

UNIVERSITY OF MANITOBA

THE PRECIPITATION BEHAVIOUR OF
Co-Cr BASE ALLOYS

by

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ABSTRACT

The precipitation behaviour of the following four alloys was studied.

Co-25% Cr-4% Ti

Co-25% Cr-5% Mo

Co-25% Cr-7% Mo

Co-25% Cr-5% Mo-2.5% Nb (compositions in wt%).

In the Co-25% Cr-4% Ti alloy the precipitates were ordered fcc Co_3Ti phase which formed on $\{100\}$ planes of the matrix. The strengthening by second phase particles improved the yield strength at peak by 60% with respect to the solution treated specimens. The growth kinetics of the γ' precipitates were diffusion controlled. The application of the LSW theory to the coarsening of the Co_3Ti precipitates gave particle size distributions which showed deviations from the theoretical distribution function mainly in terms of their broadness.

The precipitation in the Co-Cr-Mo alloys was a combination of hcp Co_3Mo and rhombohedral Co_7Mo_6 phases. The matrix of the alloys aged at 973K and 1073K was a mixture of fcc and hcp phases. While, ageing at 973K and 1073K has increased the 0.2% offset yield strength between 40% to 83% depending upon the specific ageing time and temperature, the total elongation was in the range of 18% to 35%. The elongation of the solution treated specimens was, however, lower than these values. An explanation for this behaviour of the alloys is also given.

The precipitates in the Co-25% Cr-5% Mo-2.5% Nb alloy were of the hcp Co_3Mo and hexagonal (rhombohedral) Co_7Nb_6 phases.

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CHAPTER 1 INTRODUCTION

Cobalt is an allotropic element transforming from the hexagonal close-packed to the face-centered cubic form at 690K upon heating. The addition of the refractory-type elements like Mo, W, Ta tends to stabilize the hexagonal close-packed phase, while alloying elements such as Fe, Ni and Mn which are close to cobalt in the periodic table, stabilize the face-centered allotope⁽¹⁾.

The strengthening of the cobalt-base superalloys is generally promoted by solid-solution strengthening and carbide precipitation⁽²⁾. Carbide precipitation improves both tensile and rupture strengthening, but at the same time it may lead to lower ductility properties of the cobalt-base superalloys in which it is precipitating. Another possibility of improving the strength properties of the cobalt alloys is by means of intermetallic compounds. One example is the very beneficial existence of the γ' precipitates in the nickel-base superalloys for strength purposes^(3,4). Some of the obstacles which are delaying the wide range use of the intermetallic compounds in the cobalt-base alloys are the instabilities of some precipitate phases, i.e., γ' -fcc to η -hcp transformations⁽⁵⁾ and the appearance at high temperatures of the TCP (topologically closed-packed) phases which are considered to be harmful for the strength and ductility properties.

Cobalt-base alloys, such as Vitallium, are widely used as orthopedic implants as they possess excellent corrosion resistance in the fluids in human body^(5a). Considering these factors, it was decided to study the structure and mechanical properties of Co-Cr alloys precipitation hardened by Ti, Mo, Nb bearing intermetallic compounds. The following four alloys were fabricated,

Co-25% Cr-4% Ti

Co-25% Cr-5% Mo

Co-25% Cr-7% Mo

Co-25% Cr-5% Mo-2.5% Nb (compositions in wt %).

Precipitation characteristics of the above alloys were investigated by means of optical and electron microscopy techniques. The mechanical properties were studied with hardness and room temperature tensile tests. Most of the studies were concentrated on the Co-25% Cr-4% Ti alloy. This was mainly because the presence of only one type of precipitates in this alloy made it possible to study the growth kinetics of the precipitate particles. Also, the brittleness of the Co-25% Cr-5% Mo-2.5% Nb alloy made the rolling of the material almost impossible and tensile specimens could not be made to establish its tensile properties.

CHAPTER 2 LITERATURE REVIEW

In this chapter the theories of nucleation and growth of precipitates from solid solution are first presented. This is then followed by a review of the literature concerning the precipitation behaviour of cobalt-base alloys.

2.1 Precipitation From Solid Solutions

The precipitation hardening process achieves a fine dispersion of second phase particles first by forming a solid solution, followed by rapid cooling and then heating the supersaturated solution at an intermediate temperature. The existence of precipitate particles strengthens the matrix. The increase in yield strength depends mainly on the strength, structure, spacing, size, shape and distribution of the precipitate particles, on their relative orientation and also on their level of misfit or coherency with the matrix.

The decomposition of one phase into one or more components can be considered in three different stages:

- a) The nucleation of the embryo of the new phase;
- b) The growth of the nuclei;
- c) The coarsening of the second phase particles without change in their volume fraction.

The formation of the new nuclei may proceed in two ways. If the alloy is unstable to compositional fluctuations, the reaction may occur

by spinodal decomposition. Distinctively, if the phase change involves thermal activation to overcome the nucleation barrier, the second type of phase transformation, which is the classical nucleation and growth process, may take place.

2.1.1 Spinodal decomposition

Spinodal decomposition leads to a very uniform and homogeneous dispersion of coherent second phase particles throughout the matrix. No structural changes are involved in this type of decomposition but compositional changes do occur. An alloy of initial composition C_1 and free energy F_1 in Figure 1 may decompose into a mixture of the phases M and P with an average free energy F_2 which is lower than F_1 . At an intermediate stage of decomposition, the compositions may be C'_m and C'_p with a free energy F'_1 which is lower than F_1 and higher than F_2 . Consequently the compositional fluctuations may proceed with a continuous decrease in free energy and there is no nucleation barrier to the decomposition of the solid solution. Spinodal decomposition thus occurs simultaneously, but there is no precise stage at which the new phase will form.

2.1.2 Nucleation of the precipitates

The second type of phase transformation may proceed by nucleation and growth processes. A precipitate particle can be nucleated in two distinct ways. It can form at internal lattice defects, such as, dislocations, dislocation nodes, grain and twin

boundaries; stacking faults, antiphase domain boundaries. The formation of the nuclei on the above regions of the matrix is named heterogeneous nucleation. Homogeneous nucleation is the spontaneous formation of the nuclei without the need of the previous inhomogeneities.

2.1.3 Homogeneous nucleation

The change in free energy associated with the formation of an embryo can be expressed as follows (Volmer and Weber⁽⁷⁾, Becker and Doring⁽⁸⁾)

$$\Delta F = \Delta F_v + \Delta F_s + \Delta F_m$$

where ΔF = change in free energy due to the formation of the embryo

ΔF_v = change in volume free energy

ΔF_s = interfacial energy between the new phase and the matrix

ΔF_m = strain energy arising from the formation of new particles.

For a spherical nucleus of radius r , the change in free energy becomes

$$\Delta F = 4\pi r^2(\Delta F_s) + \frac{4}{3} \pi r^3 (\Delta F_v + \Delta F_m) .$$

The critical radius r_0 can be obtained by taking the derivative of the free energy term with respect to the radius of the embryo.

$$r_0 = \frac{2\Delta F_s}{-(\Delta F_v + \Delta F_m)} \quad .$$

If the radius of the particle is less than r_0 , it may lower its free energy by decreasing its size. Consequently, particles with radius $r < r_0$ may tend to dissolve and return to the solid solution.

Considering the effect of the temperature on the critical radius r_0 , it can be assumed that the surface energy term ΔF_s does not change with temperature. The volume free energy ΔF_v is influenced by temperature becoming larger at lower temperatures. The ΔF_m term may also be assumed to be independent of temperature. The relation between the free energy of precipitate particles and ageing temperature can be seen in Figure 2.

2.1.4 Heterogeneous nucleation

Heterogeneous nucleation can occur on structural defects, such as vacancies, dislocations and also at grain boundaries. These are high free energy regions. To the extent it may lower the free energy of the system, the formation of the new nuclei at these inhomogeneities can be very preferential with respect to homogeneous nucleation.

2.1.4.1 Nucleation on vacancies

There are two ways by which the vacancies may influence the rate of nucleation of second phase particles. They can accelerate

Figure 1: Plot of free energy against composition illustrating spinodal decomposition, [6].

Figure 2: Effect of temperature of precipitation on the free energy of a precipitate particle as a function of its radius, [9].

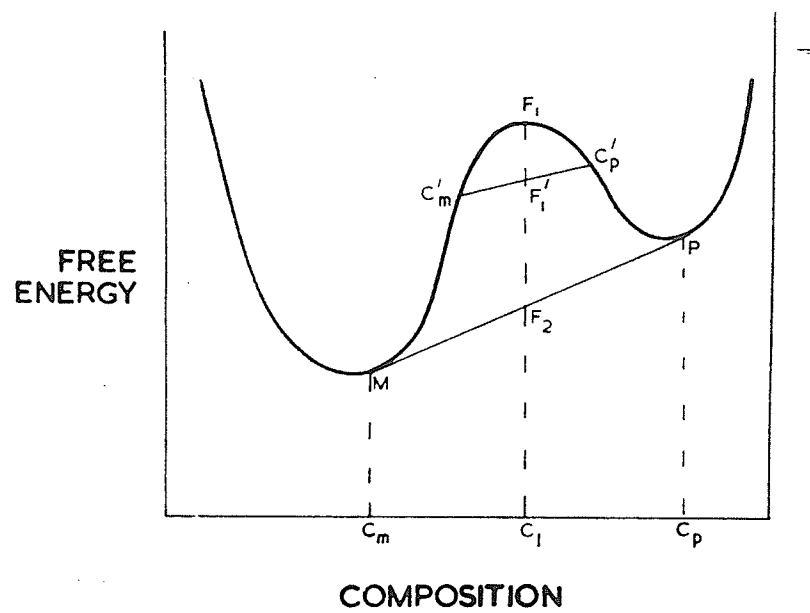


Figure 1

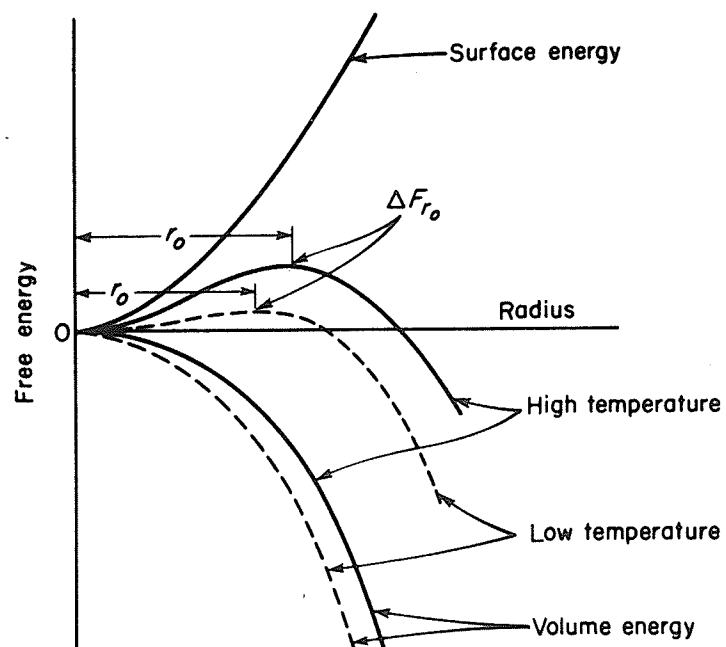


Figure 2

the diffusion rate of solute atoms which in turn increases the growth rate of new embryos. Also they can lower the nucleation barrier by becoming part of these embryos. The energy barrier to be exceeded in order to accomplish the nucleation of second phase particles in the presence of vacancies is given by⁽¹⁰⁾,

$$F_o = \frac{16 \pi (\Delta F_s)^3}{3[\Delta F_v + \Delta F_{vac} + \Delta F_{m vac}]}$$

where ΔF_{vac} = change in free energy associated with vacancy precipitation.

$\Delta F_{m vac}$ = strain energy in presence of vacancies

2.1.4.2 Nucleation on dislocations

Nucleation on dislocations was first investigated by Cahn⁽¹¹⁾.

According to Cahn the strain energy and the interfacial surface energy do favor the nucleation on dislocations and the volume energy tends to oppose it. He has defined the term α

$$\alpha = \frac{\Delta F_v Gb^2}{2\pi^2 (\Delta F_s)^2} \quad \text{for screw dislocations}$$

and

$$\alpha = \frac{\Delta F_v Gb^2}{2\pi^2 (\Delta F_s)^2 (1-v)} \quad \text{for edge dislocations}$$

where G = the shear modulus

b = Burgers vector of the dislocation

ν = the Poisson ratio.

In Figure 3, the ratio of the nucleation energy on a dislocation, to the homogeneous nucleation can be seen as a function of the parameter α .

2.1.4.3 Nucleation at grain boundaries

Grain boundaries are planar defects with high free energies. Nucleation of second phase particles at the grain boundaries of the solid solution lowers the total free energy of the system by eliminating the boundary where the embryo forms. The change in free energy is the driving force for heterogeneous nucleation at the grain boundaries.

If $\sigma^{\alpha\alpha}$ is the interfacial surface energy at a α - α grain boundary where β phase nucleates leading to $\sigma^{\alpha\beta}$ interfacial energy at the α - β interface (Figure 4), then the relation between the interfacial energies is as follows⁽¹³⁾

$$\sigma^{\alpha\alpha} = 2 \sigma^{\alpha\beta} \cos\theta \quad .$$

The ratio of the energy of nucleation at a grain boundary to that of the homogeneous nucleation becomes⁽¹³⁾

Figure 3: The ratio of the nucleation energy on a dislocation to the homogeneous nucleation energy as a function of the parameter α , [11].

ΔF^* = Change in free energy due to nucleation on a dislocation

ΔF_H^* = Free energy change associated with homogeneous nucleation

Figure 4: The formation of a β embryo on an α grain boundary surface, [12].

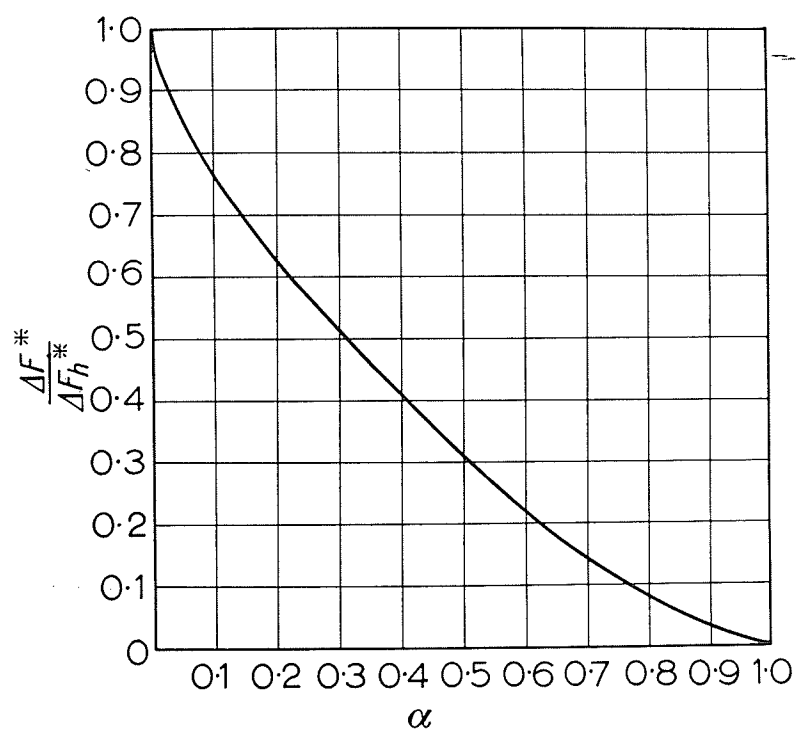


Figure 3

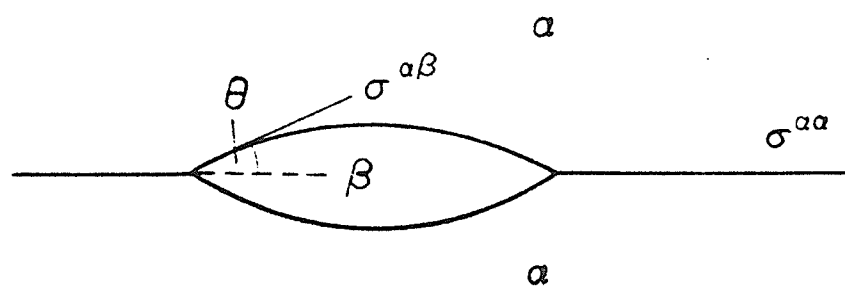


Figure 4

$$\frac{\Delta F_B}{\Delta F_H} = \frac{1}{2} (2 - 3 \cos \theta + \cos^3 \theta)$$

where ΔF_B = free energy change due to nucleation at a two-grain boundary.

ΔF_H = change in free energy due to homogeneous nucleation.

2.1.5 Coarsening of the precipitates

When the embryo reaches the stable phase, it will start to grow due to the addition of the solute atoms from the matrix. The coarsening of the precipitate particles can also occur by volume diffusion in which the large particles grow at the expense of the smaller ones. Such a coarsening process also known as "Ostwald ripening" is mainly due to the interfacial energy between the precipitate particles and the matrix. As the second phase particles are smaller their surface to volume ratio is higher, by coarsening this ratio can be reduced which renders the larger particles more stable.

The growth kinetics of the precipitate particles depends on the rate-controlling step in the process. If the rate-controlling step is the lattice diffusion, then the particle size of the precipitates is proportional to the cubic root of the ageing time. Coarsening of the second phase particles by lattice diffusion was investigated by Wagner⁽¹⁴⁾ and by Lifshitz and Slyozov⁽¹⁵⁾ (LSW

theory). The above authors describe the coarsening rate when the steady distribution is achieved as follows

$$\bar{r}^3 - \bar{r}_0^3 = \frac{8 D \sigma V_m^2 C_\alpha t}{9RT}$$

where $\bar{r}$ = average particle radius at time t

$\bar{r}_0$ = average particle radius at time $t=0$, i.e., at the onset of the coarsening process

D = the solute diffusion coefficient in the matrix

σ = interfacial free energy of the particle/matrix interface

V_m = molar volume of the particles

C_α = the solute concentration of particles with infinite radius

R = the gas constant

T = the absolute temperature.

Wagner⁽¹⁴⁾ has shown that the steady state particle size distributions can be expressed as follows

$$\rho(r,t) = \rho'(t) \rho^2 h(\rho)$$

where

$\rho'(t)$ is a function of time

$$\rho = r/\bar{r}$$

$\bar{r}$ = arithmetic mean value of spherical particles.

$$h(\rho) = \left(\frac{3}{3+\rho}\right)^{7/3} \left(\frac{3/2}{3/2-\rho}\right)^{11/3} \exp\left(\frac{-\rho}{3/2-\rho}\right) \text{ for } \rho < 3/2$$

$$h(\rho) = 0 \quad \text{for } \rho \geq 3/2 \quad .$$

The function $\rho^2 h(\rho)$ possesses the following properties

- a sharp cut-off at $\rho = 3/2$
- a maximum value at $\rho = 1.135$
- $\int_0^\alpha \rho^2 h(\rho) d\rho = 9/4$.

Ardell⁽¹⁶⁾ has modified the LSW theory by taking into consideration the effect of the volume fraction of the precipitates on their growth rate. The LSW theory of diffusion-controlled particle coarsening is applicable when the volume fraction of the precipitates is assumed to be very small. According to Ardell with increasing volume fraction of the precipitates, the mean interparticle spacing will decrease between particles. Consequently, the diffusion paths will become shorter, which should increase the coarsening rate. According to the modified LSW theory (MLSW theory) by Ardell⁽¹⁶⁾, the coarsening equation is as follows

$$\bar{r}^3 - \bar{r}_0^3 = \frac{3 \alpha D V_m \rho^3 (\phi)}{V(\phi)}$$

where ϕ = volume fraction of precipitates

$$\alpha = \frac{2\sigma V_m C_\alpha}{RT}$$

$$V(\phi) = \frac{6\sigma D V_m^2 C_\alpha dt}{RT dr^{*3}}$$

$$\rho(\phi) = \frac{\bar{r}}{r^*}$$

r^* = critical radius.

Recently, Davies et al⁽¹⁷⁾ have considered the effect of the encounters between the growing particles. The above authors have modified the LSW theory accordingly (LSEM theory). When the growing particles encounter and touch others, they will coalesce with them and the driving force for the coalescence will vary according to the surface curvatures of the particles. Consequently with increasing rate of encounters the coarsening rate of the particles will increase.

The particle size distributions of both the MLSW and LSEM theories are broader than the particle size distribution of the LSW theory, if the volume fraction of precipitates is not equal to zero. The coarsening rate constant k , in the LSEM theory is less dependent on the volume fraction of the precipitates than in the MLSW theory.

2.2 Precipitation Behaviour of Cobalt Base Alloys

The matrix of the cobalt-base alloys may consist of fcc (γ or α) or hcp (ϵ) phases, it may as well be a combination of both of the phases depending on the alloying elements present and the temperature of application. These two factors will also control the nature of second phase particles, such as carbides, TCP phases and intermetallic compounds. The following is a brief review of the various phases encountered in the cobalt-base alloys.

Generally, cobalt-base alloys contain chromium to provide resistance to oxidation and sulfidation, also chromium is a carbide former. G.P. Sullivan et al⁽¹⁸⁾ have given a summary of the effects of the various alloying elements on the cobalt-base alloys. It was reported that nickel stabilizes the γ (fcc) phase of the matrix. Zirconium increases rupture strength. Titanium is a carbide former and also can produce the intermetallic compounds Co_3Ti and Ni_3Ti . Molybdenum and tantalum are solid solution strengtheners and also they can form M_6C carbides. Aluminium can form the intermetallic compound CoAl , also it promotes oxidation resistance.

2.2.1 Carbides

The main strengthening mechanism of the cobalt-base superalloys is by carbide precipitation. Consequently, the carbon content of the cobalt-base superalloys is higher than the nickel-base alloys.

The quantity of carbon to be kept in the cobalt-base alloys is dependent on the amount of carbide forming elements which are present.

M_3C_2 and M_7C_3 type of carbides form with low amounts of Cr to C ratio. These are mainly chromium-carbon compounds, occasionally some cobalt may also be present.

$M_{23}C_6$ type of carbides exist in cobalt-base alloys where the chromium content is more than 5%. $M_{23}C_6$ carbides have cubic structure. Tungsten and molybdenum can replace chromium if they are present in the alloy. In a Mar-M 509 alloy, at the first stages of precipitation the $M_{23}C_6$ carbides are coherent with the matrix, as they grow, some of them tend to coalesce leading to long non-coherent precipitates⁽¹⁹⁾. Ageing at 973 K of a Co-25% Cr-10% Ni-0.25%C alloy has lead to the precipitation of $M_{23}C_6$ carbides on Frank partial dislocations⁽²⁰⁾. The presence of stacking faults and dislocations in the fcc matrix was related to the distribution of undissolved carbides after the solution treatment.

M_6C type of carbides appear in the cobalt-base alloys where the concentration of the refractory metals is high. The refractory metals stabilize the M_6C carbides rather than the $M_{23}C_6$ compound. In a Co-W alloy⁽²¹⁾, ageing above 1173 K transforms the coherent MC type of carbides to the non-coherent M_6C type of carbides which are formed at the grain boundaries.

