AFTER SPUTTER ETCHINGFOUR PARTICLES OF MECHANICALLY ALLOYED Ni-Cr-ThO₂ POWDER

Depth of etching	Particle A	Particle B	Particle C	Particle D
135A°	2.4	2.3	2.6	2.6
950A°	2.2	2.0	2.5	2.3

TABLE 21

AVERAGE MICROHARDNESS VALUES OF SOME ATTRITOR MILLED POWDER SAMPLES

SAMPLE HISTORY	AVERAGE MICROHARDNESS (Average of about 10 readings)	
	Load gm	HV
Ni & Cr attritor milled at 154 RPM for 48 hours (without thoria)	100	374
Ni, Cr and thoria attritor milled at 154 RPM for 48 hours	100	321
Ni & Cr attritor milled at 260 RPM for 24 hours (without thoria)	100	790
Ni, Cr and thoria attritor milled at 260 RPM for 24 hours	100	440
Only Ni powder attritor milled at 154 RPM for 25 hours	25	510
Only Ni powder attritor milled at 260 RPM for 25 hours	25	348

TABLE 22

EPMA LINE SCAN ANALYSIS OF SAMPLES WITH AND WITHOUT THORIA

Sample History	AVERAGE CHROMIUM % PICK-UP						% INHOMOGENEITY **			
	Attritor RF:	Milling time of the sample (hr)	Area* under curve (cm ²)	Mean height of line (mm)	Relative Mean %Cr**		Positive Mean Deviation (mm)	Negative Mean Deviation (mm)	Total Mean Deviation (mm)	Total Mean Deviation (Cr%) from: 26mm ht. of standard line=18.5%
					From: 26mm ht. of standard line=18.5%	From: 26mm ht. of standard line=100%				
Nickel+ Chromium no thoria	154	54	2680	28.2	20.1	108.5	15.6	5	20.6	14.7
Nickel+ chromium thoria separately added	154	54	740	7.8	5.6	30	2.7	1.3	4	2.9
Chemically predispersed thoria in nickel+ chromium	154	60	340	3.6	2.6	13.9	2.2	0.7	2.9	2.1
Nickel+ chromium no thoria	260	24	2550	26.8	19.8	103.0	1.6	1.0	2.6	1.8
Nickel+ chromium thoria separately added	260	24	2390	25.2	17.9	96.9	2.6	1.6	4.2	3.2

TABLE 23

DIFFUSIVITY OF CHROMIUM IN NICKEL FROM CHROMIUM LAMELLAE THICKNESS

Milling time interval of the sample	Approximate reduction in thickness of Cr lamellae (Average of 10 readings)	Corresponding Diffusion Coefficient for Cr in Ni based on
	Microns	$D \approx \frac{x^2}{t}$
		x = Cr thickness reduction
		t = milling time in seconds
From 6th hr to 18th hr	1.0	$2.3 \times 10^{-13} \text{ cm}^2/\text{sec.}$
From 12th hr to 24th hr	0.9	$1.9 \times 10^{-13} \text{ cm}^2/\text{sec.}$
From 24th hr to 30th hr	0.5	$1.2 \times 10^{-13} \text{ cm}^2/\text{sec.}$

Average diffusivity $\approx 2 \times 10^{-13} \text{ cm}^2/\text{sec.}$

TABLE 24
SEMI-QUANTITATIVE EDAX ANALYSIS IN SEM OF COATED BALLS AND LOOSE
POWDER WITH PROGRESSIVE ATTRITOR MILLING TIME

Attritor Milling Time at which sample was drawn Hours	Relative concentration of Cr as $\frac{\text{Cr}}{\text{Ni}}$ ratio, of the welded layer sticking to the ball	Relative concentration of Cr as $\frac{\text{Cr}}{\text{Ni}}$ ratios of the loose powders of the sample
3	0.0298	0.0366
6	0.0466	0.0821
12	0.254	0.171
19	0.500	0.492
23	0.465	0.530
30	0.452	0.490
38	0.461	0.471
48	0.461	0.471