MC type of carbides can form by reactions with group IV and group V elements. They make a major contribution to the strength of cobalt alloys. MC carbides in a Co-W alloy⁽²¹⁾ precipitating at the grain boundaries are coarse and non-coherent with the matrix, the carbides which are within the grains are coherent and they are aligned along (111) planes of the fcc matrix.

2.2.2 TCP phases

The existence of the TCP (topologically closed-packed) phases in the cobalt-base alloys is considered to be harmful for the rupture strength of the alloys at high temperatures. They can also decrease the tensile strength and lower the ductility properties at room temperature. TCP phases are electronic compounds. σ , μ and Laves phases have been observed in the cobalt-base alloys⁽²²⁾. These compounds form if the ratio of the sum of the chromium and refractory metals to cobalt exceeds certain values.

Sigma (σ) phase is body-centered tetragonal with 30 atoms per unit cell. σ phase is brittle and if it precipitates at the grain boundaries it can constitute a site for initiation of the fracture⁽²³⁾. Another disadvantage of the sigma phase is that the amount of the refractory metals in its unit cell is very high. Since, the refractory metals are removed from the matrix of the alloy, their strengthening effect is decreased considerably.

Mu (μ) phase has 13 atoms per unit cell and it is of rhombohedral structure. In a Co-W alloy⁽²¹⁾, μ phase precipitates as Co_7W_6 compound.

Laves phase is of A_2B type. In a Co-9% Ti alloy⁽⁵⁾ addition of Mn was reported to lead to the formation of Co_2Ti laves phase.

It is possible to evaluate if an austenitic matrix may be susceptible to the precipitation of TCP compounds. A process called PHACOMP analysis is applied for this purpose. This technique basically consists of calculating average electron hole number $\bar{N}_v$ of the alloy. If the $\bar{N}_v$ value is higher than, 2.5 for nickel-base alloys and 2.75 for cobalt-base alloys, the alloy system can form TCP compounds. Wagenheim⁽²⁴⁾ has applied the PHACOMP analysis to the Co-Cr-Ni-Ta-C (Disco) alloys. The presence of σ phase was encountered with $\bar{N}_v$ values of 2.89 and 2.78. When the $\bar{N}_v$ values were lower than 2.75 no σ phase was present. Biss et al⁽²⁵⁾ have investigated the relative effects of chromium, molybdenum, tungsten and tantalum for the formation of σ compound in Ni-Co-Cr alloys. They have reported that on the atomic percentage basis regarding the minimum amount of each refractory element which is necessary to initiate the σ phase precipitation, molybdenum, tungsten and tantalum have the same potential. In 2% - 4% range of refractory metals, greater quantities of σ phase are formed by equal amounts of molybdenum and tungsten than tantalum. Also tantalum is suggested to cause the

precipitation of μ phase in addition to the σ phase.

2.2.3 GCP phases

Geometrically close-packed (GCP) phases have the A_3B form. B is a smaller atom than A. The GCP phase precipitates are very effective strengtheners of the nickel-base alloys⁽³⁾. For the cobalt-base alloys, the mismatch between the matrix and the γ' (fcc) and η (hcp) GCP phases is generally observed to be higher than 1%⁽²²⁾. When the misfit is higher than 1%, the precipitation of the GCP phases is considered not very effective for improving the strength properties of the cobalt-base superalloys^(22, 26).

Some of the investigations on the GCP phase precipitates in the cobalt-base alloys are reviewed in the following section.

The presence of γ' Co_3Ti precipitates have been reported to contribute to the strengthening, at intermediate temperatures, in a CM-7 (Co-20% Cr-15% Ni-15% W-1.3% Ti-0.5% Al-0.1%C) alloy⁽²⁷⁾. Ageing for longer times between 1023K to 1098K transformed the above γ' (fcc) precipitates to an ordered η (hcp) phase. Co_3Ti phase precipitates were observed also by Berezina et al⁽²⁸⁾ in a Co-7.8% W-3.6% Ti alloy. Ageing at 1123K for long periods of time showed the presence of γ' type Co_3Ti and Co_3W precipitates. In this system Co_3Ti was still fcc at 1123K while it transformed to η phase in the CM-7 alloy at lower temperatures. The shape of γ' precipitates did not exhibit considerable changes in the temperature range of

923K - 1273K in the Co-W-Ti alloy. The stability of the γ' compound was attributed to the relatively low coherency strains. The γ' -Co₃Ti phase of precipitates in a 53% Co-43.3% Ni-3.7% Ti alloy⁽²⁹⁾ were observed to have a lattice mismatch of 1.3% with the matrix. The increase in strength of the above alloy was related to the interaction of the glissile dislocations with the elastic stresses resulting from the coherent precipitation of Co₃Ti phase. In a Co-20% Cr-15% W-10% Ni-1% Ti-0.2%C alloy⁽³⁰⁾, no precipitation of Co₃Ti phase was observed. When the Ti concentration of the above alloy was increased to 2%, Co₃Ti phase was observed. Because of the high temperature service of this alloy, TiC precipitates were considered to be the main strengthening phase. For this purpose the Ti content was kept at 1%. If the Co₃Ti precipitates were present, they altered the precipitation of the TiC phase. Co₃W- η precipitates were observed in a W233(Co-15% Cr-15%W) alloy⁽³¹⁾ aged at 973K for 100 and 1000 hours. The matrix of this alloy was a mixture of γ and ϵ phases and the precipitation occurred in the hcp regions. Ageing of a Co-15% Cr-8%Ta alloy⁽³²⁾ at 973K for 16 hours produced coherent Co₃Ta γ' cubic precipitates in the $\langle 100 \rangle$ fcc directions. While γ' precipitates were present in the fcc regions of the matrix, some regions of the matrix were of hcp structure. At 1073K the Co₃Ta particles coalesced and gradually lost their coherency with the matrix. They eventually transformed to the rhombohedral Co₃Ta compound. The matrix of a Co-5% Cr-5% Nb alloy⁽³³⁾

aged at 873K for 16 hours consisted of fcc and hcp phases. The existence of very fine ordered precipitates in the {111} planes of the fcc matrix of this alloy was also observed. The precipitates in the hcp regions were of Co_2Nb Laves structure. Mechanical properties and structure of various cobalt-nickel-niobium alloys was investigated by Piercey et al⁽³⁴⁾. The precipitates in 6 Co-Ni-Cr-Nb alloys of different compositions, were the Laves Co_2Nb phase. The precipitates extracted from 13 different Co-Ni-Nb alloys were of hexagonal Laves phase with an axial ratio of 1.615 ($a = 5.190 \text{ \AA}$, $c = 8.384 \text{ \AA}$)⁽³⁴⁾. The precipitates in the both alloy systems were of needle-like shape.

2.2.4 Experimental investigations of the coarsening of the γ' precipitates

The growth kinetics of γ' precipitates in cobalt-base superalloys has not been a subject of many detailed analyses. Most of the work however has been in the nickel-base alloys.

The coarsening of γ' precipitates in cobalt-base alloys was investigated by Chaturvedi et al⁽³⁵⁾ in a 40% Co-38% Ni-17% Cr-5% Ti alloy. The γ' precipitates were of $(\text{Co}, \text{Ni})_3\text{Ti}$ formula. The coarsening kinetics of the precipitates obeyed the predictions of the LSW theory. The same authors have applied the MLSW theory to Co-Ni-Cr-Ti alloys⁽³⁶⁾ in which the concentration of Ti was 4, 5 and

6%. The variation in the volume fraction of the precipitates was reported not to modify the coarsening behaviour of the γ' precipitates, and the LSW theory governed the growth kinetics.

CHAPTER 3 EXPERIMENTAL TECHNIQUES

3.1 Fabrication of the Alloys

The compositions of the alloys used during the course of this study were as follows

Co-25% Cr-4%Ti

Co-25% Cr-7%Mo

Co-25% Cr-5%Mo

Co-25% Cr-5% Mo-2.5%Nb .

The purity of the materials used was: Co 99.99%, Cr 99.99%, Mo 99.99%, Ti 99.7%, Nb 99.95%. All the alloys were made in an induction furnace in argon atmosphere. First two alloys which were used for tensile tests, besides the other investigations, were cast as 15 mm square ingots. The other two alloys were cast in cylindrical shapes of 200 grams weight. The ingots were cast in sand molds. All the alloys were homogenized at 1373K for three days. The first two alloys were hot rolled at 1373K until their thickness was reduced to 5 mm. The other two alloys were hot swaged at 1373K down to 5 mm diameter.

There were partial cracks observed in the Co-Cr-Mo-Nb alloy resulting from hot swaging. Attempts of cold and hot rolling were not successful in avoiding these cracks. Still, portions of

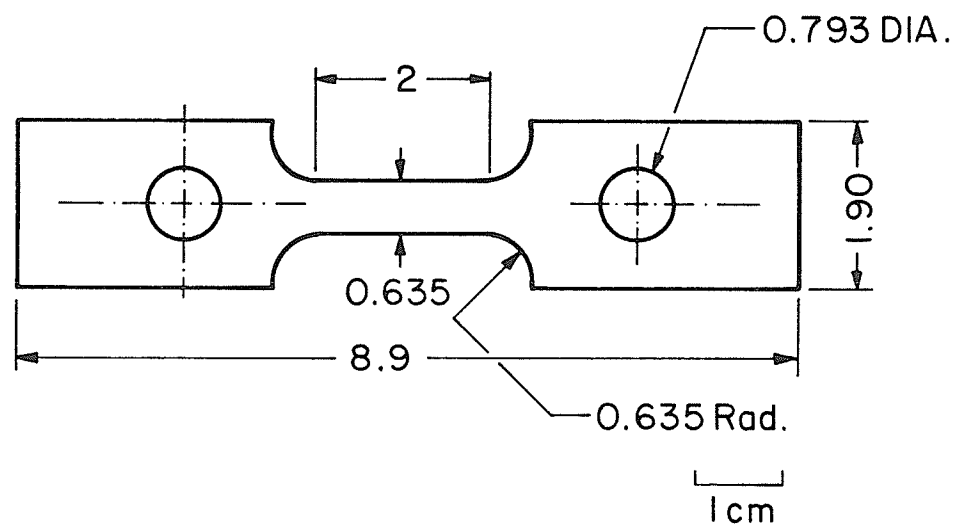
the alloy which did not crack were used for metallography and hardness studies.

The surface oxides on the alloys were removed by grinding, and all the four alloys were further homogenized at 1473K for 24 hours. Subsequently, they were cold rolled down to a 1.2 mm thickness for tensile and hardness specimens, with several intermediate anneals at 1473K. For the preparation of the thin foils, the cold rolling was continued down to a 0.2 mm thickness. All the samples were given a final solution treatment at 1473K for 1.5 hours. The heat treatments were conducted in sealed vycor capsules filled with argon gas. The specimens were quenched by breaking the capsules in water. It should be noted that the amount of cold deformation given to the Co-Cr-Mo-Nb alloy was kept less than the other three alloys.

3.2 Mechanical Properties

Hardness measurements were performed with a Vickers pyramid indenter at a load of 10 kg. Seven to eight indentations were made on the mounted and polished samples.

The tensile specimens were of the shape given in Figure 5. The pin holes were made by a spark-cutting machine. The specimens were machined to the final shape in a numerical controlled milling machine. As mentioned before, after reaching the final shape, the



THE TENSILE SPECIMEN

Figure 5: The standard specimen used for tensile tests.

tensile specimens were solution treated at 1473K for 1.5 hours. Tensile tests were conducted at room temperature, at a strain rate of 4.16×10^{-4} /sec in an Instron testing machine.

3.3 Optical Microscopy

Mounted samples were polished successively with emery papers and diamond pastes down to the 0.25 micron size. The polished samples were chemically etched by immersion in a solution of 80% HCl, 10% HNO₃, 10% alcoholic ferric chloride, by volume. They were later examined in a Vickers 55 Optical microscope.

3.4 Electron Microscopy

3.4.1 Carbon extraction replicas

Polished and etched samples were placed in a vacuum coating unit. Thin layer of carbon was deposited on the surface of these samples. Their surface was then scratched into square divisions. These samples were electrolytically etched in a 90% methanol, 10% perchloric acid solution at 5-6 volts for a few seconds. Then, they were washed in ethanol baths and the carbon layer was floated in distilled water. These films were collected on 200 mesh copper grids and examined in a Philips EM 300 electron microscope.

3.4.2 Thin foils

Disc-shaped specimens of 3 mm diameter and ≈ 0.2 mm thickness were electropolished in a Tenupol polishing unit. A solution of 92.5% methanol and 7.5% perchloric acid was used at 233K with a voltage of 15-17 volts. When a hole was detected, the specimen was removed from the polishing unit and cleaned in successive methanol and ethanol baths. Thin foils were examined in the same Philips EM 300 electron microscope.

3.5 Extraction of The Precipitates

In order to be able to compute the weight fraction of the γ' precipitates and their chemical composition, the Co_3Ti precipitates were extracted from the Co-25% Cr-4%Ti alloy by anodic dissolution of the matrix. An aqueous solution of 1% ammonium sulfate and 1% citric acid⁽³⁷⁾ with a current density of 0.03 Amps/cm², was used. As observed by Kriege and Baris⁽³⁷⁾, the separation of particles with average particle sizes larger than $300 \text{ \AA}$ (in the present system the average edge lengths $\bar{a}$ of the cubic particles) was successful. The extraction of the precipitates with $\bar{a}$ values lower than $300 \text{ \AA}$ has given doubtful results. The extracted precipitates were separated from the solution by centrifuging first with distilled water and then with ethanol. Finally the ethanol was evaporated in order to obtain the dried precipitates.

3.6 Particle Size Measurements

The average particle size of the γ' precipitates in the aged Co-25% Cr-4%Ti alloy was obtained by means of carbon extraction replicas. A minimum of 300 individual particles were measured for a given ageing time and temperature.

CHAPTER 4 EXPERIMENTAL RESULTS

The solution treated and water quenched specimens of all the alloys were aged at 973K and 1073K for varying lengths of time. Their ageing kinetics and mechanical properties were followed by hardness measurements except for the Co-25% Cr-4% Ti and the Co-25% Cr-7% Mo alloys whose tensile properties were also determined. The structure of the aged specimen was then examined by optical and electron microscopy techniques. In this chapter, the experimental results are presented separately for each alloy, except for the Mo alloys both of which showed similar precipitation behaviour and mechanical properties.

4.1 Co-25% Cr-4% Ti Alloy

4.1.1 Mechanical properties

The Vickers hardness values of the solution treated and aged specimens are plotted against ageing time in Figure 6. It is observed that ageing at 973K leads to a higher peak hardness value with respect to that observed at 1073K. The peak hardness at 973K is 90 VPH higher than the solution treated specimen while the peak hardness at 1073K shows an increase of 65 VPH. The hardness of the aged alloys starts to decrease after 5 and 100 hours at 1073K and 973K, respectively. The hardness behaviour of the Co-25% Cr-4% Ti alloy is in agreement with the general effects of ageing temperature

Figure 6: Variation in hardness with ageing time at the ageing temperatures of 973K and 1073K.

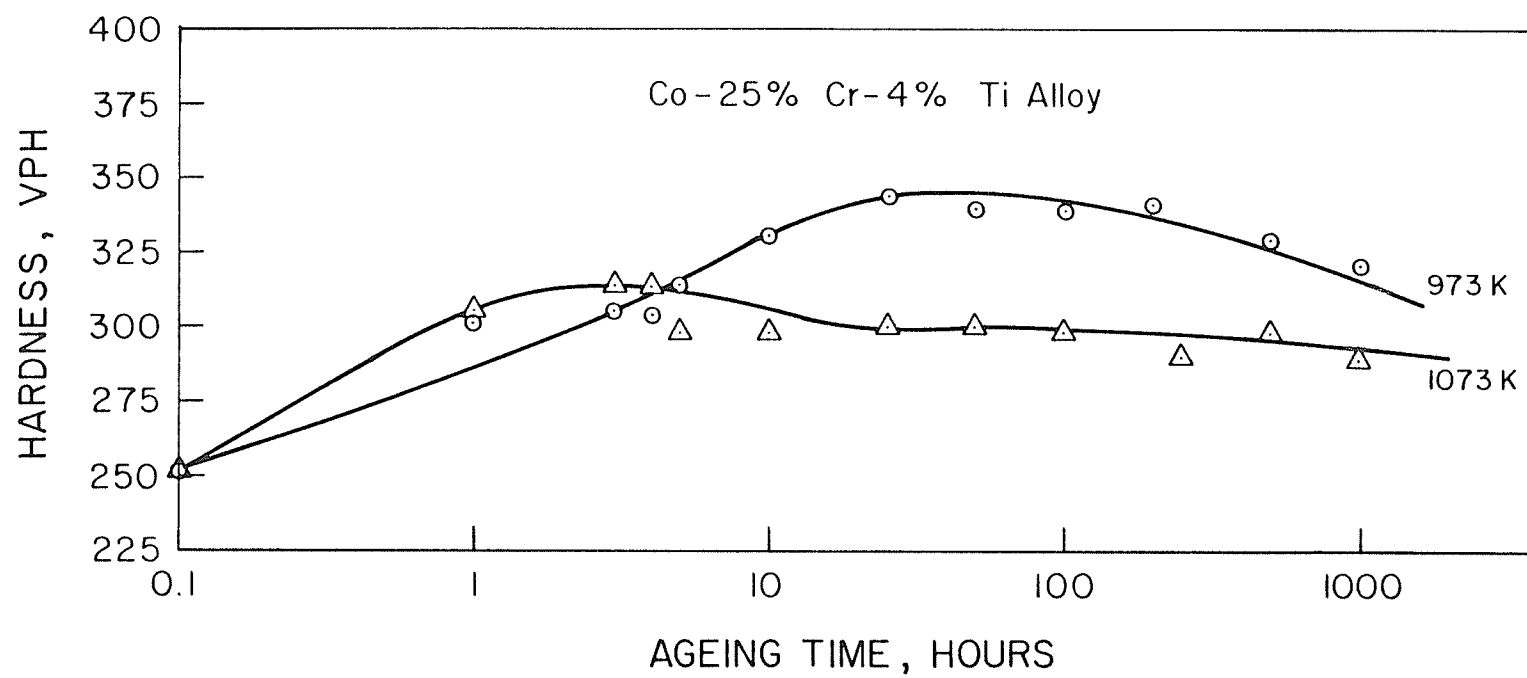


Figure 6

Figure 7: Room temperature tensile properties against ageing time for different ageing temperatures.

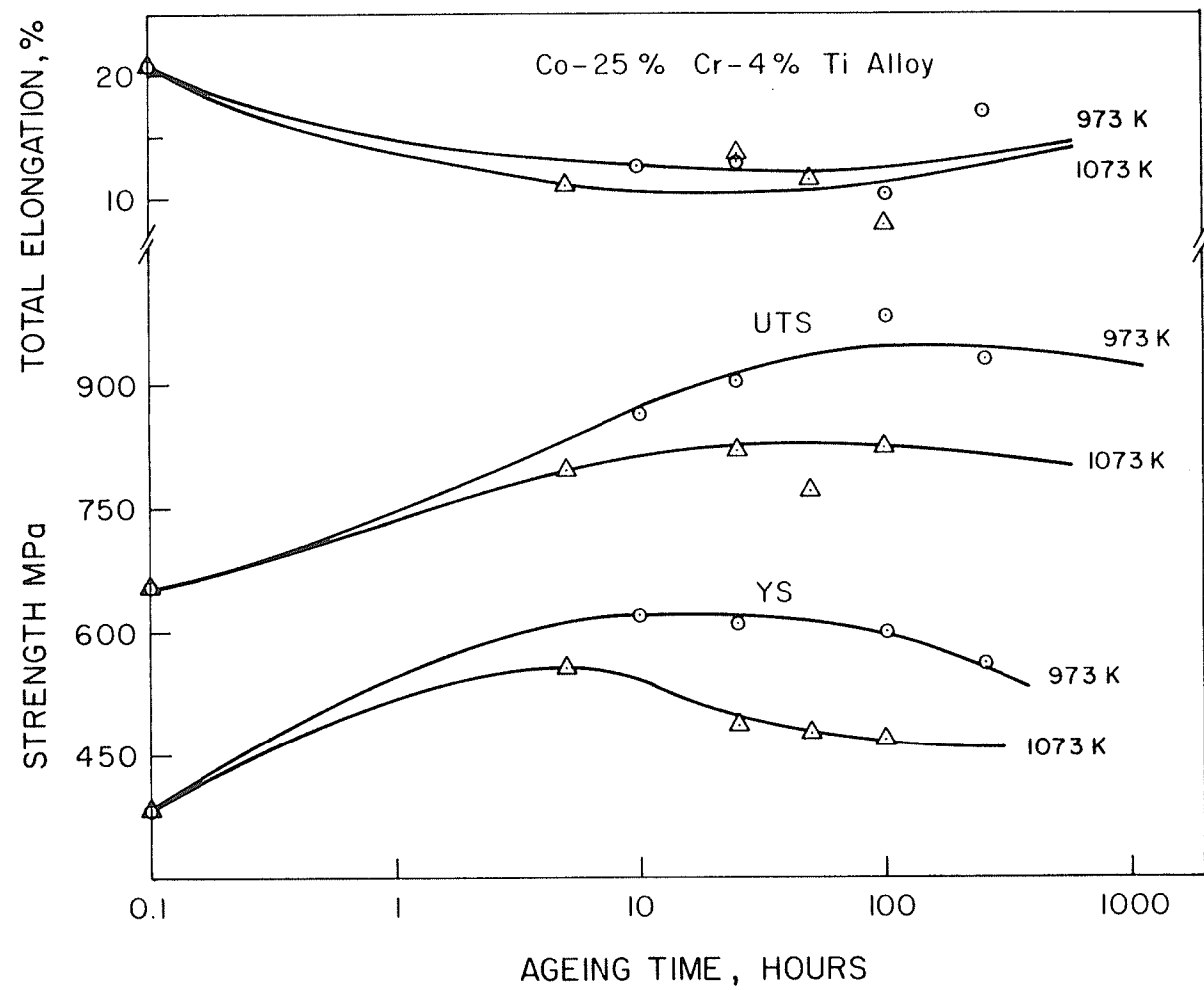


Figure 7

on the hardness properties, i.e., a higher peak hardness at lower ageing temperature which requires a longer ageing time.

The tensile tests were conducted at room temperature. The plots of the 0.2% offset yield strength, ultimate strength and total elongation as a function of ageing time for specimens aged at 973K and 1073K can be seen in Figure 7. The 0.2% offset yield strength of the Co-25% Cr-4% Ti alloy exhibits the same trend as its hardness behaviour. The % increase in yield strength is 60% for the samples aged at 973K for 10 hours with respect to the solution treated ones. The increase in yield strength of the samples aged at different ageing times and temperatures varies in the range of 25% to 60%. Total elongation of the aged tensile specimens is between 8% to 13% while it is 20% for the solution treated sample.

4.1.2 Optical metallography

The optical microstructure of the solution treated and aged specimens of the Co-25% Cr-4% Ti alloy were studied (Figures 8-11).

The metallographic study of the solution treated specimen in Figure 8, reveals a single phase with polygonal grains. The presence of twins or transformation bands within the grains is also observed. Some dark undissolved particles can be seen in the solution treated sample. No change in the grain structure of the aged specimens is noticed with respect to the solution treated one (Figures 9-11). The twins or transformation bands are conserved in the aged specimens

Figure 8: Optical microstructure of the Co-25% Cr-4% Ti alloy solution treated at 1473K. (150 x).

Figure 9: Optical microstructure of the Co-25% Cr-4% Ti alloy aged at 973K for 100 hours. (210 x).

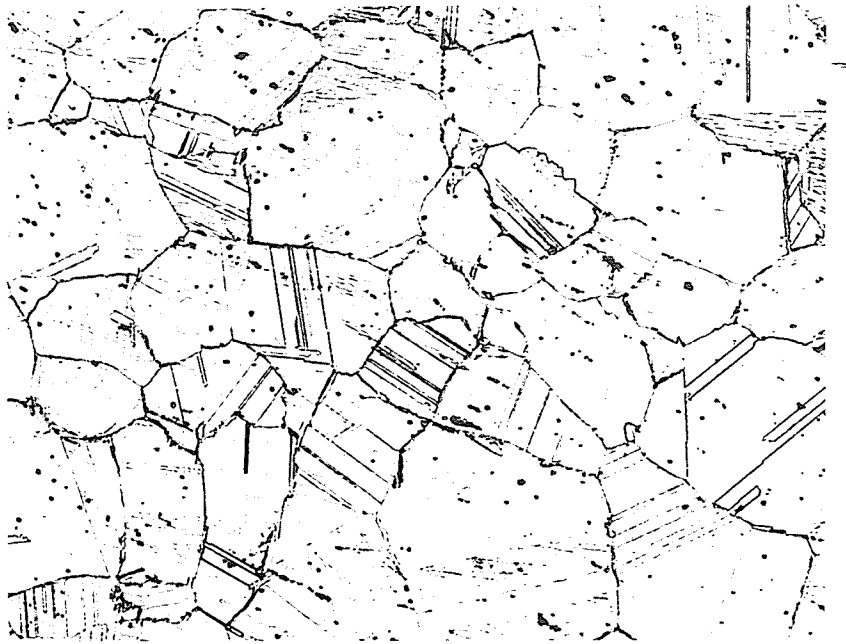


Figure 8

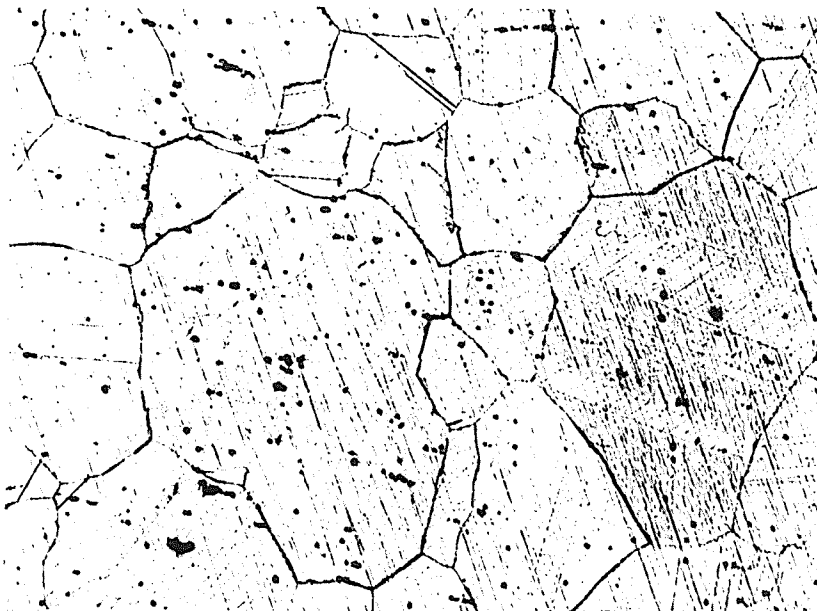


Figure 9

Figure 10: Optical microstructure of the Co-25% Cr-4% Ti alloy aged at 1073K for 10 hours. (250 x).

Figure 11: Optical microstructure of the Co-25% Cr-4% Ti alloy aged at 1073K for 50 hours. (250 x).

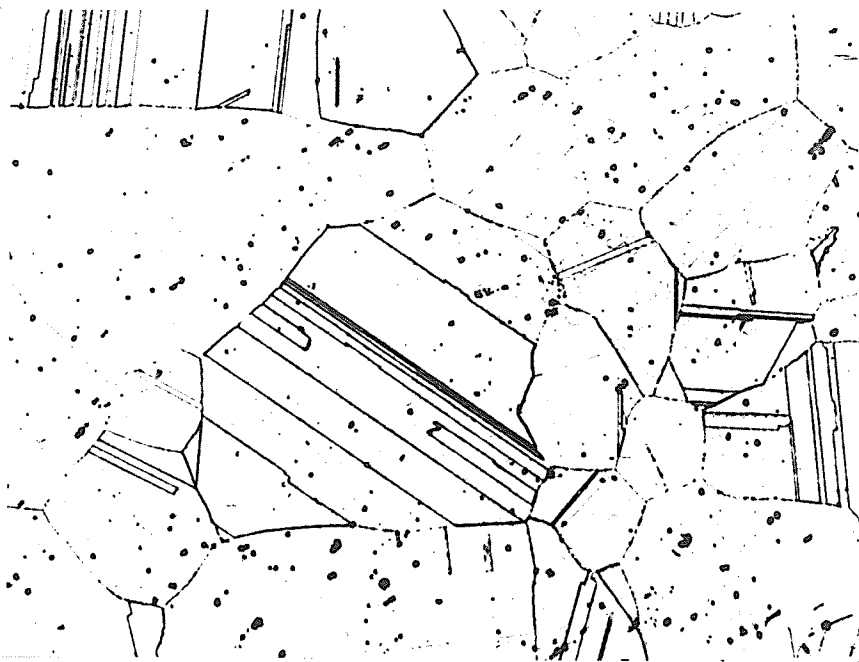


Figure 10

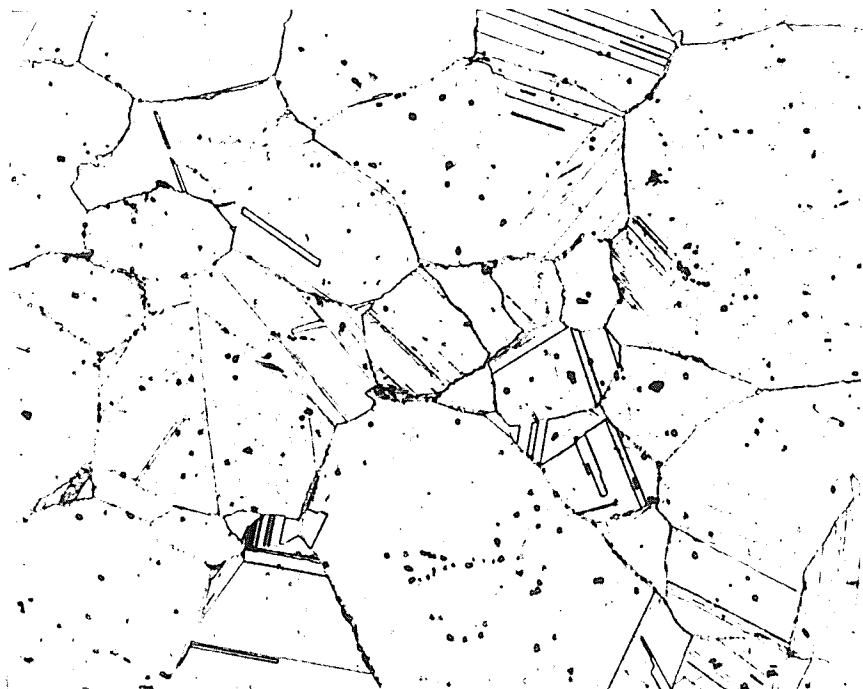


Figure 11

and no considerable change is noticed in their density with respect to the solution treated sample. The undissolved particles are still present in the aged specimens. Optical microstructures do not reveal the presence of second phase particles either within the grains or at the grain boundaries.

4.1.3 Electron microscopy

4.1.3.1 Carbon extraction replicas

The identification of the second phase particles, the observation of their shapes and also size measurements of these precipitates were conducted by means of carbon extraction replicas.

The d-spacing values of the precipitates were calculated by using camera constant for each of the ring diffraction patterns. The camera constant was determined by using aluminium replica as a standard.

In the Co-25% Cr-4% Ti alloy, the precipitates in the samples aged at 973K and 1073K for 50, 100, 500 hours were identified. These precipitates are cubic in shape, as seen in Figures 12-14, and their "d" values match with those of cubic Co_3Ti phase⁽³⁸⁾. The lattice parameter of the Co_3Ti precipitates is computed to be in the range of $3.60 \text{ \AA} - 3.62 \text{ \AA}$. One of the many ring patterns used for identification of the extracted precipitates can be seen in Figure 15. All the examinations reveal the presence of only one type of precipitates. The cubic shape of the precipitates is conserved and no phase transformations of the γ' precipitates is observed up to 500 hours of ageing

Figure 12: Carbon extraction replica of the Co-25% Cr-4% Ti alloy aged at 973K for 500 hours. (40500 x).

Figure 13: Carbon extraction replica of the Co-25% Cr-4% Ti alloy aged at 1023K for 500 hours. (40500 x).

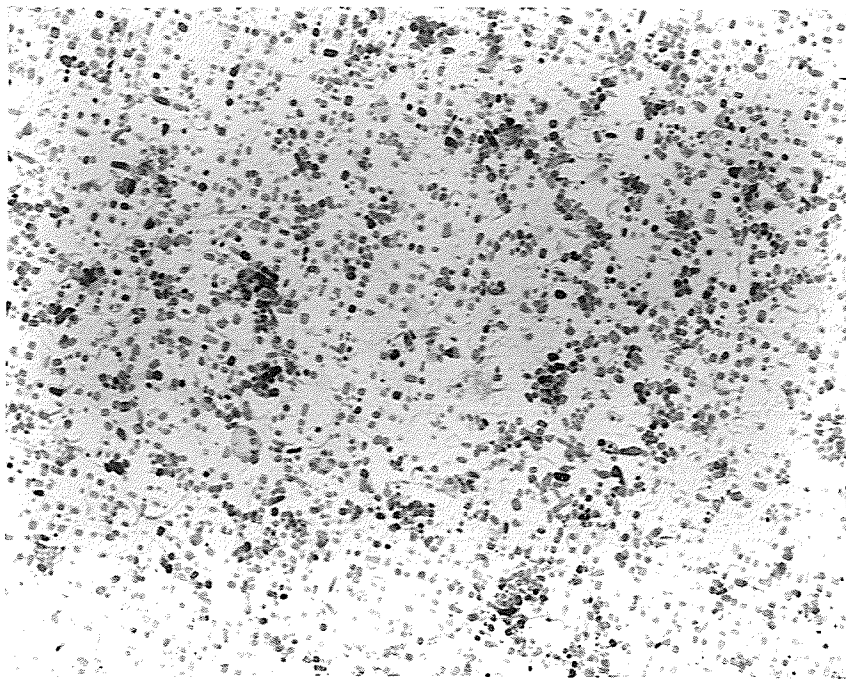


Figure 12

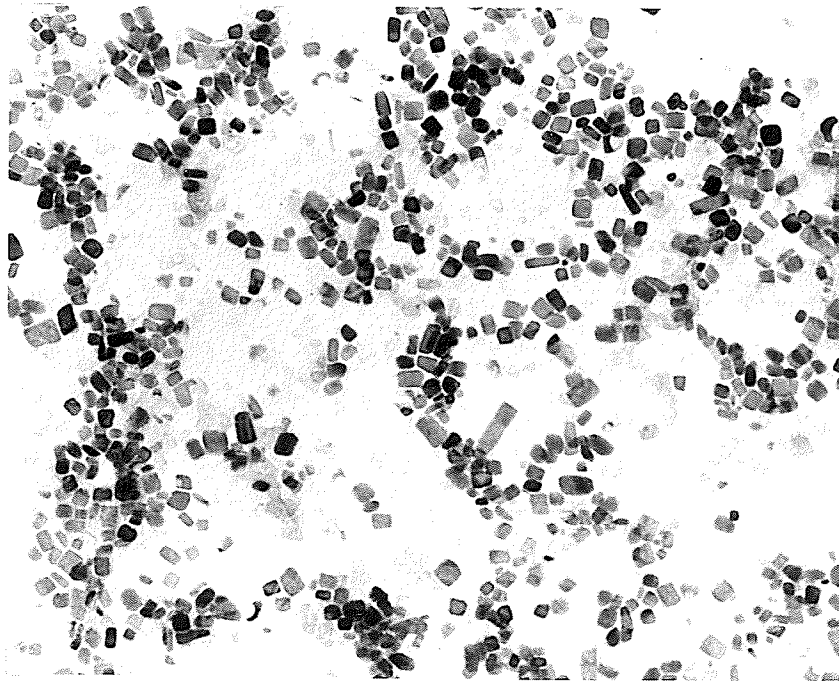


Figure 13

Figure 14: Carbon extraction replica of the Co-25% Cr-4% Ti alloy aged at 1073K for 50 hours. (59900 x).

Figure 15: Ring pattern of the carbon extraction replica of the alloy aged at 1073K for 50 hours (Figure 14).

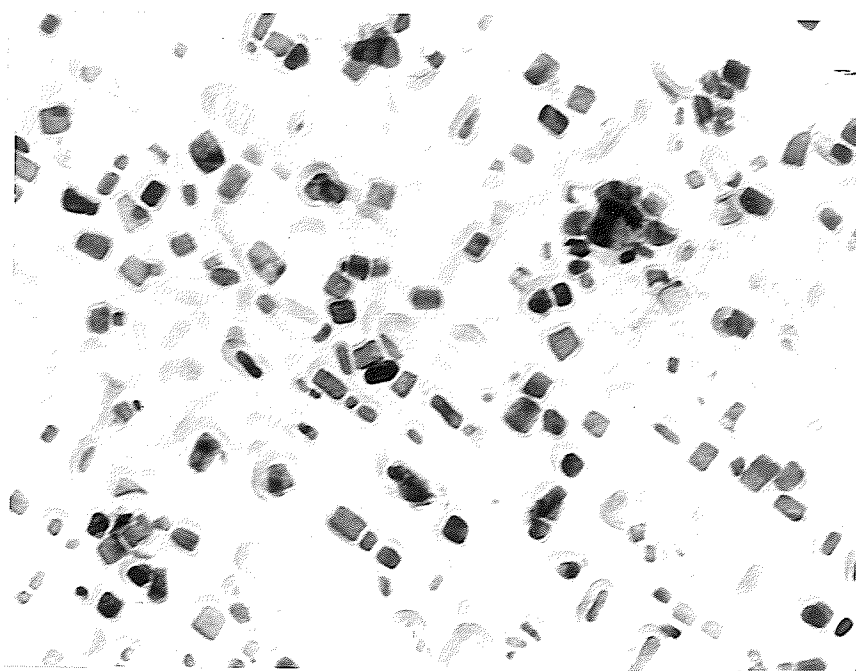


Figure 14



Figure 15

at 973K and 1073K.

In order to determine the coarsening kinetics of these cubic Co_3Ti precipitates, a third ageing temperature of 1023K was also selected. The precipitates which occur at 1023K show the same characteristics as the other two temperatures. At all the three temperatures the precipitates are distributed uniformly within the grains. Although carbon extraction replica technique is not suitable to make a final statement, no preferential precipitation at the grain boundaries is observed in the examined specimens. The average edge length $\bar{a}$ of the cubic Co_3Ti precipitates varies in the range of 90 Å (100 hours at 973K) to 880 Å (500 hours at 1073K) for the examined specimens. The more detailed analysis of the particle size of the Co_3Ti precipitates is presented in the section concerning the coarsening kinetics of these precipitates.

4.1.3.2 Thin foil electron microscopy

Electron microscopic studies of the Co-25% Cr-4% Ti alloy were conducted for the solution treated and aged specimens.

The examination of the solution treated thin foils reveals the existence of stacking faults (Figures 16, 17) and twins (Figures 19, 20). The matrix of the solution treated samples is of fcc phase with a lattice parameter of 3.59 Å. No hcp phase is noticed in the solution treated specimens.

Figure 16: Bright-field micrograph of the Co-25% Cr-4% Ti alloy solution treated at 1473K. (33900 x).

Figure 17: Dark-field of Figure 16, showing stacking faults by BF-DF contrast. (33900 x).

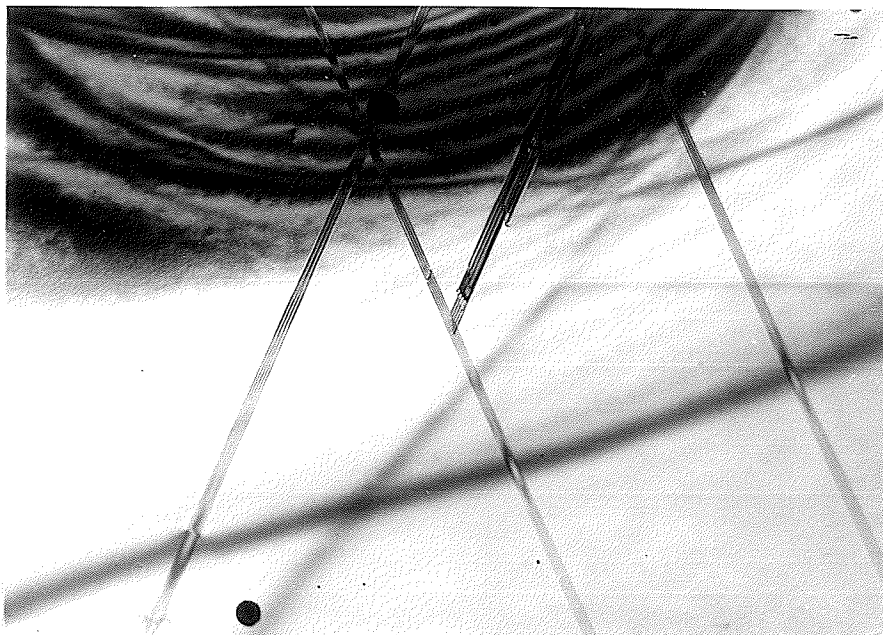


Figure 16

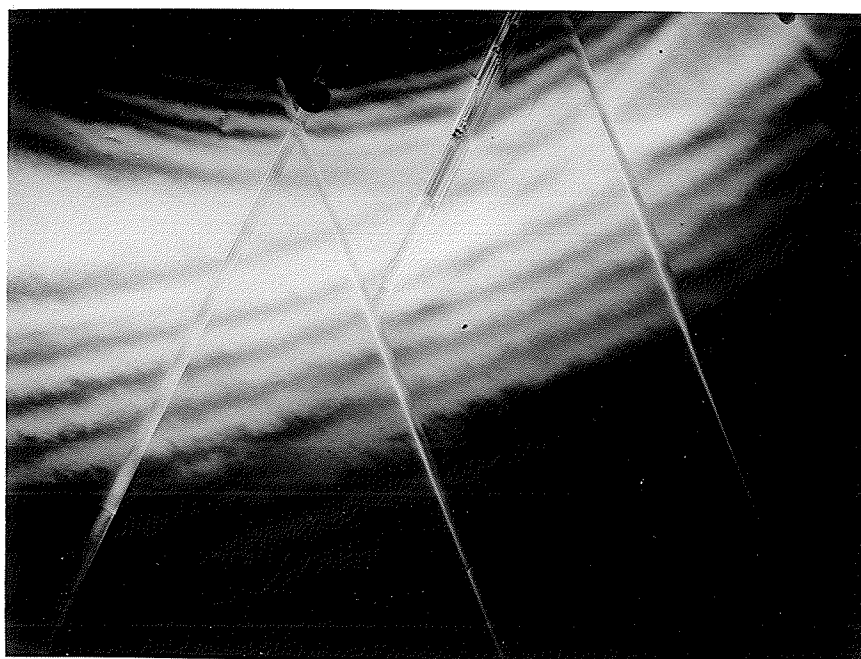


Figure 17

Figure 18: SADP of Figure 16.

Interpretation of Figure 18.

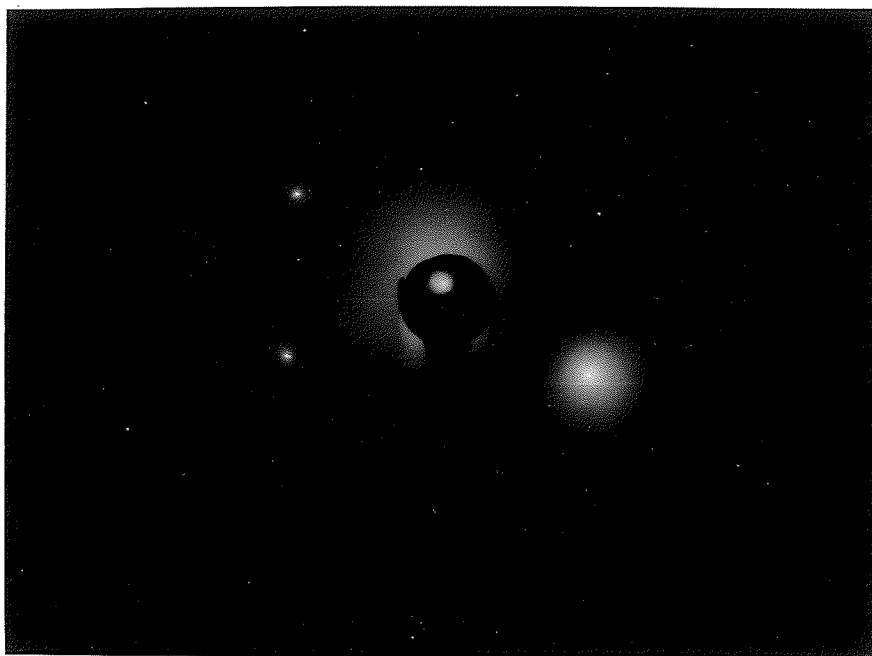


Figure 18

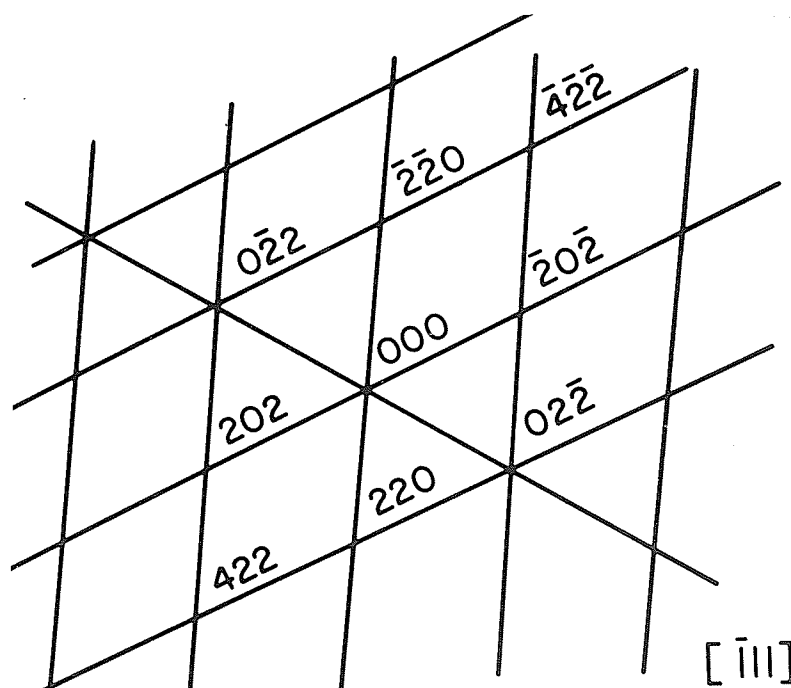


Figure 19: Bright-field micrograph of the Co-25% Cr-4% Ti alloy solution treated at 1473K. (35300 x).