TABLE 25

'SOFT SPOTS' IN THE MICROHARDNESS SURVEY OF ATTRITOR MILLED POWDERS

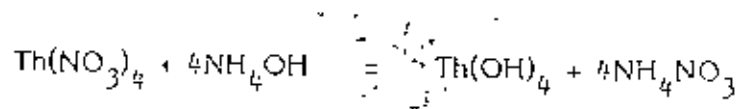
SAMPLE HISTORY	MICROHARDNESS VALUES*	
	LOAD gms	Hv
Ni, Cr & ThO ₂ attritor milled at 154 RPM, 6mm balls in 100/1 ball ratio for 30 hours	50	780, <u>550</u> , 770, 825, 730, 665, 655 ALL IN ONE PARTICLE
	50	790, 800, 850, <u>560</u> , 880, 725 ALL IN ONE PARTICLE
Ni, Cr and ThO ₂ attritor milled at 260RPM, 6mm balls in 18/1 ball ratio for 42 hours	100	442, 552, <u>355</u> , 489, 443, <u>352</u>
	100	<u>325</u> , <u>321</u> , 439, 394 ALL IN ONE PARTICLE
Only Ni powder attritor milled at 260RPM, for 25 hours		296, 330, 392, 398, <u>179</u> , 244, 411, <u>217</u> , 405, <u>203</u> , <u>381</u> , <u>286</u>

* Underlined values are the 'soft spots' which are significantly lower than the rest

APPENDIX I

A. PREPARATION OF THORIA

Thoria in fine, particulate form is generally prepared by the decomposition of thorium hydroxide. The method followed in this work for obtaining thorium hydroxide was to precipitate it by adding ammonium hydroxide to thorium nitrate. One litre of 0.4M solution of ammonium hydroxide was added to one litre of a mechanically stirred solution 0.1M thorium nitrate solution at 90°C. Thorium hydroxide in a gel like form was precipitated as per the following reaction:

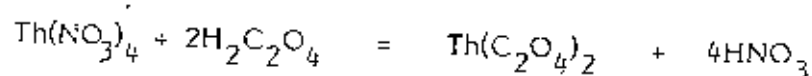
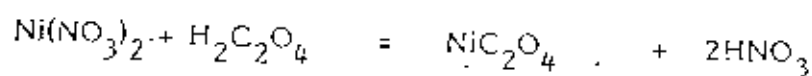


It was filtered, washed thoroughly with hot water and dried at 100°C. It was subsequently decomposed at 600°C to get ThO_2 . It was then crushed in a laboratory grinder. The average particle size of the thoria as measured by X-ray diffraction was found to be 330Å.

B. PREPARATION OF Ni-2ThO₂

Co-precipitation and selective reduction method was used to prepare powder of nickel containing a uniform dispersion of fine thoria particles. The aim was to prepare nickel containing 2 volume % (2.3% by weight) of thoria.

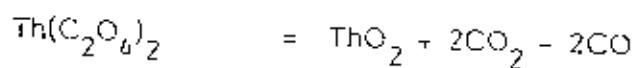
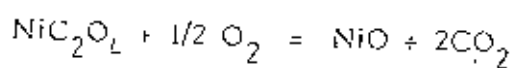
To 0.55M nickel nitrate solution, appropriate quantity of thorium nitrate was added to make 3 litres solution, which was brought to a pH of 6 with 5N NH_4OH solution. The resulting solution was heated to about 90°C and 2 litres of a hot solution of 1M oxalic acid was added to it, while it is being mechanically stirred. Stirring was continued for about 3 hours. The precipitate is an intimate mixture of nickel and thorium oxalates. The precipitation reactions are:



The precipitate was filtered and washed several times with hot water and dried at about 100°C . The dried oxalate mixture was then heated slowly in air to about 600°C and maintained at this temperature for about 3 hours. An intimate mixture of nickel and thorium oxides was thus obtained.