Figure 20: Dark-field of Figure 19, showing presence of twins by BF-DF contrast. (35300 x).

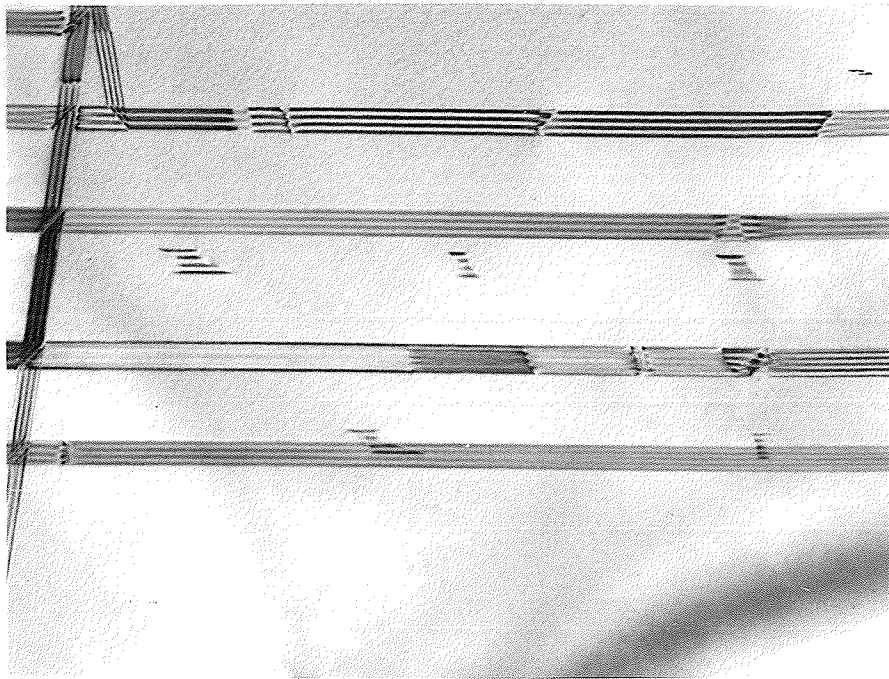


Figure 19

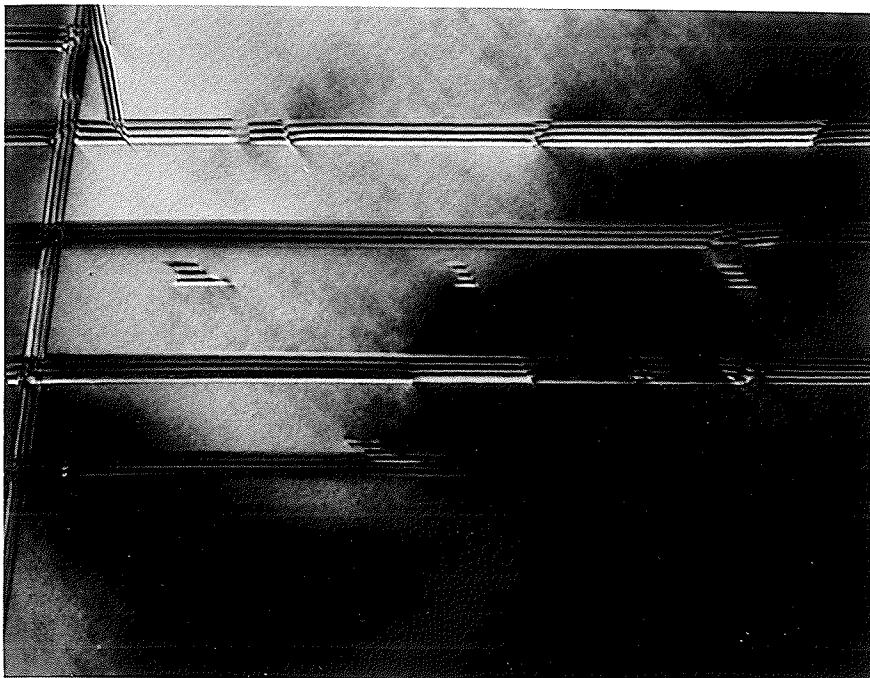


Figure 20

Figure 21: SADP of Figure 19.

Interpretation of Figure 21.

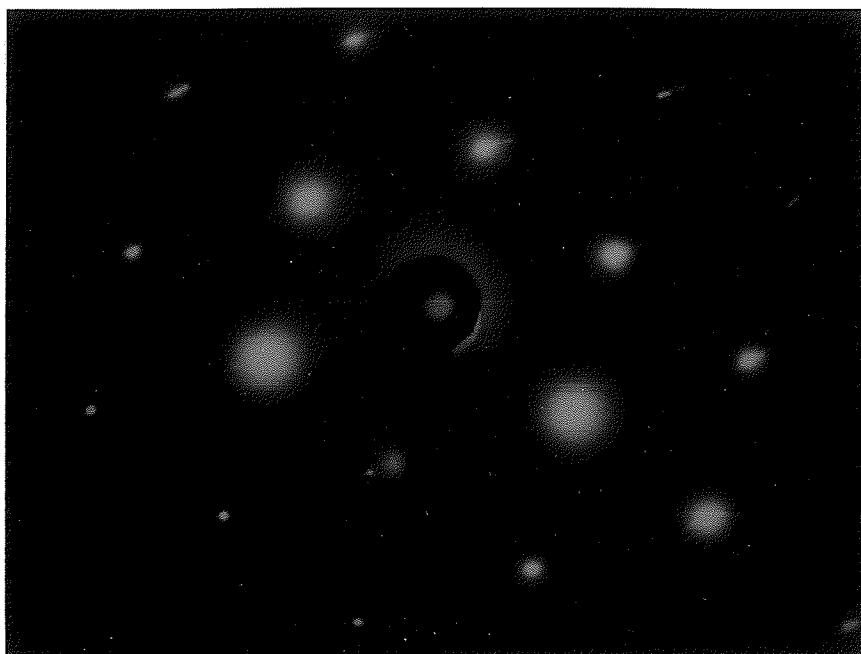
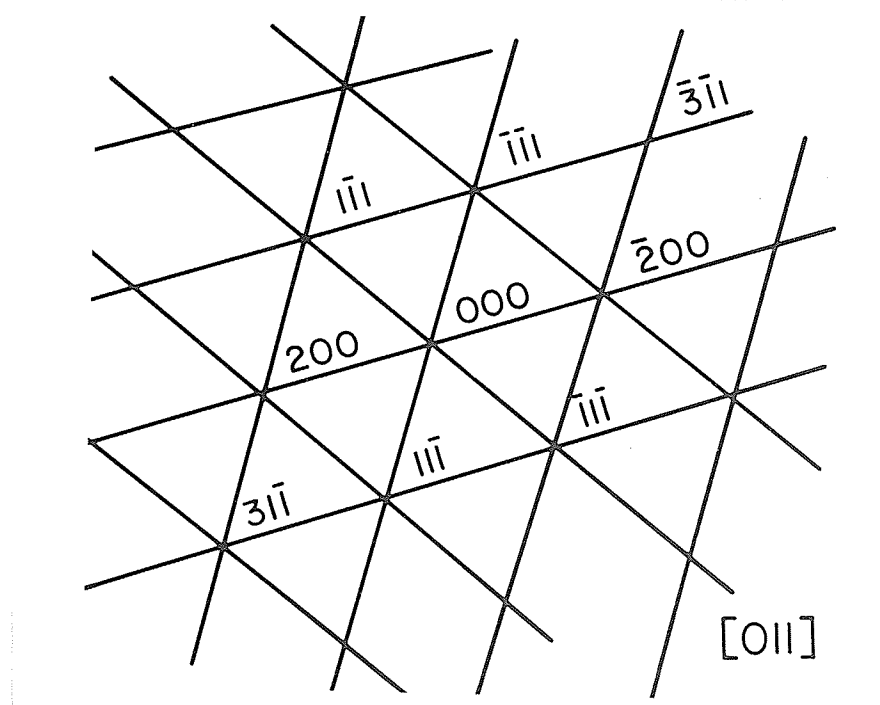


Figure 21



Studies of the aged specimens (Figures 22-34) reveal the existence of the γ' - Co_3Ti precipitates dispersed homogeneously within the grains (Figures 22, 24, 27, 29, 33). No preferential precipitation at the stacking faults, twins or grain boundaries is observed. The diffraction patterns of the aged specimens (Figures 26, 30, 31, 34) show very weak superlattice spots. These spots correspond to those due to the ordered fcc structure of Co_3Ti . The crystallographic habit of these precipitates is also similar to that observed in other Ni base alloys, i.e., they form on $\{100\}$ planes and are aligned along $\langle 100 \rangle$ directions. Occasionally, however, no reflections were obtained from the second phase particles (Figure 26). A specimen aged at 1073K for 1000 hours has a lattice parameter of $3.585 \text{ \AA}$ for the matrix and $3.612 \text{ \AA}$ for the cubic precipitates. The misfit between the matrix and the precipitate particles $\left(\frac{a_{\gamma'} - a_{\text{matrix}}}{a_{\text{matrix}}} \right)$ is 0.75%. The lattice misfit changes between 0.6% to 1.0% for the examined specimens. No fcc γ' to hcp η phase transformation occurred for the Co_3Ti precipitates aged up to 1000 hours at 1073K. The precipitate-matrix interfaces do not reveal any dislocation to suggest the loss of coherency of the γ' precipitates. The density of the stacking faults and twins in the matrix does not change considerably on ageing. The matrix of the aged specimens was also fcc.

Figure 22: Bright-field micrograph of the Co-25% Cr-4% Ti alloy aged at 973K for 10 hours. (35300 x).

Figure 23: Dark-field of Figure 22, showing stacking faults by BF-DF contrast. (35300 x).

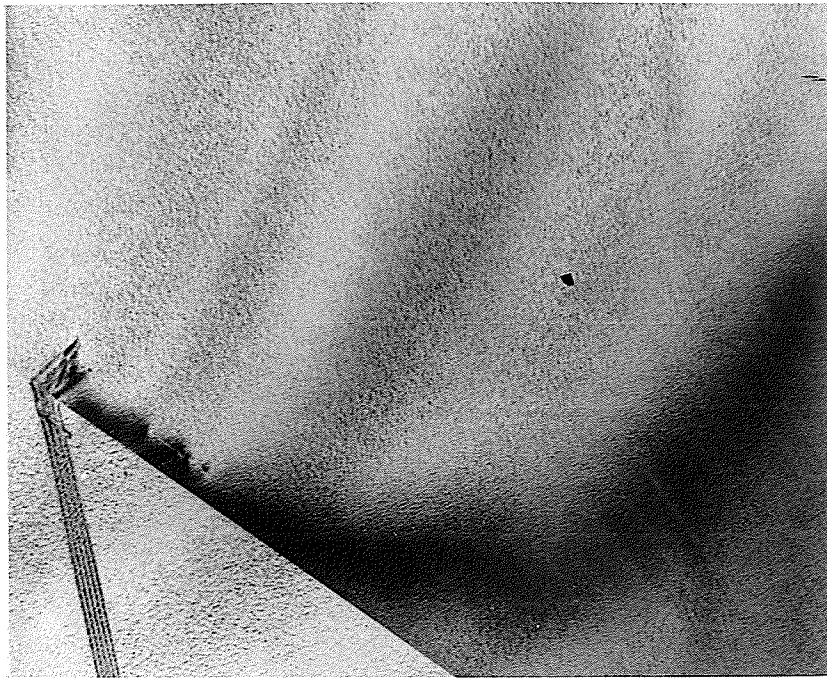


Figure 22

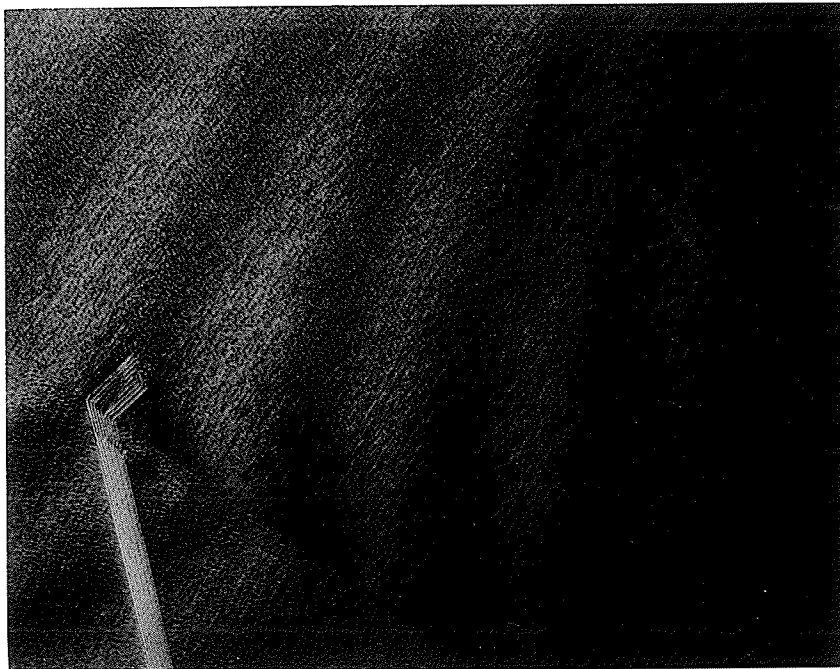


Figure 23

Figure 24: Bright-field of Co-25% Cr-4% Ti alloy aged at 973K for 50 hours. (14800 x).

Figure 25: Dark-field of Figure 24, showing stacking faults by BF-DF contrast. (14800 x).

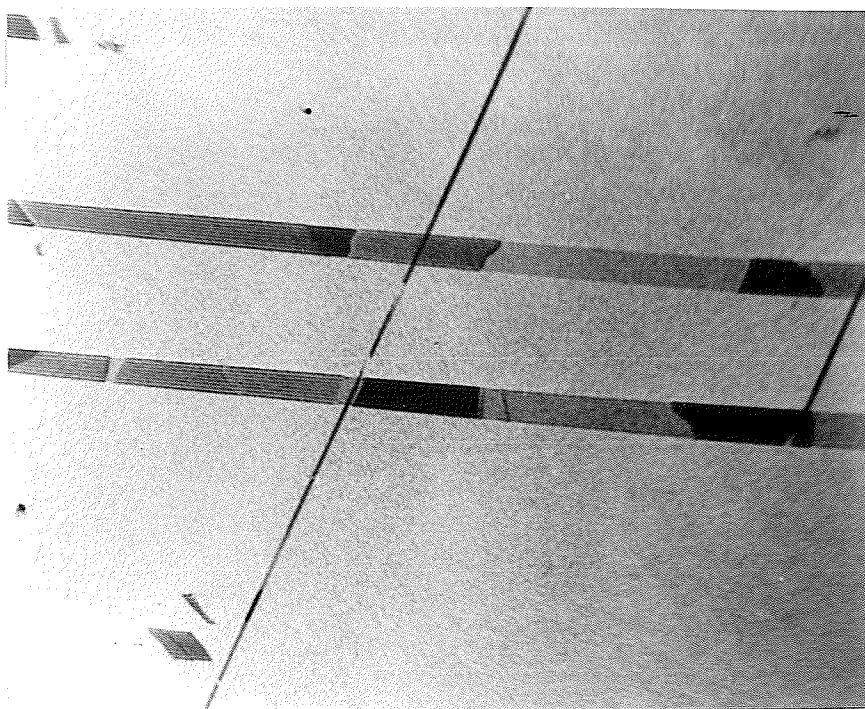


Figure 24

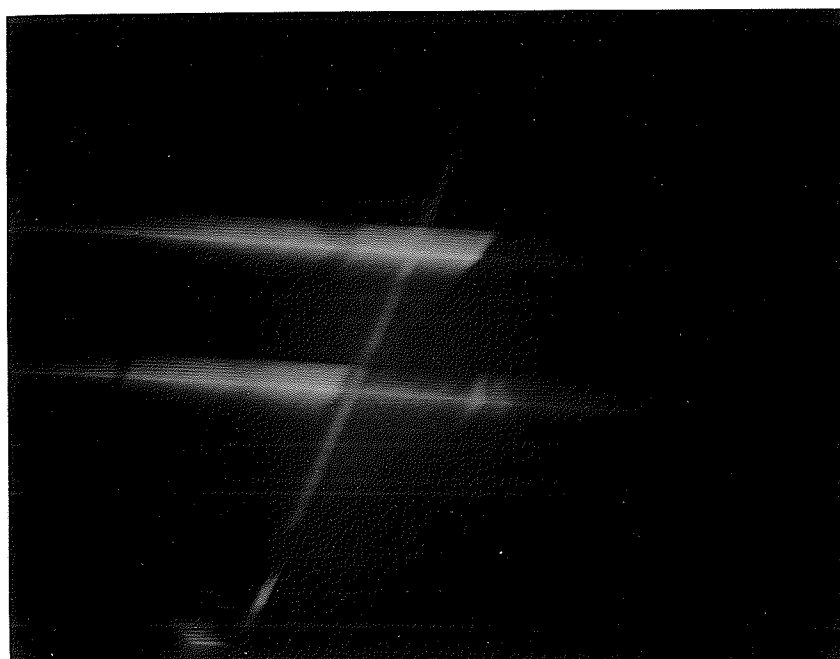


Figure 25

Figure 26: SADP of Figure 24.

Interpretation of Figure 26.



Figure 26

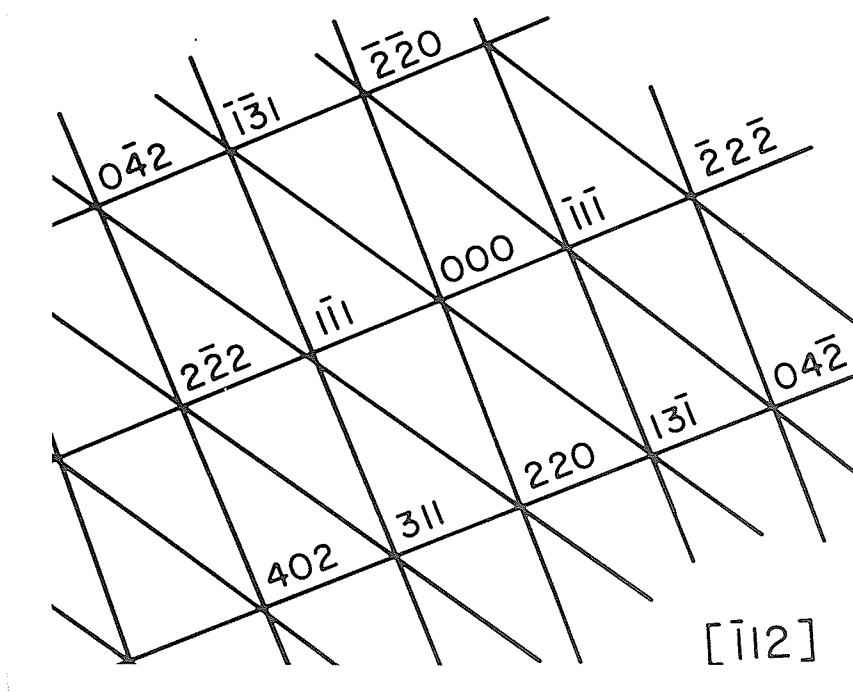


Figure 27: Bright-field micrograph of the Co-25% Cr-4% Ti alloy aged at 973K for 100 hours. (20700 x).

Figure 28: Dark-field of Figure 27, showing the presence of twins by BF-DF contrast. (20700 x).

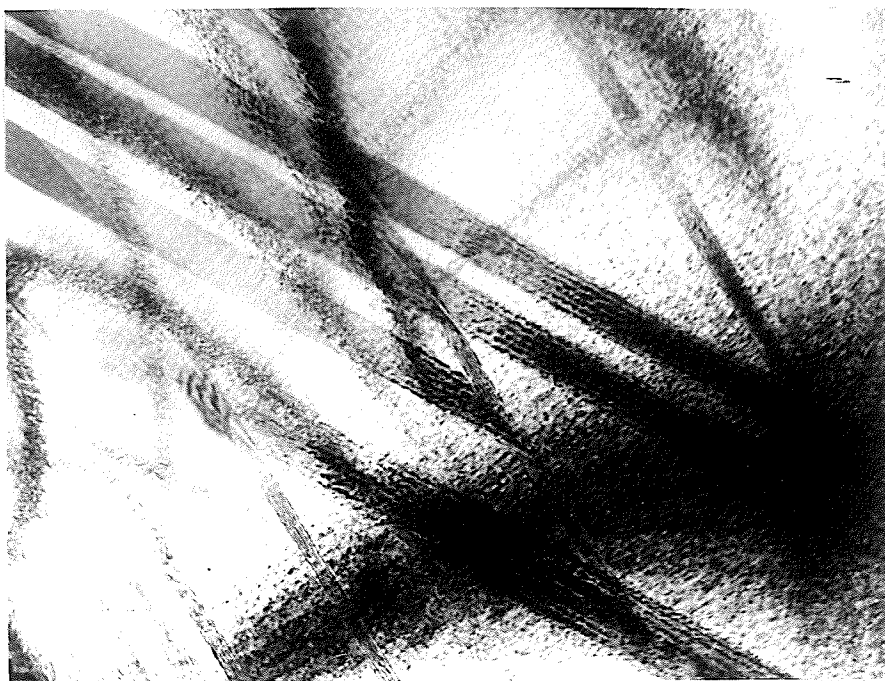


Figure 27

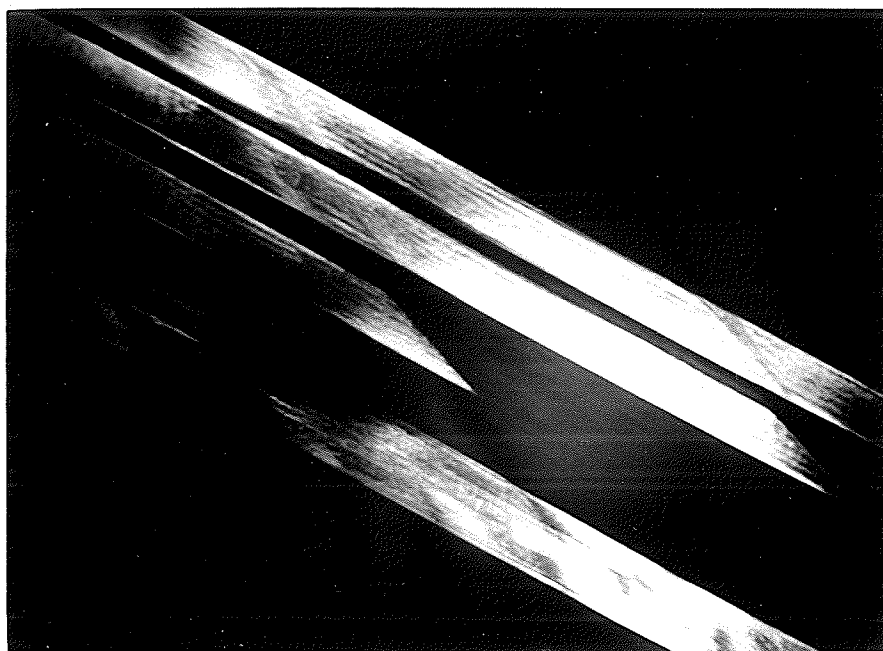


Figure 28

Figure 29: Bright-field micrograph of the Co-25% Cr-4% Ti alloy aged at 1073K for 10 hours. (20700 x).

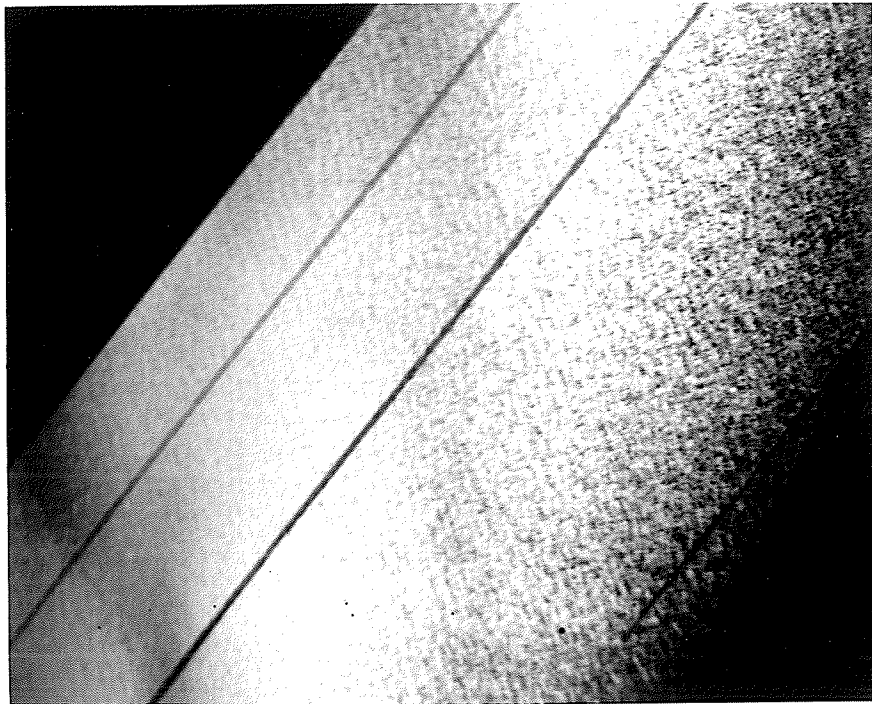


Figure 29

Figure 30: SADP of Figure 29.

Interpretation of Figure 30.



Figure 30

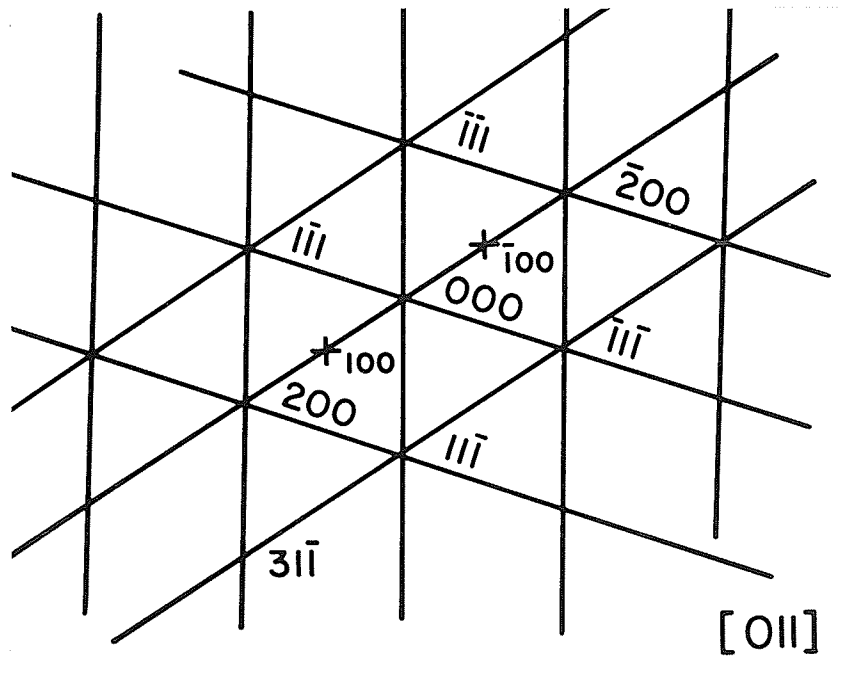


Figure 31: SADP of the Co-25% Cr-4% Ti alloy aged at 1073K for 500 hours.

Interpretation of Figure 31.



Figure 31

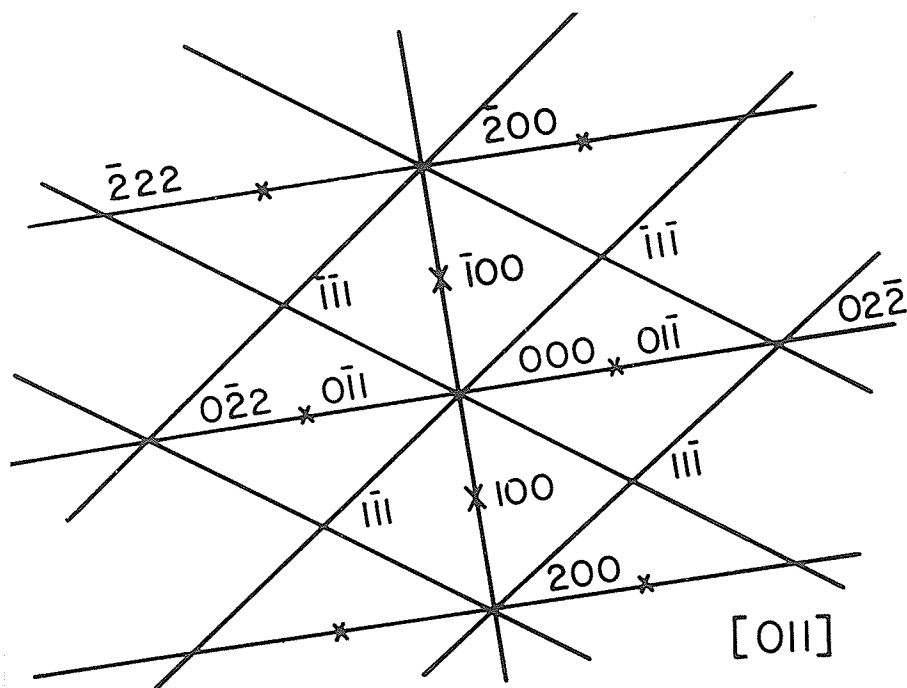


Figure 32: Dark-field from (100) superlattice reflection of Figure 31. (37000 x).

Figure 33: Bright-field micrograph of the Co-25% Cr-4% Ti alloy aged at 1073K for 1000 hours. (20700 x).

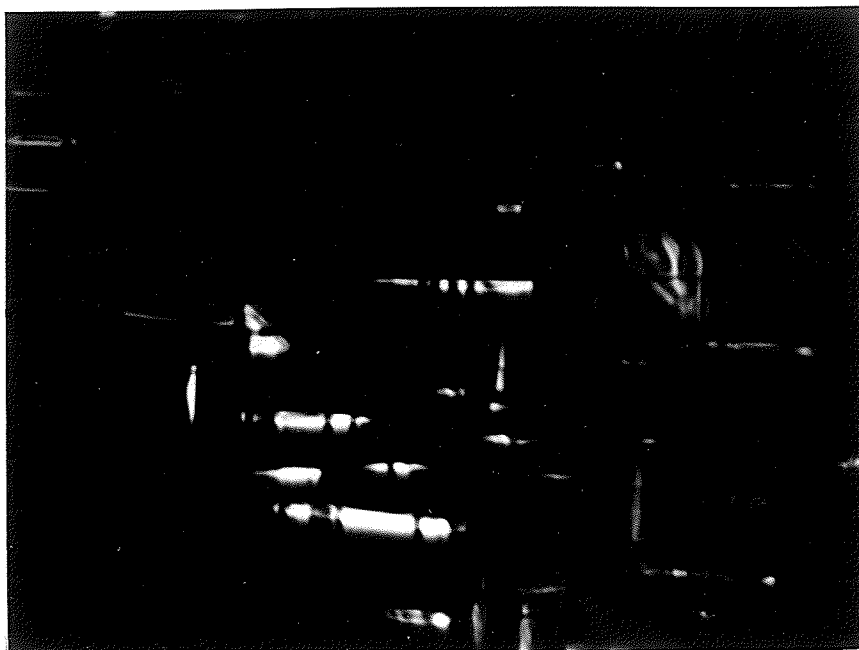


Figure 32

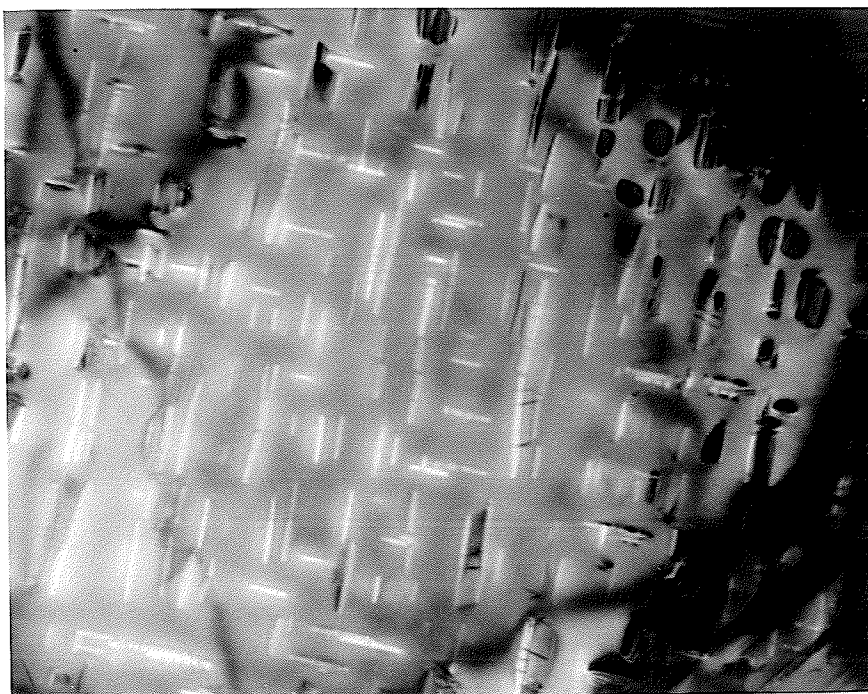


Figure 33

Figure 34: SADP of Figure 33.

Interpretation of Figure 34.

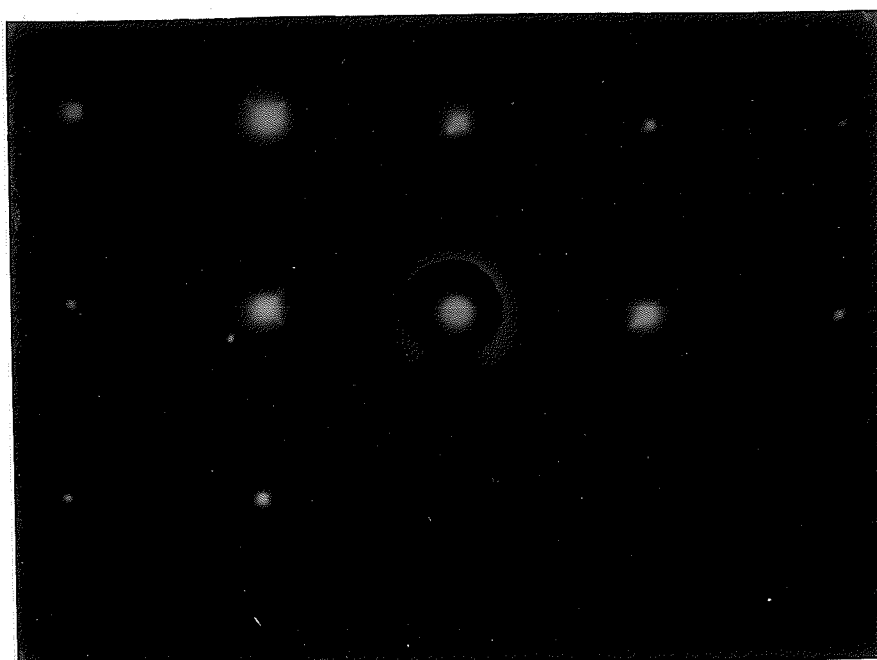
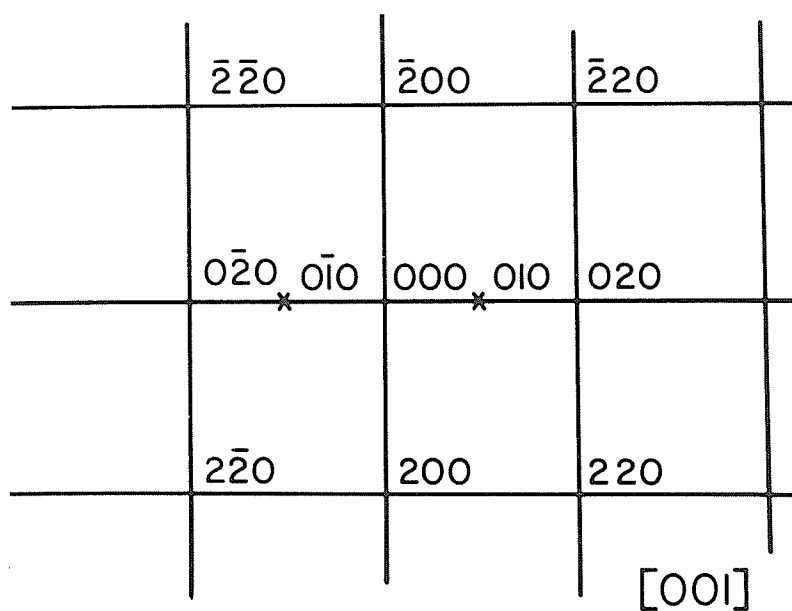


Figure 34



4.1.4 Coarsening kinetics of the Co₃Ti precipitates

In addition to the mechanical properties and structural studies of the solution treated and aged specimens by means of optical and electron microscopy techniques, the growth kinetics of the Co₃Ti precipitates were also studied. This section presents the results obtained by application of the LSW theory to the growth kinetics of the cubic γ' precipitates.

4.1.4.1 Growth kinetics

As stated earlier, according to the LSW theory the growth of precipitate particles by volume diffusion can be expressed as:

$$\bar{r}^3 - \bar{r}_0^3 = \frac{8 D \sigma C_{\alpha} V_m^2 t}{9RT}$$

which can also be written as:

$$\bar{r}^3 - \bar{r}_0^3 = k t$$

where $k = \left(\frac{8 D \sigma C_{\alpha} V_m^2}{9RT} \right)$ is the rate constant.

In the present investigation, since the particles are cuboid in shape, r term is replaced by $\frac{\bar{a}}{2}$ ⁽³⁹⁾. The applicability of the LSW theory can be studied by plotting $\frac{\bar{a}}{2}$ vs log time (Figure 35). The slopes of the straight lines in Figure 35 are .336, .334 and .312 respectively for ageing temperatures of 973K, 1023K and 1073K. These values suggest that, within the limits of experimental inaccuracies, the coarsening of the γ' precipitates obeys the predictions of diffusion controlled growth and the LSW

Figure 35: Log-log plot of the half the mean particle edge length against ageing time at different ageing temperatures.

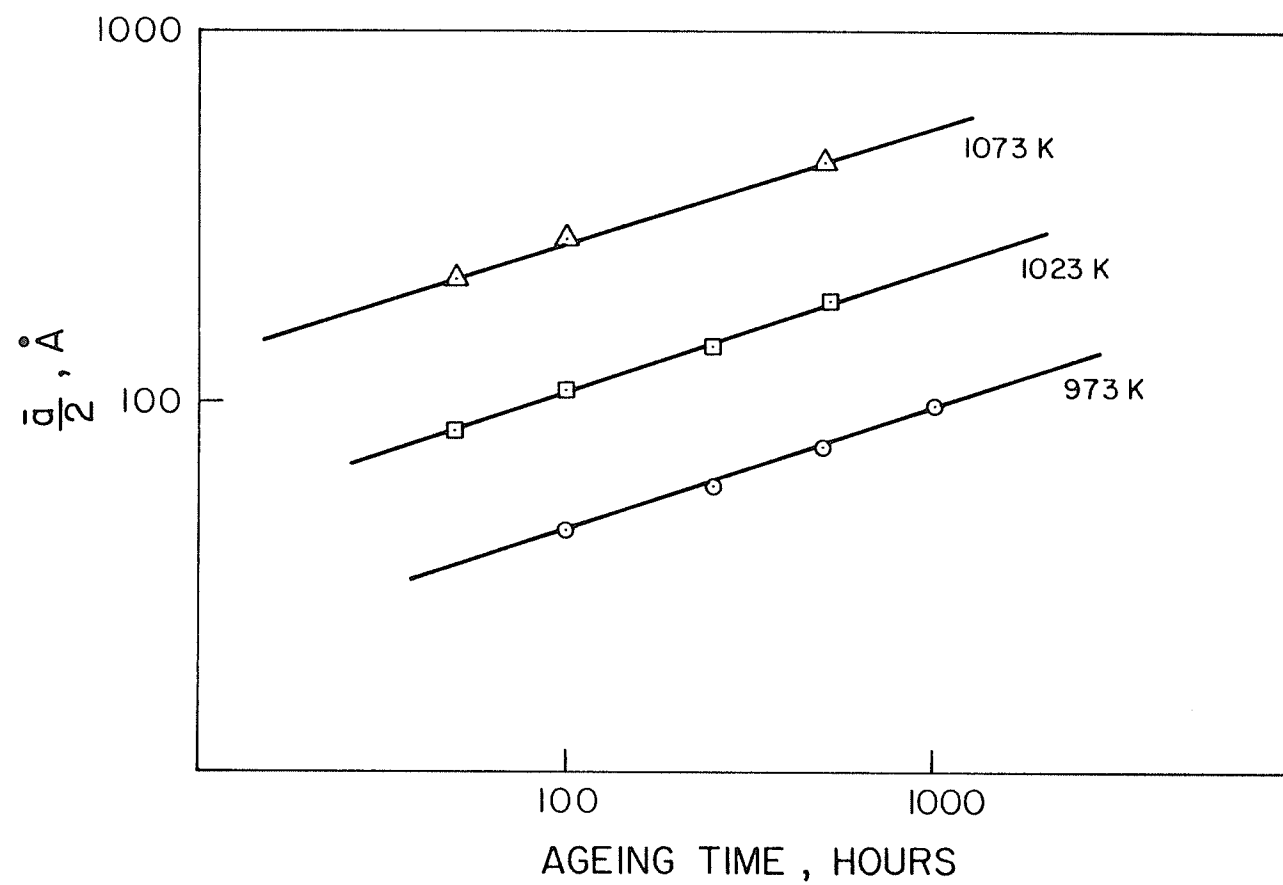


Figure 35

theory is applicable.

4.1.4.2 Activation energy measurements

The diffusion coefficient D in the expression for the rate constant k can be expressed as:

$$D = D_0 \exp \left(\frac{-Q}{RT} \right) .$$

Therefore,

$$k = \frac{64 \sigma C_{\alpha} V_m^2 D_0 \exp \left(\frac{-Q}{RT} \right)}{9RT} .$$

A plot of $(\bar{a})^3$ vs ageing time for the three temperatures can be used to compute the rate constants k , which are equal to the slopes of the straight lines in Figure 36. The C_{α} term in the above expression for the rate constant k can be computed by means of the weight fraction of the electrochemically extracted γ' precipitates. The value obtained for the weight fraction of the undissolved particles in the solution treated specimens is subtracted from the weight fraction of the aged specimens. The weight fraction of the extracted Co_3Ti precipitates can be seen in Figure 37. It should be noted that the calculation of concentration of the solute atoms from weight fraction is based on the assumption that the exact chemical composition of the precipitates is Co_3Ti .

As can be seen in the equation for the rate constant k , the

Figure 36: Variation of the cube of the average particle edge length with time at various ageing temperatures.

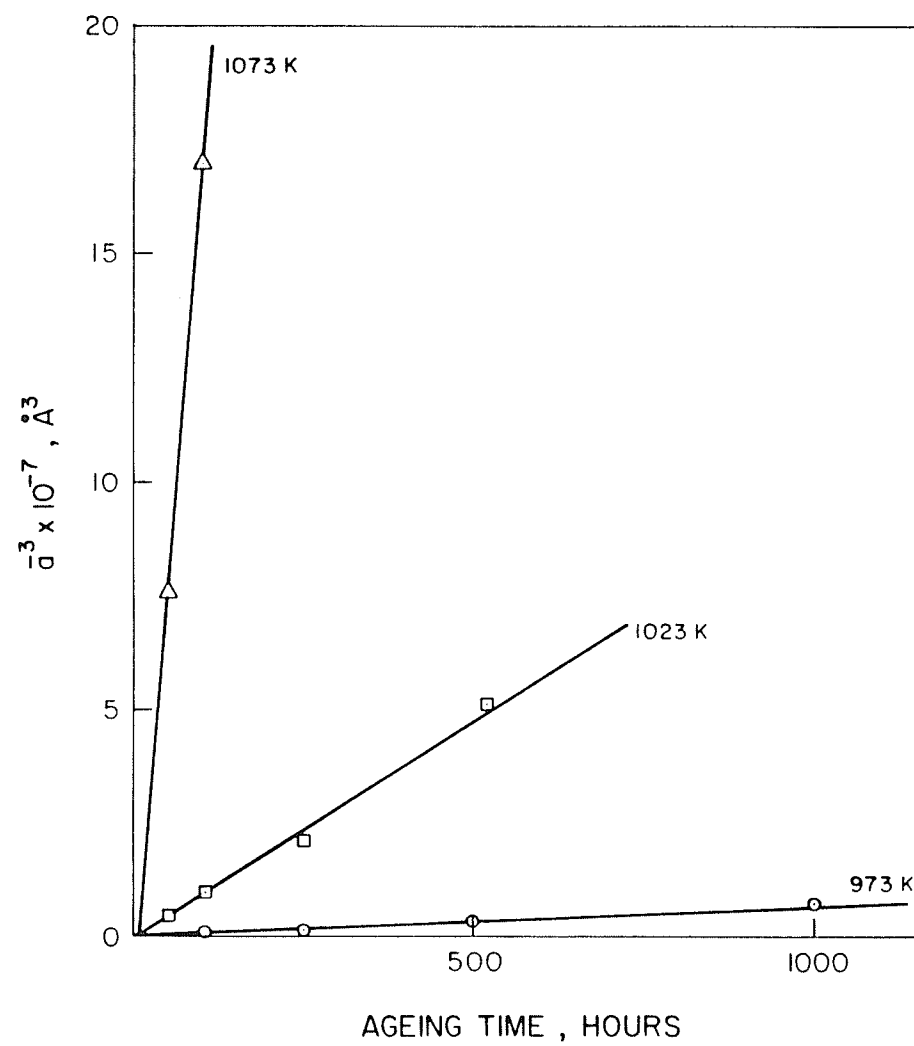


Figure 36

Figure 37: The weight fraction of γ' at various ageing temperatures.