The oxide mixture was reduced in flowing, dry hydrogen at about 930°C for about 2 hours. While thorium oxide remained unreduced, nickel oxide was reduced to nickel. It contains the thorium in a finely dispersed form.

The decomposition and reduction reactions are:



Thoria distribution in the resultant powder was checked by transmission electron microscopy. The average particle size of thoria in the Ni-2 ThO₂ was found to be about 1000A°.

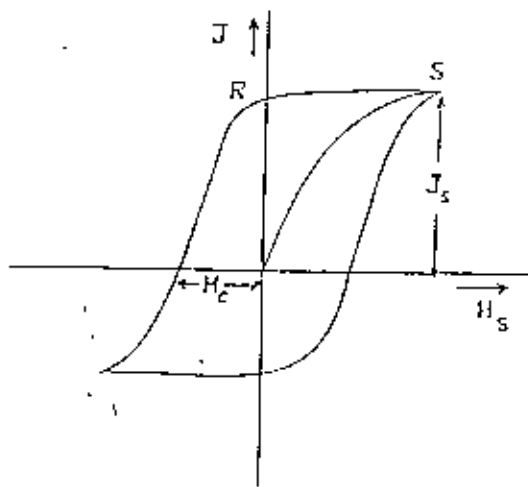
APPENDIX 2

COERCIVITY MEASUREMENT

This Appendix briefly describes the principle of coercivity measurement with the Precision Coercive Force Meter Type 1.094 of Institut Dr. Foster, Reutling (Fig. 17).

Coercive force is the opposing field strength H_C required to bring the magnetization intensity J or the induction B to zero in a material following previous saturation magnetization. Physical material characteristics such as saturation, remanence, conductivity, density, etc., may vary through values of, at the most, two orders of magnitude, while coercive force and permeability values may vary by five orders of magnitude. However, while permeability measurements are sensitive to the physical shape of the sample, coercivity is essentially independent on the geometry of the sample.

For H_C measurement, the sample is magnetized to saturation, then the saturation field strength is reduced to zero. A magnetic field with opposite polarity is then applied to the sample and increased until the magnetization J is zero. The field strength required to cause the magnetization J to go to zero is the coercivity, H_C .



- J = Magnetization Intensity
- J_s = Saturation Magnetization
- R = Remanence Point
- S = Saturation Point
- H_s = Saturation Field Strength
- H_c = Coercivity

For determination of H_c , it is necessary that the device which indicates the magnetization J does not also indicate the opposing field required for the H_c measurement. The Precision Coercive Force Meter is constructed to meet this requirement. The H_c value on the panel meter is the factor H_c expressed in Oersteds.

The principle of operation of the instruments is briefly as follows: an A.C. voltage from a variable control transformer is rectified, filtered, and then as a D.C. voltage is applied through a polarity reversal switch to the field coil or to the electromagnetic yoke which produces the saturation field strength. The sample may be saturated in both the coil or the magnetization yoke if the necessary saturation induction is attained.

When measuring samples with coercive force values more than 1-2 Oe, it is not necessary to compensate the magnetic earth field, it is only necessary to orient the longitudinal axis of the test coil in East-West direction.

APPENDIX 3

ANALYSIS OF EPMA LINE SCANS

This Appendix describes the method used in calculating (i) % average chromium pick-up, and (ii) % average inhomogeneity from the photographic records of line scans of chromium in Electron Probe Micro Analysis (EPMA).