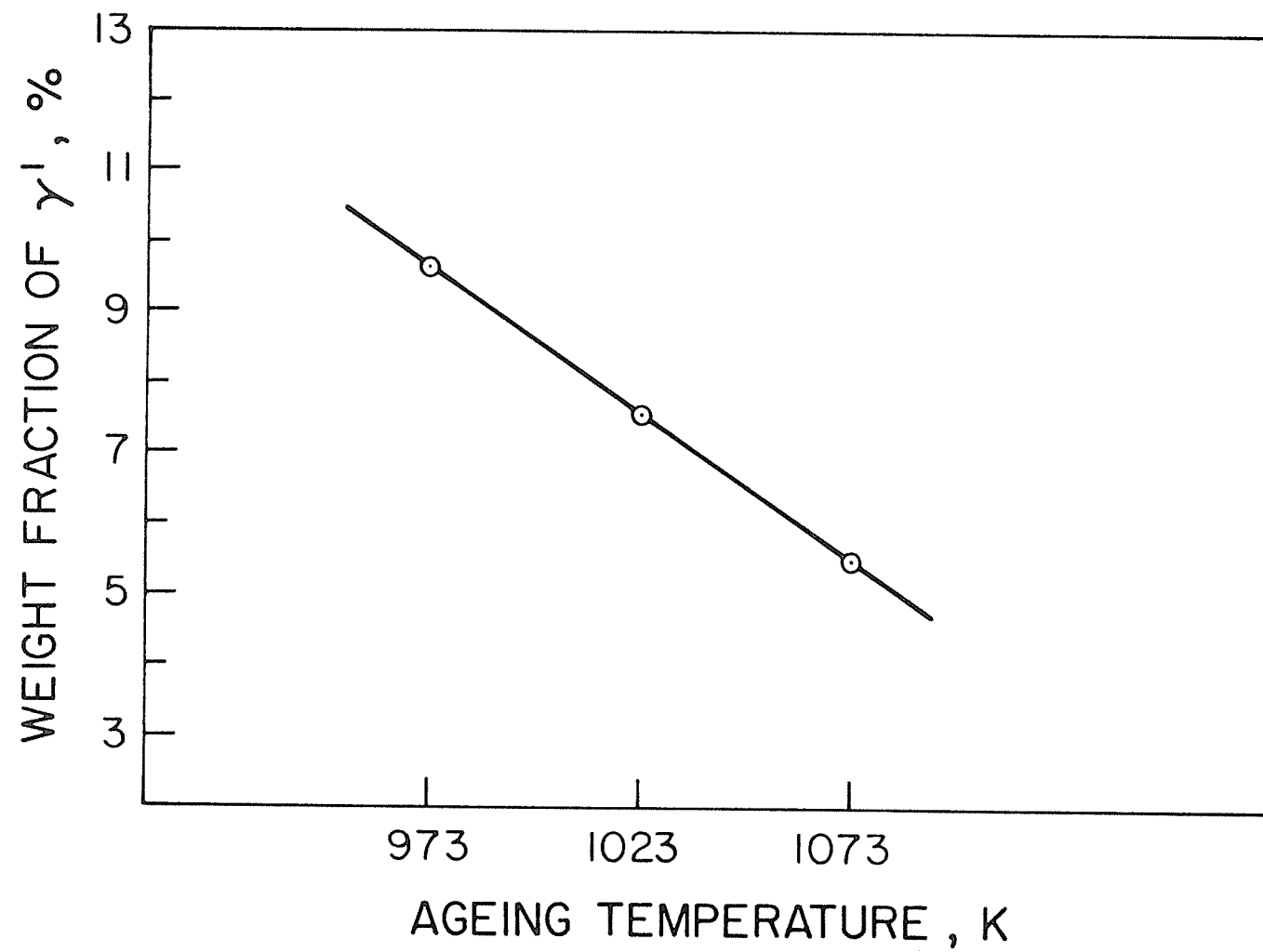


Figure 37

Figure 38: Arrhenius plot for the determination of activation energy for coarsening of γ' .

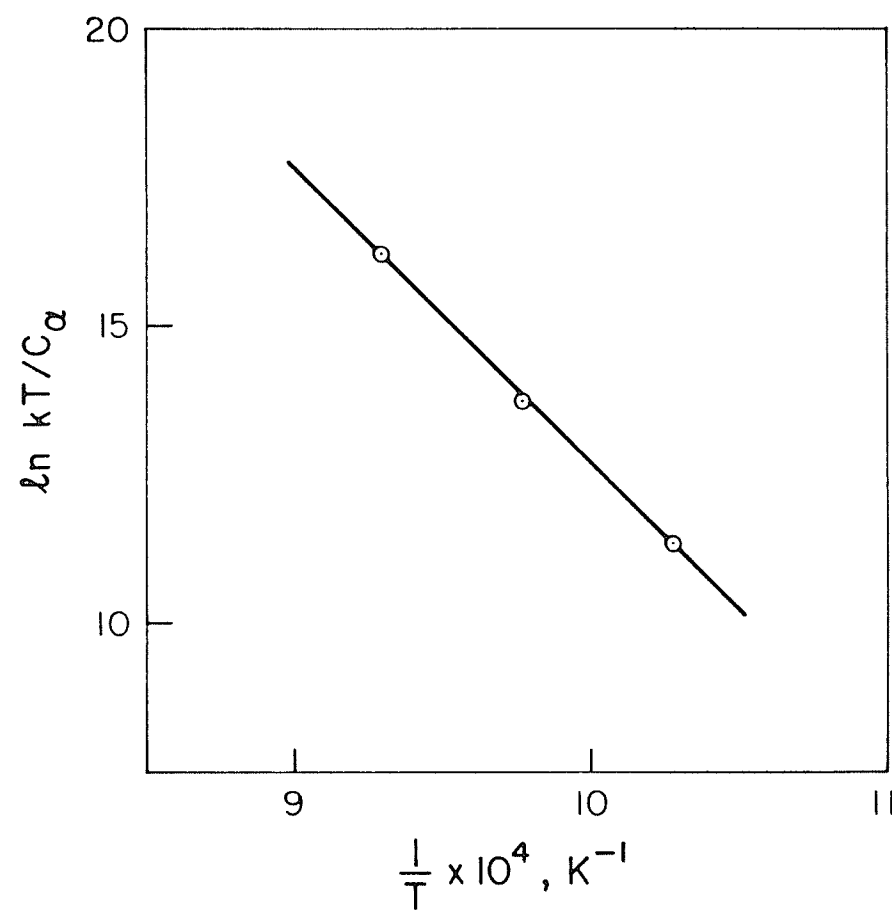


Figure 38

temperature dependent terms are C_α , T and k . Knowing the values of these terms, it is possible to plot the Arrhenius plot $\ln \frac{kT}{C_\alpha}$ vs $\frac{1}{T}$ (Figure 38). The slope of the Arrhenius plot is equal to $-Q/R$, where Q is the activation energy for coarsening of γ' precipitates in the Co-Cr-Ti matrix. The activation energy Q is calculated to be 425.1 kJ/mole. Table 1 shows the data used in the calculations.

Ageing Temperature	$k(\text{\AA}^3/\text{s})$	C_α	$kT/C_\alpha(\text{\AA}^3/\text{s})$
973K	2.12	2.5%	8.25×10^4
1023K	27.48	3.03%	9.27×10^5
1073K	370.69	3.5%	11.36×10^6

Table 1

4.1.4.3 Particle size distributions

The particle size distributions at 973K, 1023K, 1073K are normalized in order to be able to compare them with the theoretical particle size distribution.

It was already mentioned in Chapter 2 that Wagner⁽¹⁴⁾ has expressed the particle size distribution as a function of particle size and ageing time. Ardell and Nicholson⁽³⁹⁾ have normalized the distribution function $\rho(r,t)$ by defining a new function $g'(r,t)$ where

Figure 39: Histograms showing the γ' particle size distribution. The histograms are plotted as $\frac{9}{4} \bar{a} g(a, t)$ for comparison with the theoretical distribution function $\rho^2 h(\rho)$.

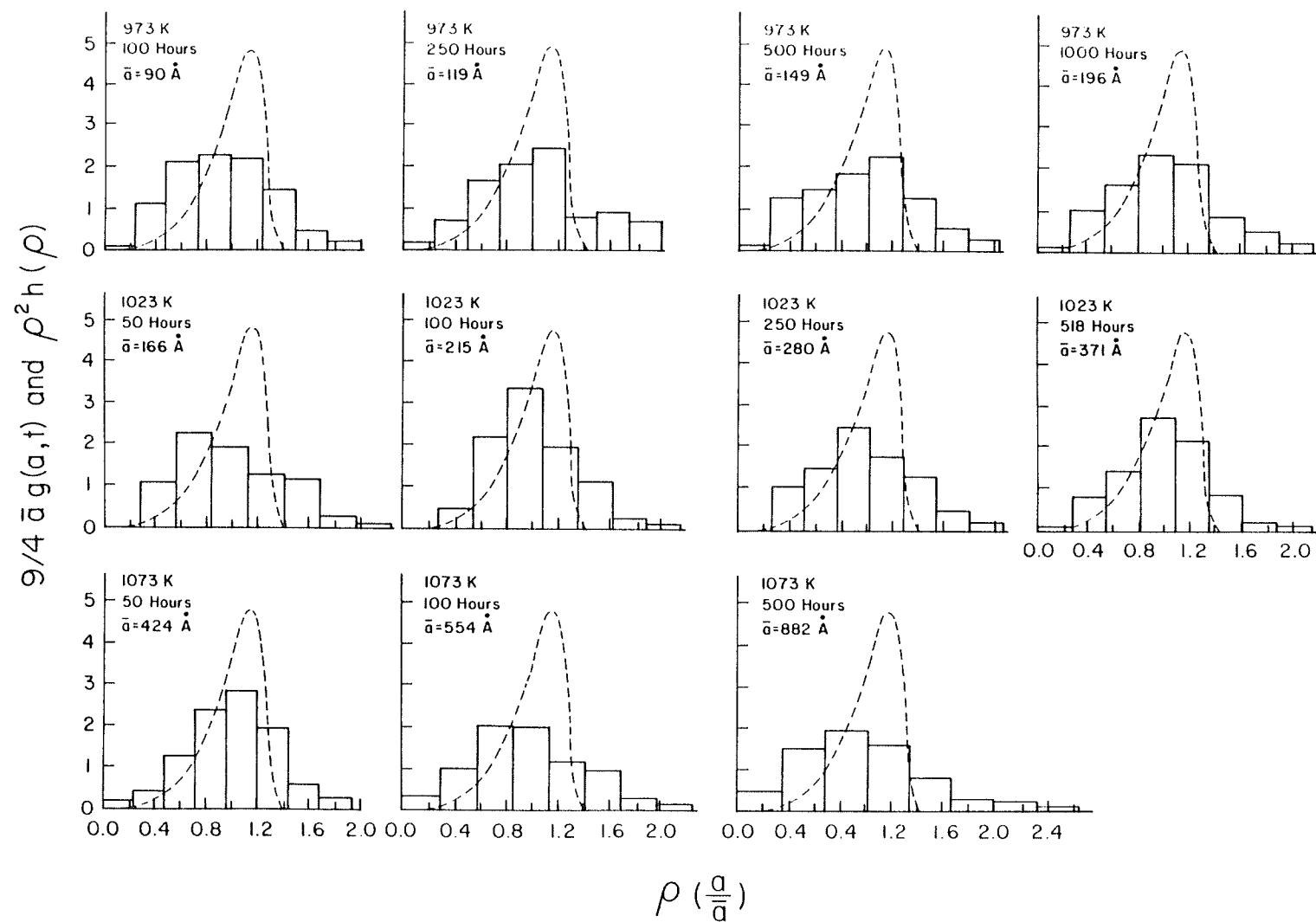


Figure 39

$$g'(r,t) = \frac{\rho^2 h(\rho)}{\left(\frac{9}{4}\right) \bar{r}} \quad .$$

And the normalized distribution function for the present investigation becomes

$$g(a,t) = \frac{\rho^2 h(\rho)}{\left(\frac{9}{4}\right) \bar{a}} \quad .$$

The normalized particle size distributions are shown in Figure 39. It is observed that the experimental particle size distributions are broader than the theoretical distribution. The cut-offs occur at ρ values of approximately 2, which is larger than 1.5. The maximum values of the normalized distribution functions are much lower than the values of the theoretical function, the highest value does not exceed 3.5. These maxima do not occur at the theoretically predicted values of $\rho = 1.135$.

4.2 Co-Cr-Mo Alloys

Because of the similarities in the hardness behaviour and ageing characteristics of the Co-25% Cr-5% Mo and Co-25% Cr-7% Mo alloys, in this section the experimental results concerning these two alloys are presented jointly.

4.2.1 Mechanical properties

The Vickers hardness values of the two alloys can be seen in Figures 40 and 41. The maximum increase in peak hardness for the 5% Mo alloy is 50 VPH which at 1073K occurs after ageing for 25 hours. The corresponding increase for the 7% Mo alloy at the same temperature is 75 VPH and occurs after ageing for 50 hours. It should also be noticed that 2% increase in Mo content does not lead to any increased strengthening of the solution treated specimen. A deviation from the classical ageing temperature-hardness relation is observed. No improvement in the peak hardness value of the specimens aged at 973K occurs with respect to those aged at 1073K. Although the peak hardness is reached after longer ageing times for lower temperatures, its value is not higher. In these two alloys, the precipitates become overaged and the hardness starts to decrease after 50 hours at 1073K and 250-500 hours at 973K.

Since both the alloys exhibited similar hardness characteristics and the increase in strength for the 7% Mo alloy was superior to that of 5% Mo alloy after ageing, the tensile tests were conducted only for the Co-25% Cr-7% Mo alloy. The plots of the 0.2% offset yield strength, ultimate strength and total elongation as a function of ageing time at 973K and 1073K can be seen in Figure 42. The increase in yield strength of the Co-25% Cr-7% Mo alloy varies from 50% to 80% depending on the ageing time and temperature. Whereas sample aged to peak at 1073K shows an improvement of 83.3% in yield strength with respect to solution treated ones, the specimen aged to peak at 973K has an increase of only 69.7%. A similar trend was also observed by hardness measurements. It is also

Figure 40: Variation in hardness of the Co-25% Cr-5% Mo alloy with ageing time at the ageing temperatures of 973K and 1073K.

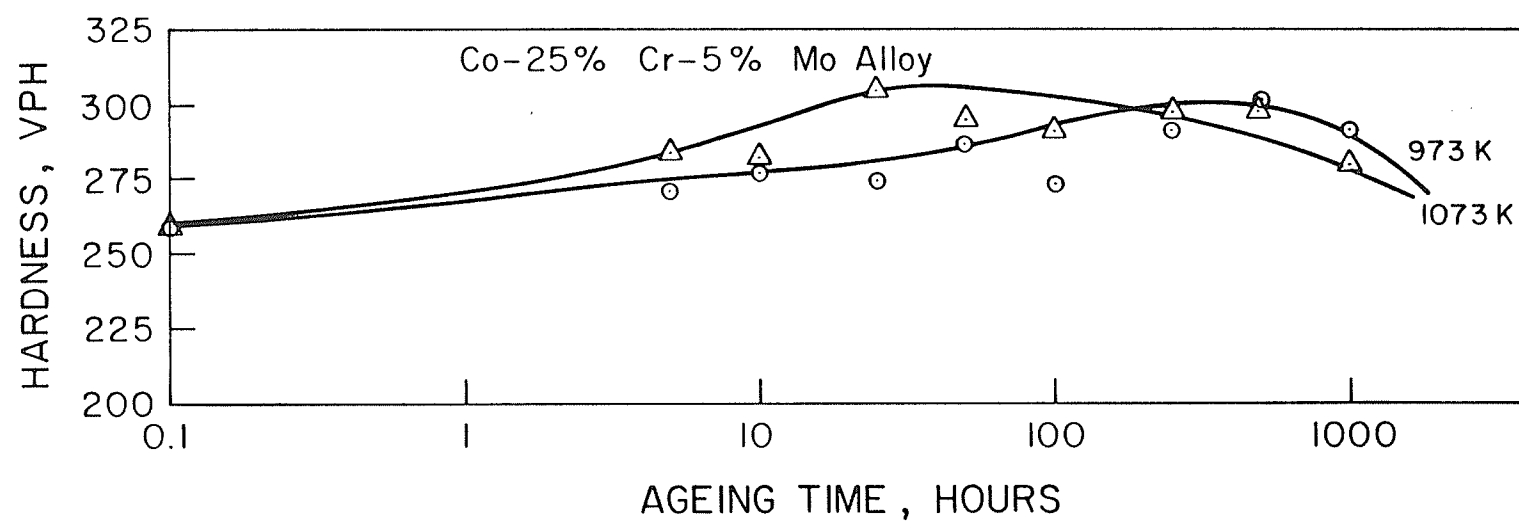


Figure 40

Figure 41: Variation in hardness of the Co-25% Cr-7% Mo alloy with ageing time at the ageing temperatures of 973K and 1073K.

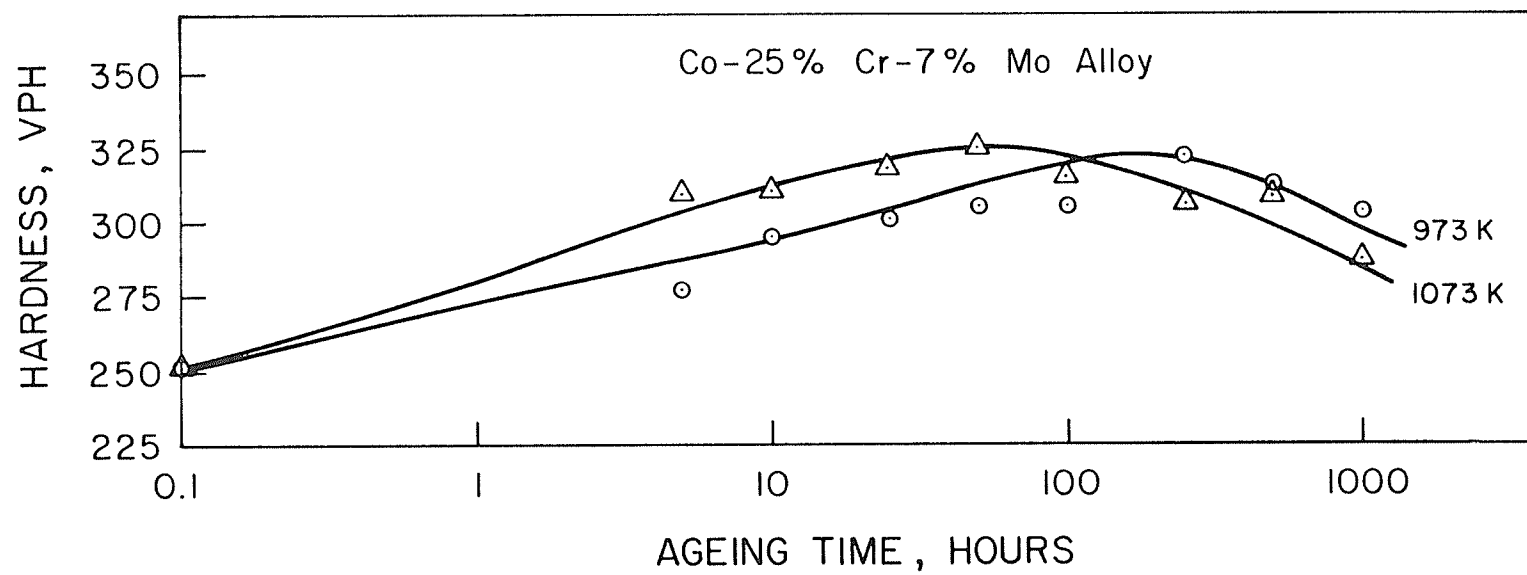


Figure 41

Figure 42: Room temperature tensile properties of the Co-25% Cr alloy against ageing time for different ageing tempe

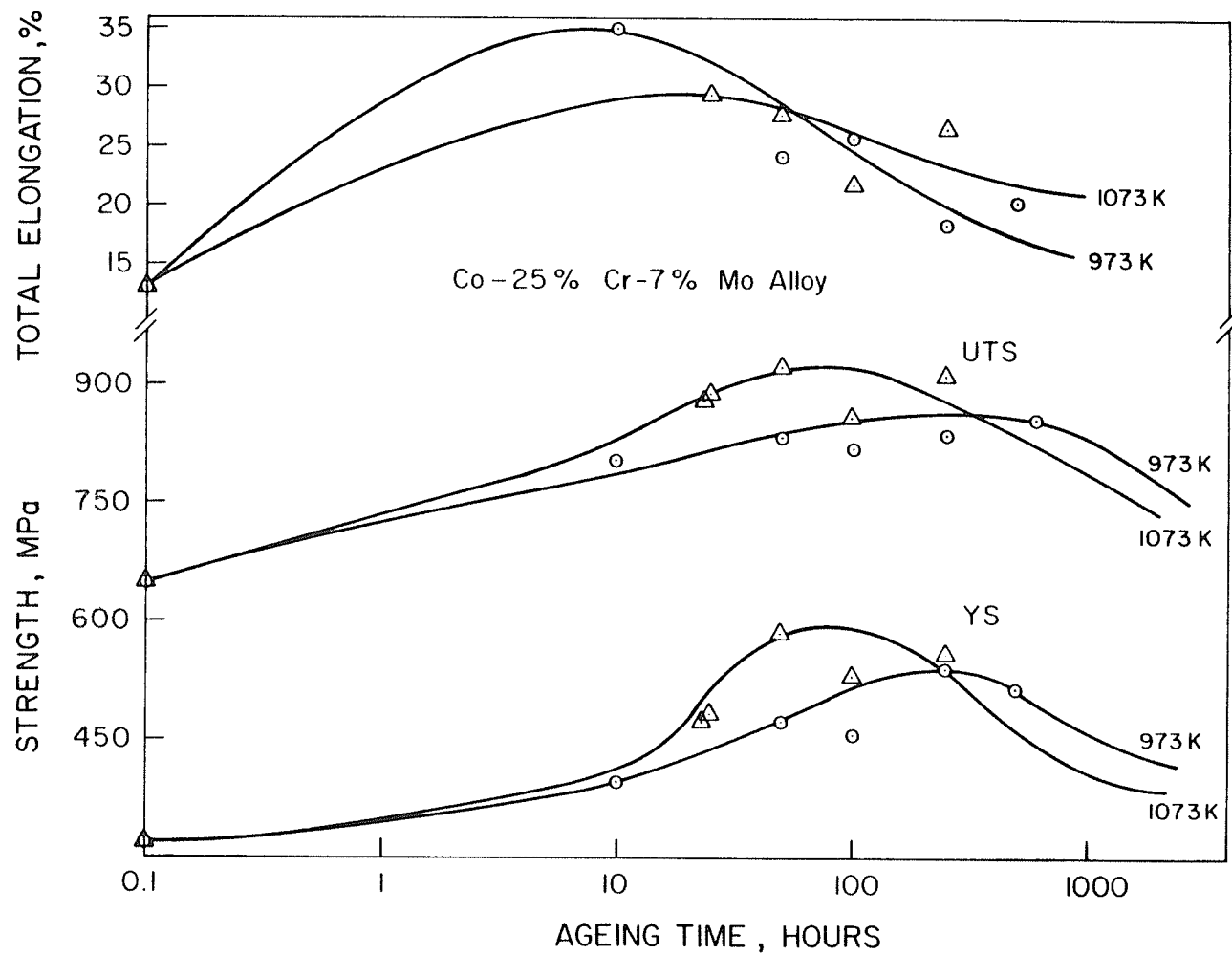


Figure 42

observed that the elongation of the aged specimens is higher than that of the solution treated ones.