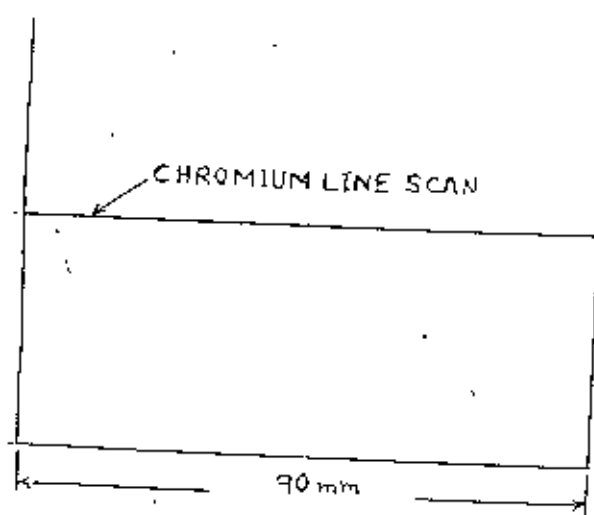


FIG. A

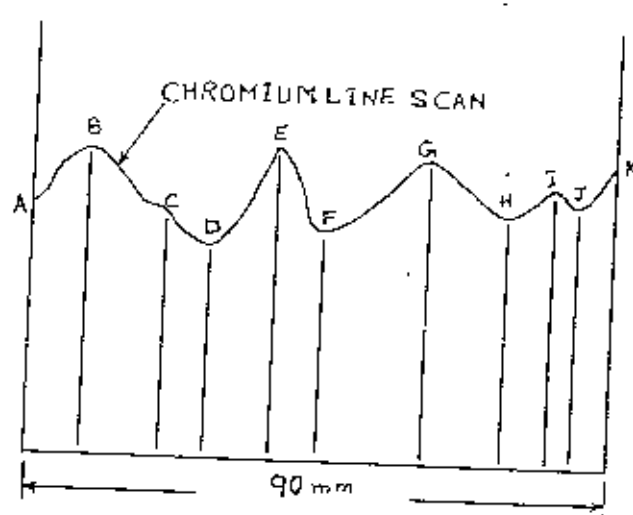


FIG. B

Chromium pick-up calculation

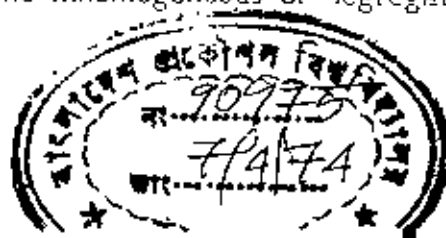
Fig. A is the chromium line scan of the homogenised 'standard' alloyed powder of Ni-Cr containing 18.5%Cr (by chemical analysis). This is at 26 mm from the base line and thus any straight line scan, obtained

under same conditions, appearing at 26 mm height represents 18.5% chromium in the sample, in other words, 100% of the 'standard'. A straight chromium line at any other height can therefore be converted to actual percentage of chromium or expressed as a percentage of the chromium content of the 'standard' line and this accordingly gives the 'average chromium pick-up' in either % chromium itself or % of standard sample's chromium content.

Since the line scans of the actual samples are often wavy due to inhomogeneity of distribution of the chromium in the matrix, the wavy line scan must first be 'converted' to a representative straight line whose height from the base level can then be used to get the average chromium pick-up. As the scanned distance in the particle given by the base length is kept constant at 50 in all the cases of analysis, the area under a wavy curve is notionally equivalent to the average of a rectangle whose length is the scanned distance in the particle and whose height is the representative mean height of the chromium line scan had it been a straight line. Thus when the measured area enclosed by the wavy line of an EPMA line scan photograph of chromium is divided by the base line length of 90 mm, one gets the mean height of the wavy line which is then converted to the % average chromium pick-up.

Inhomogeneity calculation

The waviness of the EPMA line scan such as the one shown in Fig.B is a result of the inhomogeneous or segregated distribution of the scanned



ement. To estimate the degree of inhomogeneity, the heights of the 'peaks' and 'valleys', such as points A to K in Fig.B are measured. The differences which each of these heights is more or less than the mean height of the line scan, previously determined, are averaged to give positive and negative average deviations from the mean height level. The sum of these two averages is the total mean deviation of the line scan, which is converted to % chromium by using the calibrated height of the 'standard' chromium line (i.e., 26 mm height = 18.5% Cr). The extent of average inhomogeneity can thus be expressed in terms of % chromium.