4.2.2 Optical metallography

The optical microstructures of the Co-25% Cr-5% Mo and Co-25%-7% Mo alloys present similar characteristics (Figures 43-50). In the solution treated specimens (Figures 43, 47), the matrix shows polygonal grains with some twins or hexagonal phase ϵ . The specimens aged at 973K show large amounts of twins or transformation bands (Figures 44, 48, 49). Qualitatively the density of transformation bands seem to be less in specimens aged at 1073K as compared to those aged at 973K. On specimens aged at 1073K, optical micrographs also show presence of "islands" at the grain boundaries which were not seen in specimens aged at 973K (Figures 45, 46, 50).

4.2.3 Electron microscopy

Electron microscopic studies were conducted for both the alloys. While the carbon extraction replica technique was used to identify the second phase particles in the two alloys, the thin foil examinations were performed only for the Co-25% Cr-7% Mo alloy.

4.2.3.1 Carbon extraction replicas

These precipitates were identified by electron ring diffraction patterns, two of which are shown in figures 53 and 57, by the same method used for Co-Cr-Ti alloys. Two types of precipitates were

Figure 43: Optical microstructure of the Co-25% Cr-5% Mo alloy solution treated at 1473K. (110 x).

Figure 44: Optical microstructure of the Co-25% Cr-5% Mo alloy aged at 973K for 500 hours. (200 x).



Figure 43

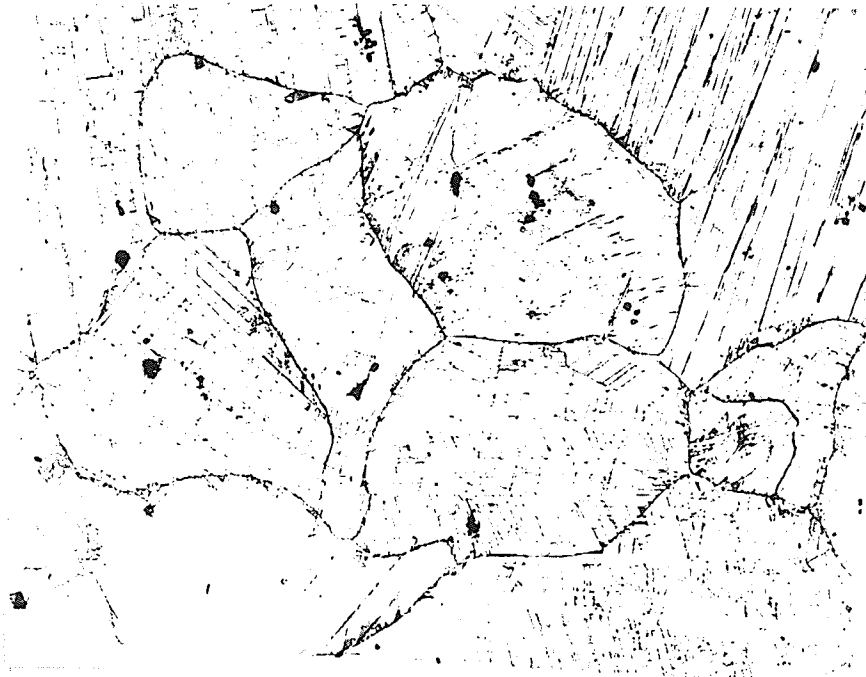


Figure 44

Figure 45: Optical microstructure of the Co-25% Cr-5% Mo alloy aged at 1073K for 50 hours. (180 x).

Figure 46: Optical microstructure of the Co-25% Cr-5% Mo alloy aged at 1073K for 500 hours. (300 x).

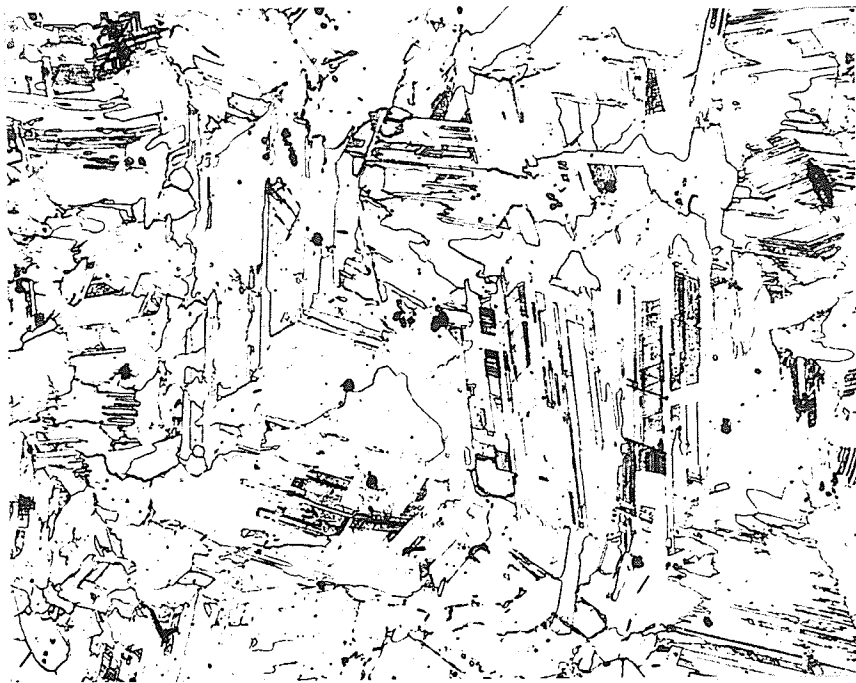


Figure 45

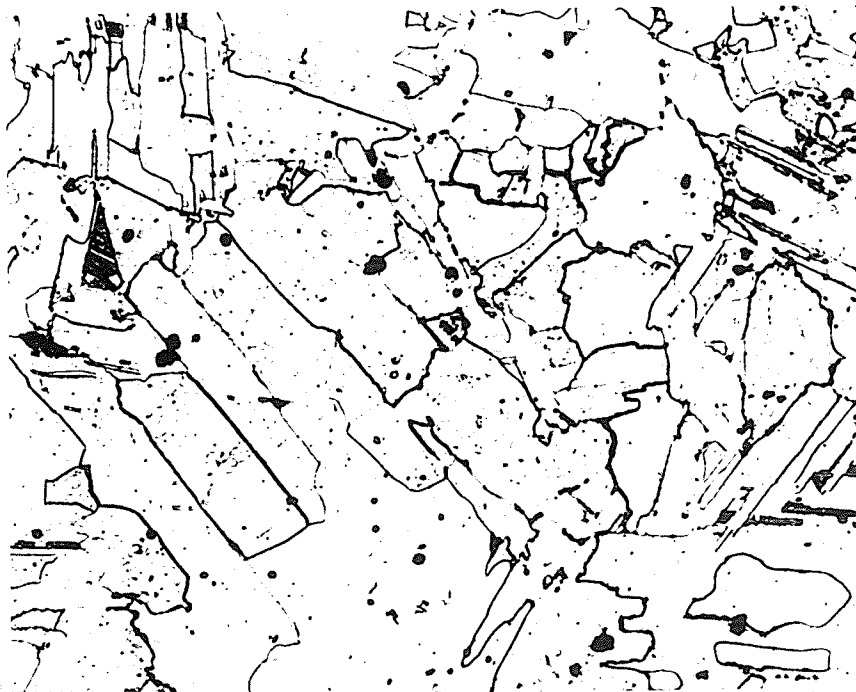


Figure 46

Figure 47: Optical microstructure of the Co-25% Cr-7% Mo alloy solution treated at 1473K. (130 x).

Figure 48: Optical microstructure of the Co-25% Cr-7% Mo alloy aged at 973K for 50 hours. (300 x).

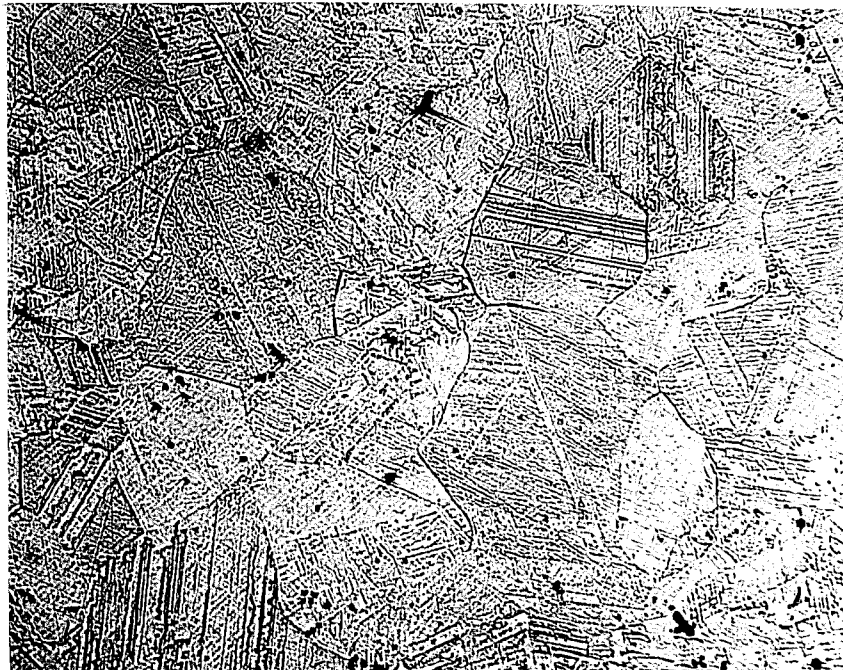


Figure 47



Figure 48

Figure 49: Optical microstructure of the Co-25% Cr-7% Mo alloy aged at 973K for 100 hours. (260 x).

Figure 50: Optical microstructure of the Co-25% Cr-7% Mo alloy aged at 1073K for 100 hours. (280 x).

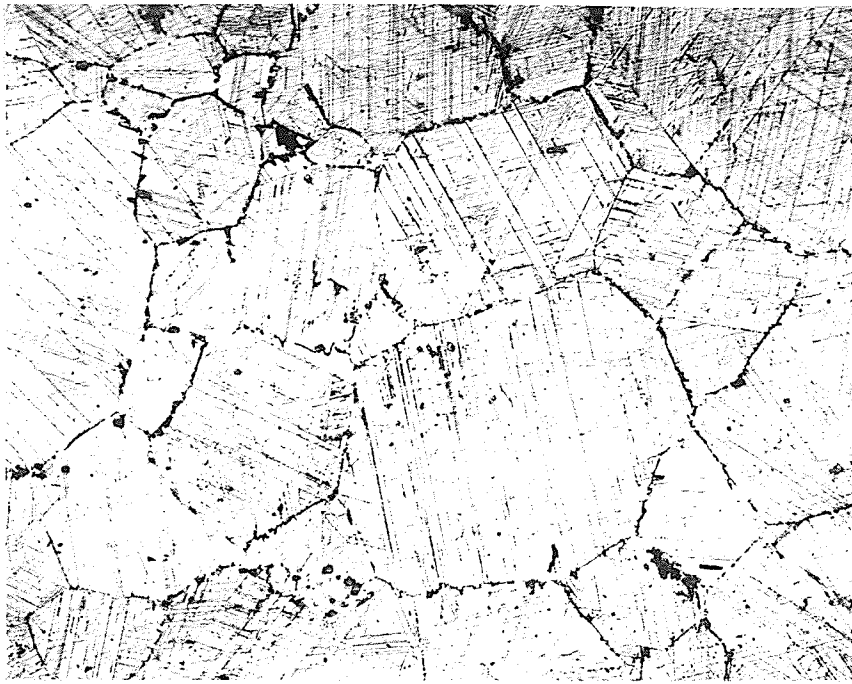


Figure 49

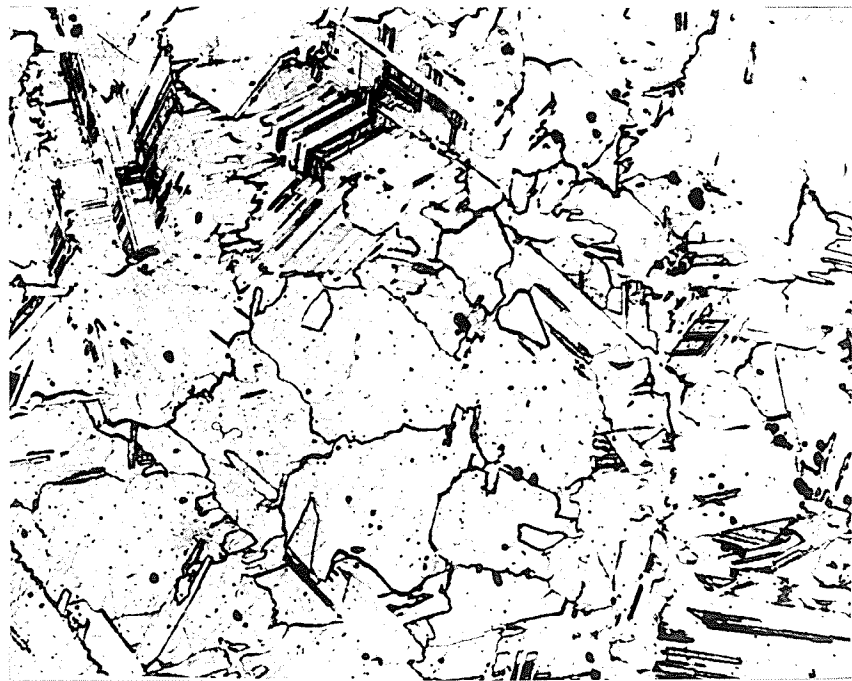


Figure 50

identified. They were, a hcp Co_3Mo phase with $a = 5.12$ and $c = 4.11$ Å(40), and a rhombohedral Co_7Mo_6 phase with $a = 8.980$ Å and $\alpha = 30^\circ$ 48'(40). As shown in Figures 51, 52, 54, 55, 56, the precipitates are observed to be plate-shaped and occasionally they appear in a cellular configuration, which seems to form by the close alignment of the plate-like precipitates. The shape of the precipitates for both the alloys is noticed to be the same, while their size, qualitatively, seems to be larger for the Co-25% Cr-7% Mo alloy.

4.2.3.2 Thin foil electron microscopy

The electron microscopic studies of the solution treated thin foils of the Co-25% Cr-7% Mo alloy revealed the presence of a high density of stacking faults and transformation bands (Figures 58-61), as was also observed by optical micrographs. In the matrix of the aged specimens, however, stacking faults were not observed but hexagonal phase was detected (Figures 64, 69, 71). In thin foils of specimens aged at 973K and 1073K the precipitates, already identified to be a combination of hexagonal Co_3Mo and rhombohedral Co_7Mo_6 phases by carbon extraction replica, were also observed. No precipitates were observed in the thin foils aged up to 10 hours. The precipitation occurred within the grains and also at the grain boundaries. In some grains no precipitates were observed, but still hcp phase was detected (Figure 71). In some cases dislocations were observed at the precipitate-matrix interfaces (Figures 63, 65, 68, 70).

Figure 51: Carbon extraction replica of the Co-25% Cr-5% Mo alloy aged at 973K for 50 hours. (11800 x).

Figure 52: Carbon extraction replica of the Co-25% Cr-5% Mo alloy aged at 973K for 500 hours. (14000 x).

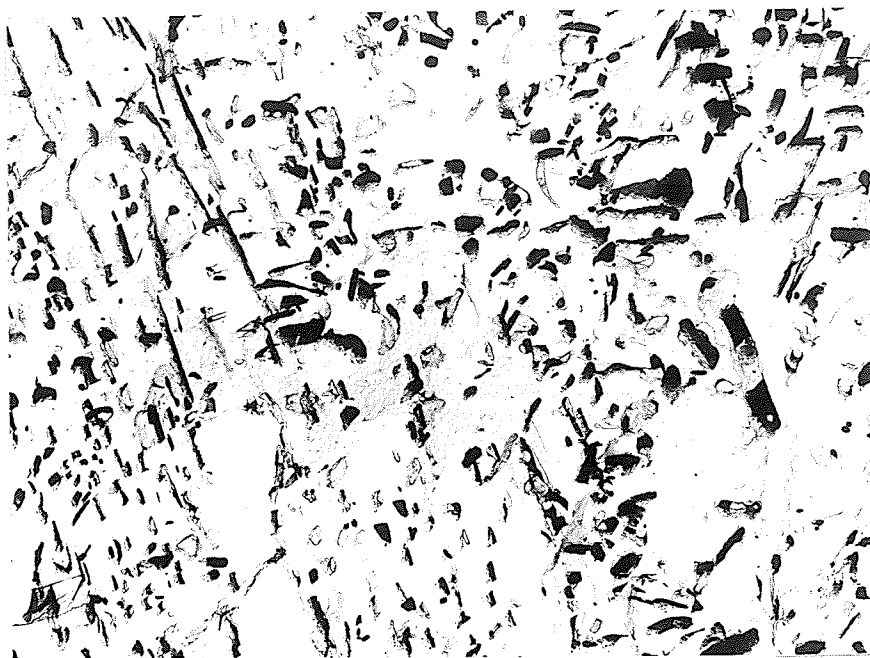


Figure 51

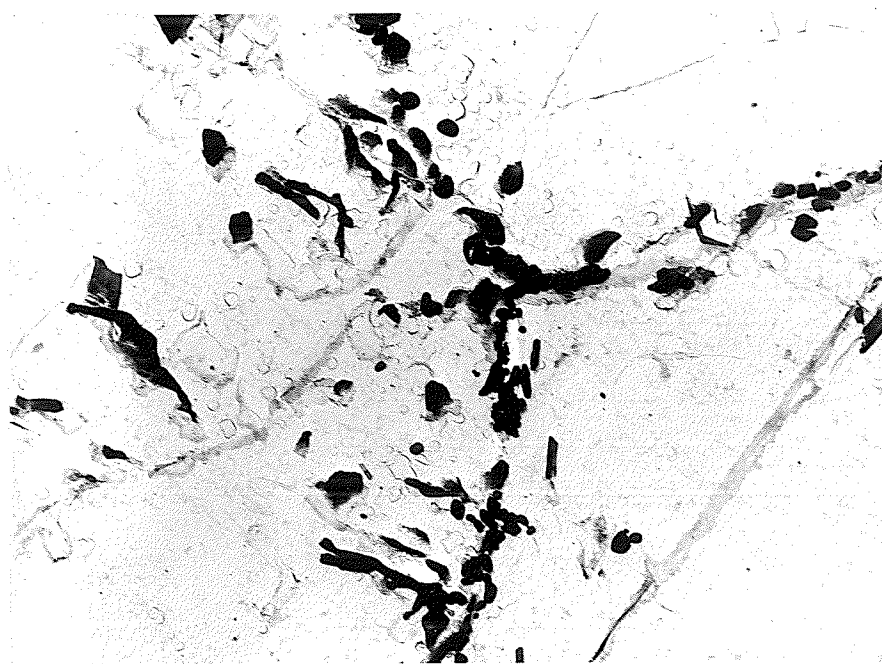


Figure 52

Figure 53: Ring pattern for carbon extraction replica of Co-25% Cr-5 Mo alloy aged at 973K for 500 hours (Figure 52).

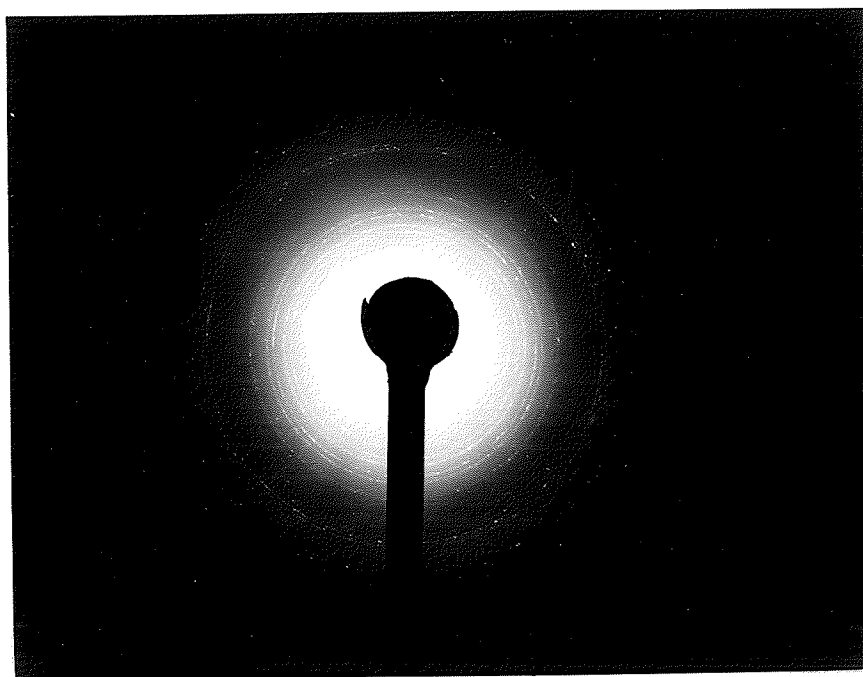


Figure 53

Figure 54: Carbon extraction replica of the Co-25% Cr-7% Mo alloy aged at 973K for 250 hours. (9700 x).

Figure 55: Carbon extraction replica of the Co-25% Cr-7% Mo alloy aged at 973K for 500 hours. (9700 x).



Figure 54

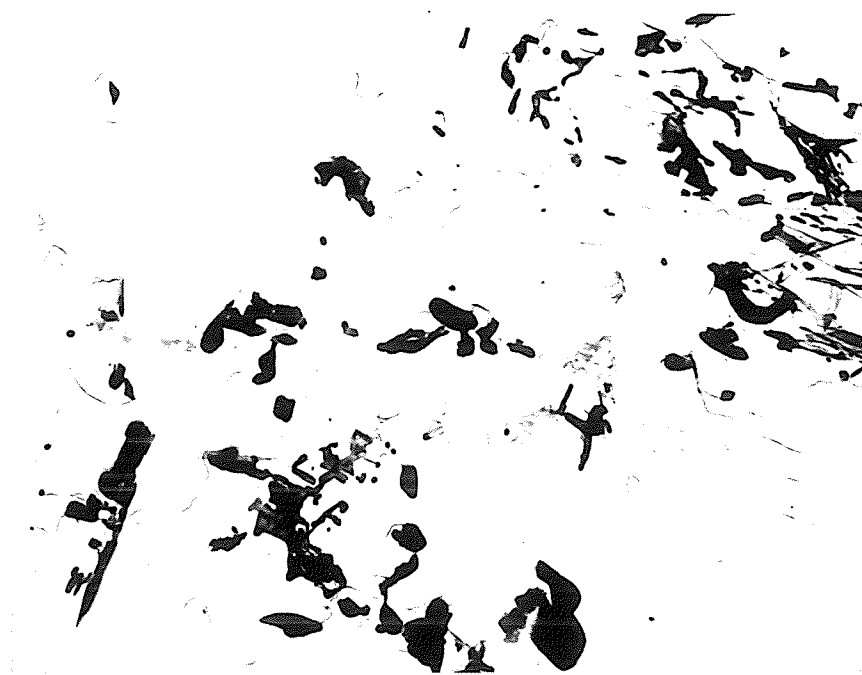


Figure 55

Figure 56: Carbon extraction replica of the Co-25% Cr-7% Mo alloy aged at 1073K for 250 hours. (9700 x).

Figure 57: Ring pattern of the carbon extraction replica of the Co-25% Cr-7% Mo alloy aged at 973K for 250 hours (Figure 54).



Figure 56



Figure 57

Figure 58: Bright-field micrograph of the Co-25% Cr-7% Mo alloy solution treated at 1473K. (20700 x).

Figure 59: Dark-field of Figure 58, showing stacking faults by BF-DF contrast. (20700 x).



Figure 58



Figure 59

Figure 60: Bright-field micrograph of the Co-25% Cr-7% Mo alloy solution treated at 1473K. (37000 x).

Figure 61: Dark-field of Figure 60, showing stacking faults by BF-DF contrast. (37000 x).

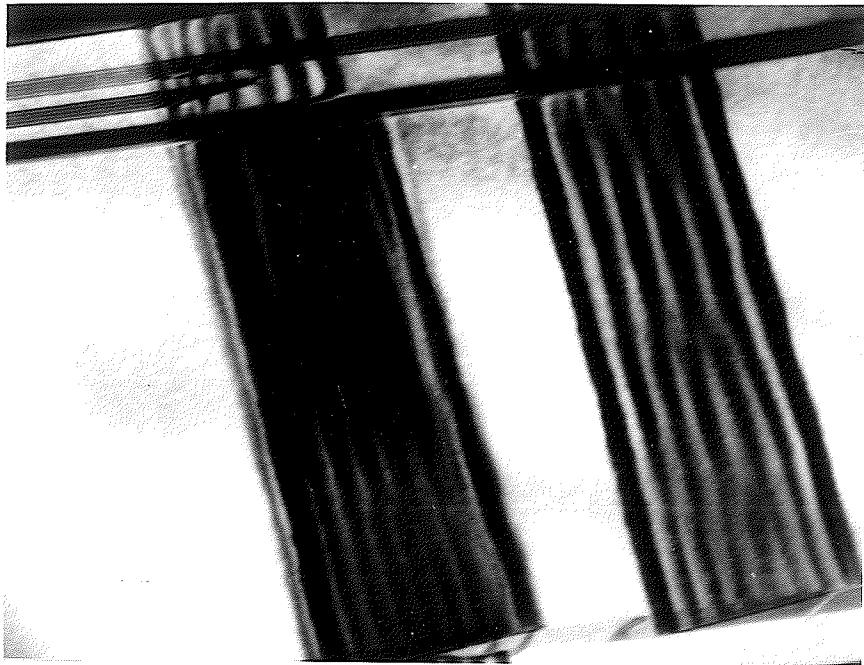


Figure 60

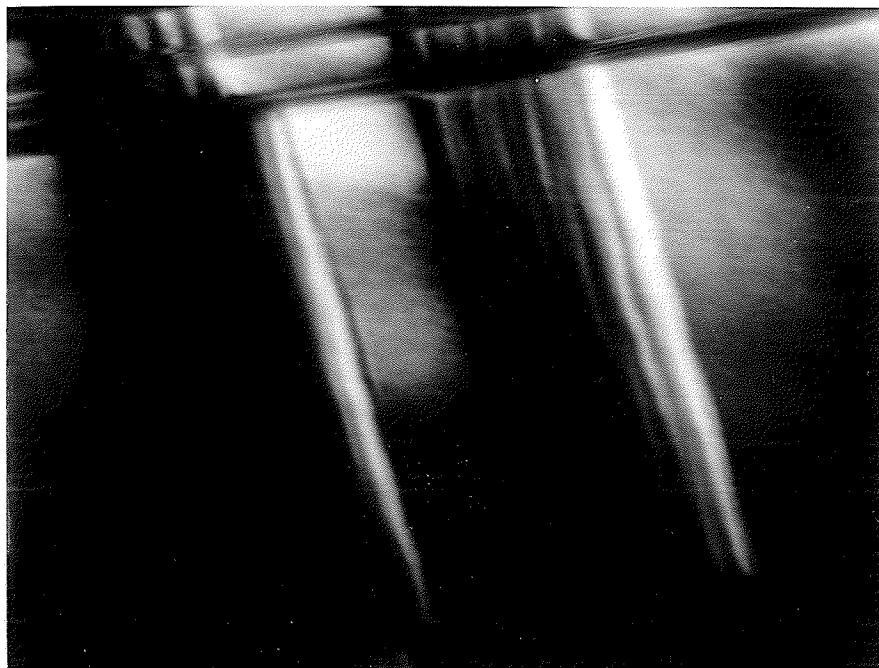


Figure 61

Figure 62: SADP of Figure 60.

Interpretation of Figure 62.

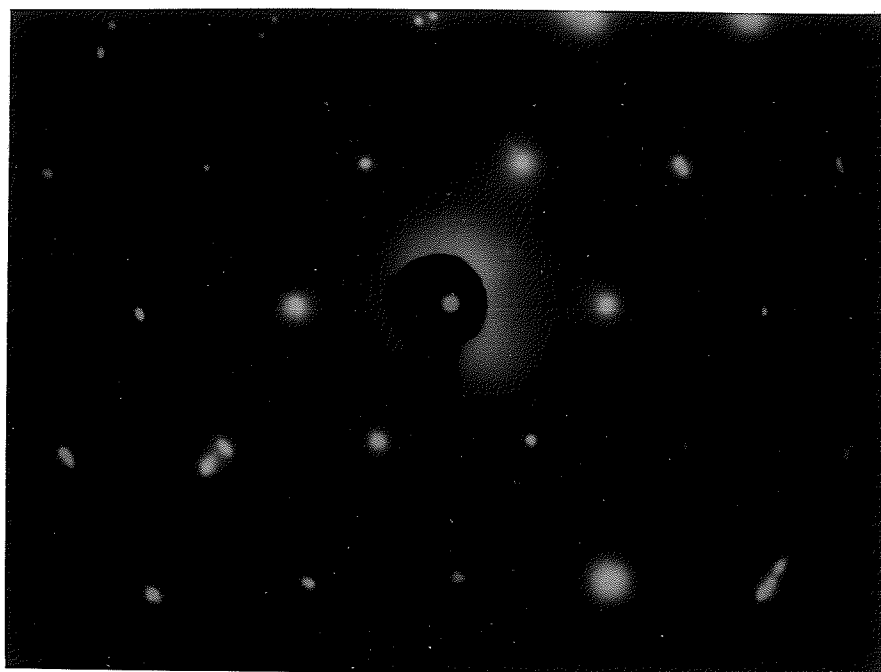


Figure 62

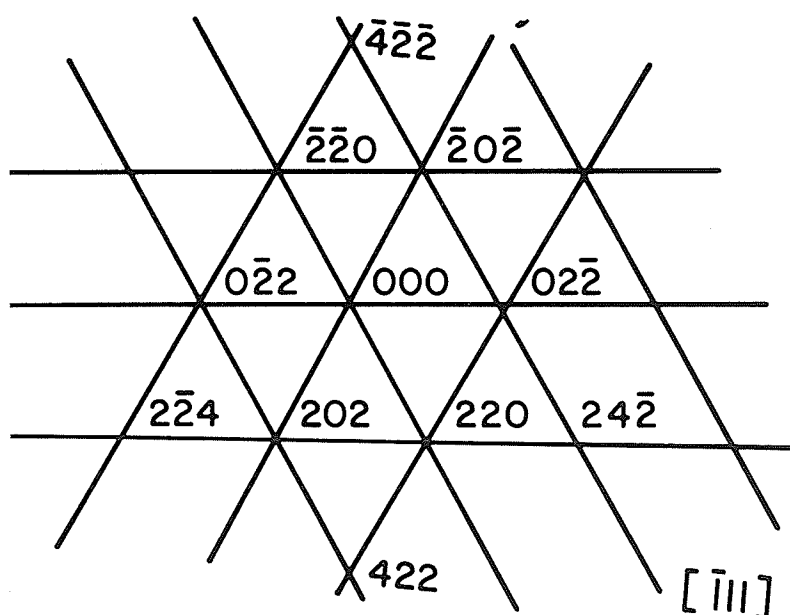


Figure 63: Bright-field micrograph of the Co-25% Cr-7% Mo alloy aged at 973K for 50 hours. (20700 x).

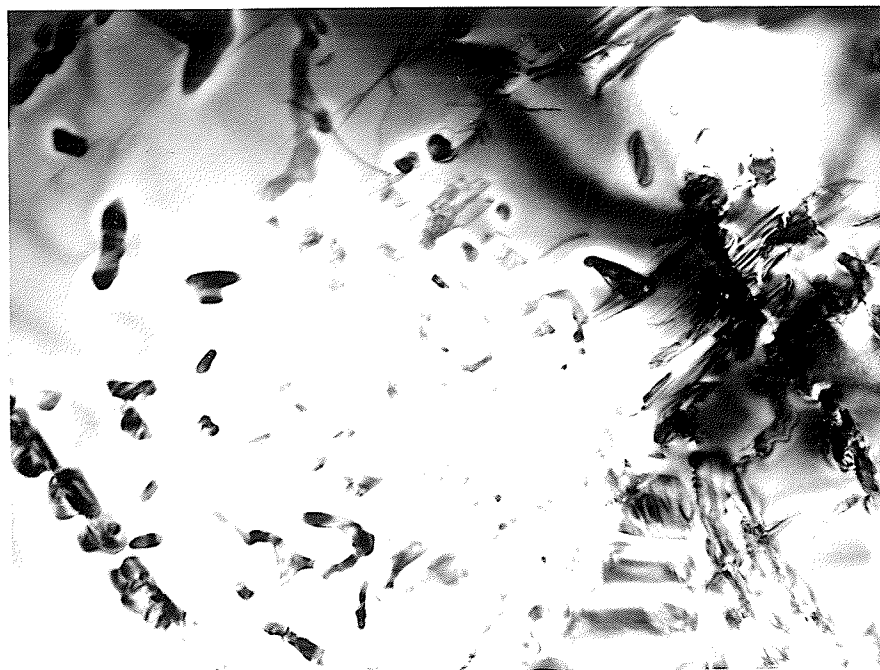


Figure 63

Figure 64: SADP of Figure 63.

Interpretation of the hcp matrix in Figure 64.



Figure 64

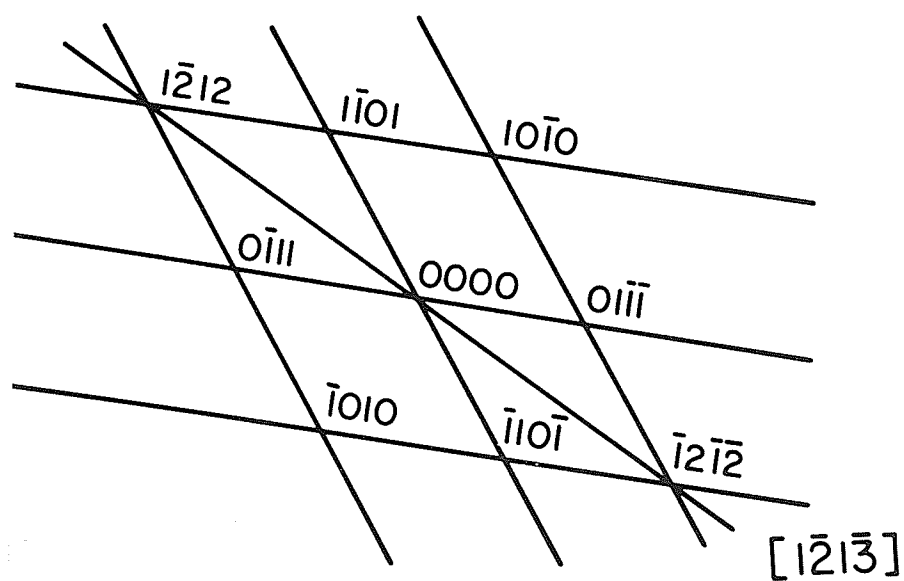


Figure 65: Bright-field of the Co-25% Cr-7% Mo alloy aged at 973K for 300 hours. (16700 x).



Figure 65

Figure 66: Bright-field micrograph of the Co-25% Cr-7% Mo alloy aged at 1073K for 50 hours. (28200 x).

Figure 67: Dark-field of Figure 66. (28200 x).



Figure 66

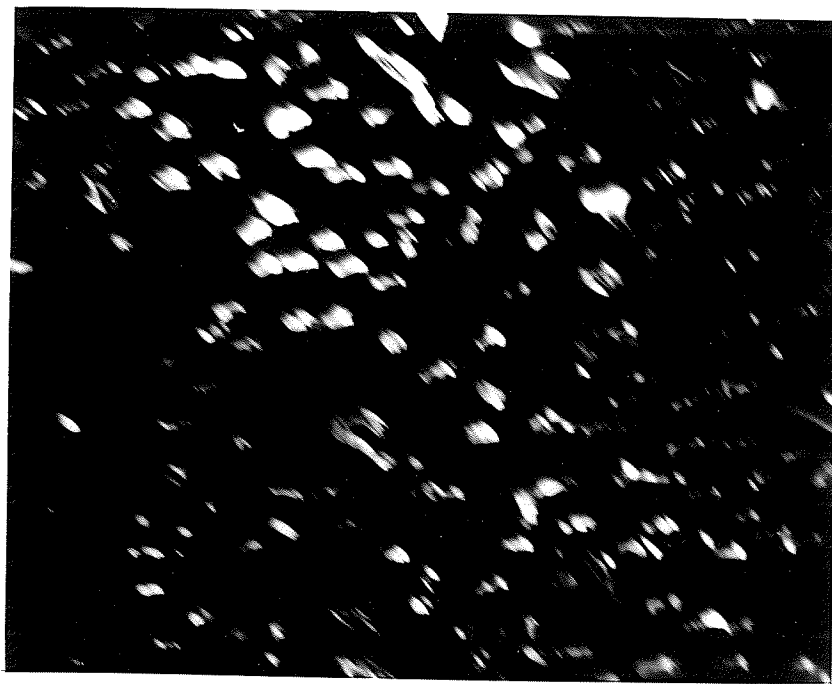


Figure 67

Figure 68: Bright-field micrograph of the Co-25% Cr-7% Mo alloy aged at 1073K for 85 hours. (12600 x).

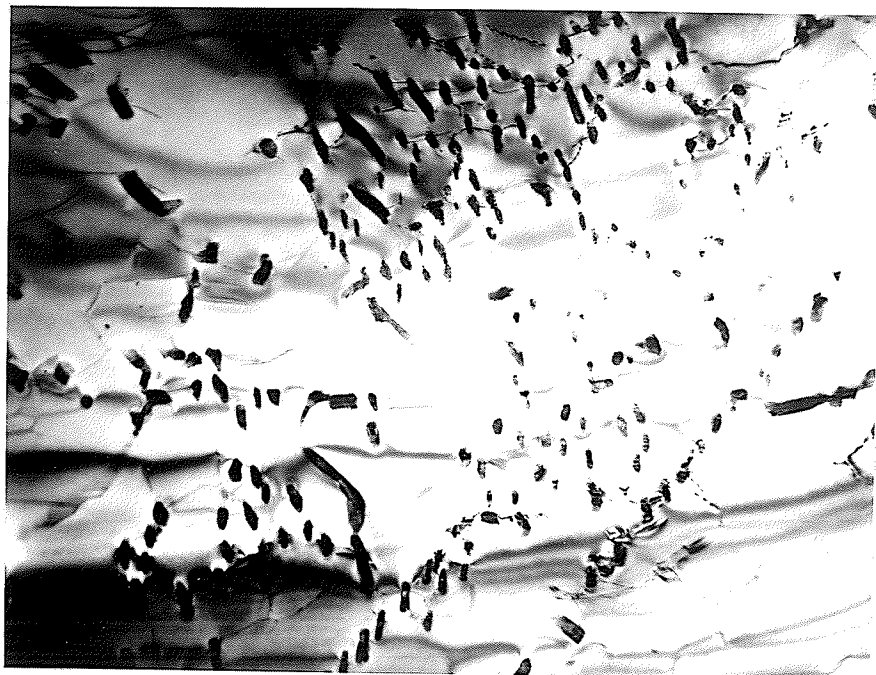


Figure 68

Figure 69: SADP of Figure 68.

Interpretation of the hcp matrix in Figure 69.



Figure 69

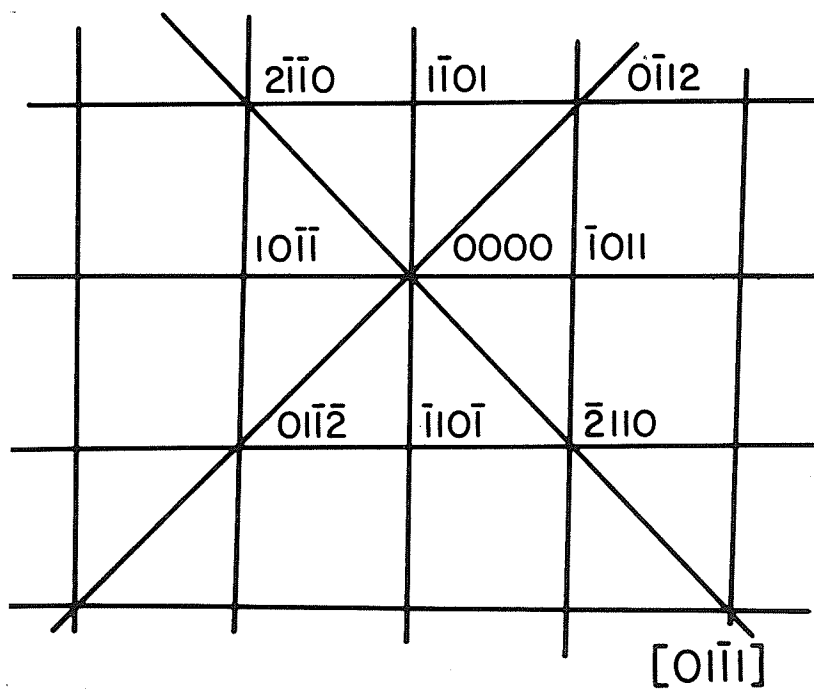


Figure 70: Bright-field micrograph of the Co-25% Cr-7% Mo alloy aged at 1073K for 142 hours. (12600 x).



Figure 70

Figure 71: SADP of a precipitate free area of the Co-25% Cr-7% Mo alloy aged at 1073K for 85 hours.

Interpretation of Figure 71.

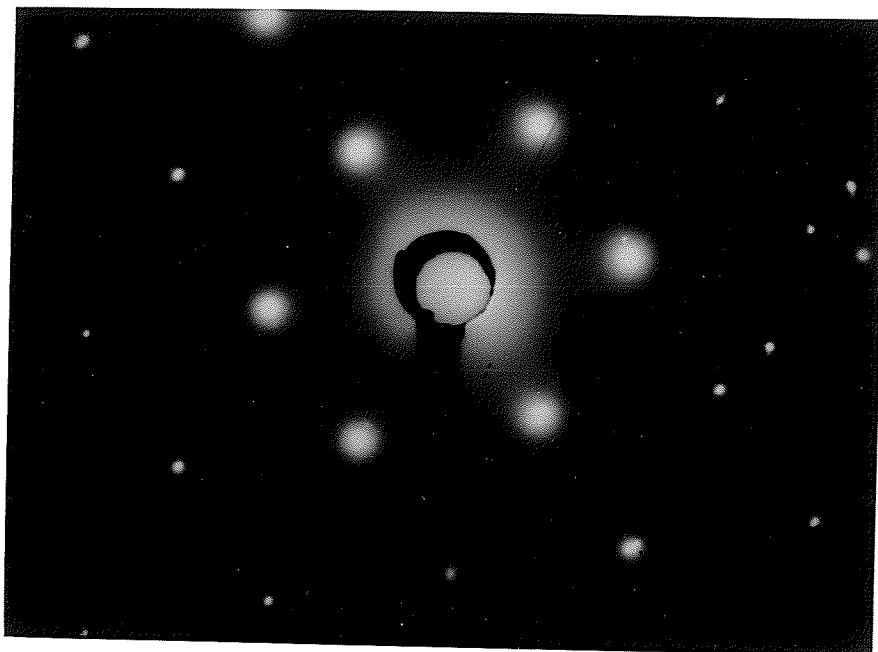
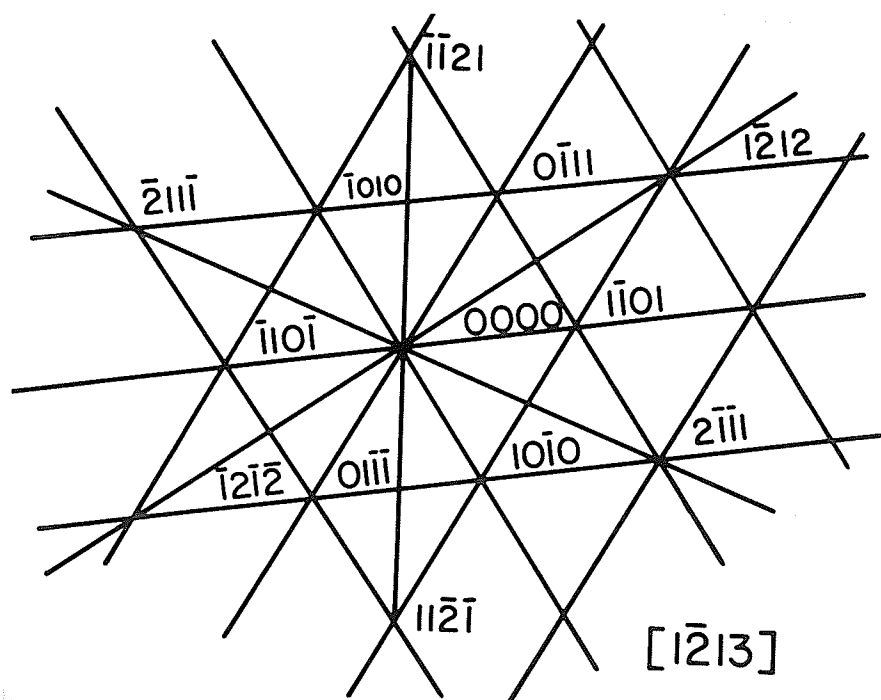


Figure 71



4.3 Co-25% Cr-5% Mo-2.5% Nb Alloy

The mechanical properties of the Co-25% Cr-5% Mo-2.5% Nb alloy were examined by means of hardness tests only. The structural investigations were conducted by optical metallography and carbon extraction replica techniques.

4.3.1 Mechanical properties

The Vickers hardness values of the specimens aged at 973K and 1073K against ageing time are shown in Figure 72. An increase of 145 VPH is observed in the peak aged specimen at 1073K which occurred after ageing for 100 hours. As it was the case in the Co-Cr-Mo system, in this alloy also the hardness values attained after ageing at 973K are lower than those at 1073K. But the peak hardness at 973K occurs after a longer ageing time than at 1073K.

4.3.2 Optical metallography

In the Co-25% Cr-5% Mo-2.5% Nb alloy the optical microstructure of the solution treated specimens (Figure 73) is similar to those of the Co-Cr-Mo alloys. The matrix consists of polygonal grains with some twins or transformation bands in them. The specimens aged at 973K (Figure 74) exhibit a high density of transformation bands.

4.3.3 Electron microscopy

The second phase particles in the aged Co-Cr-Mo-Nb alloy were identified by means of carbon extraction replica techniques. The

Figure 72: Variation in hardness with ageing time at ageing temperature of 973K and 1073K.

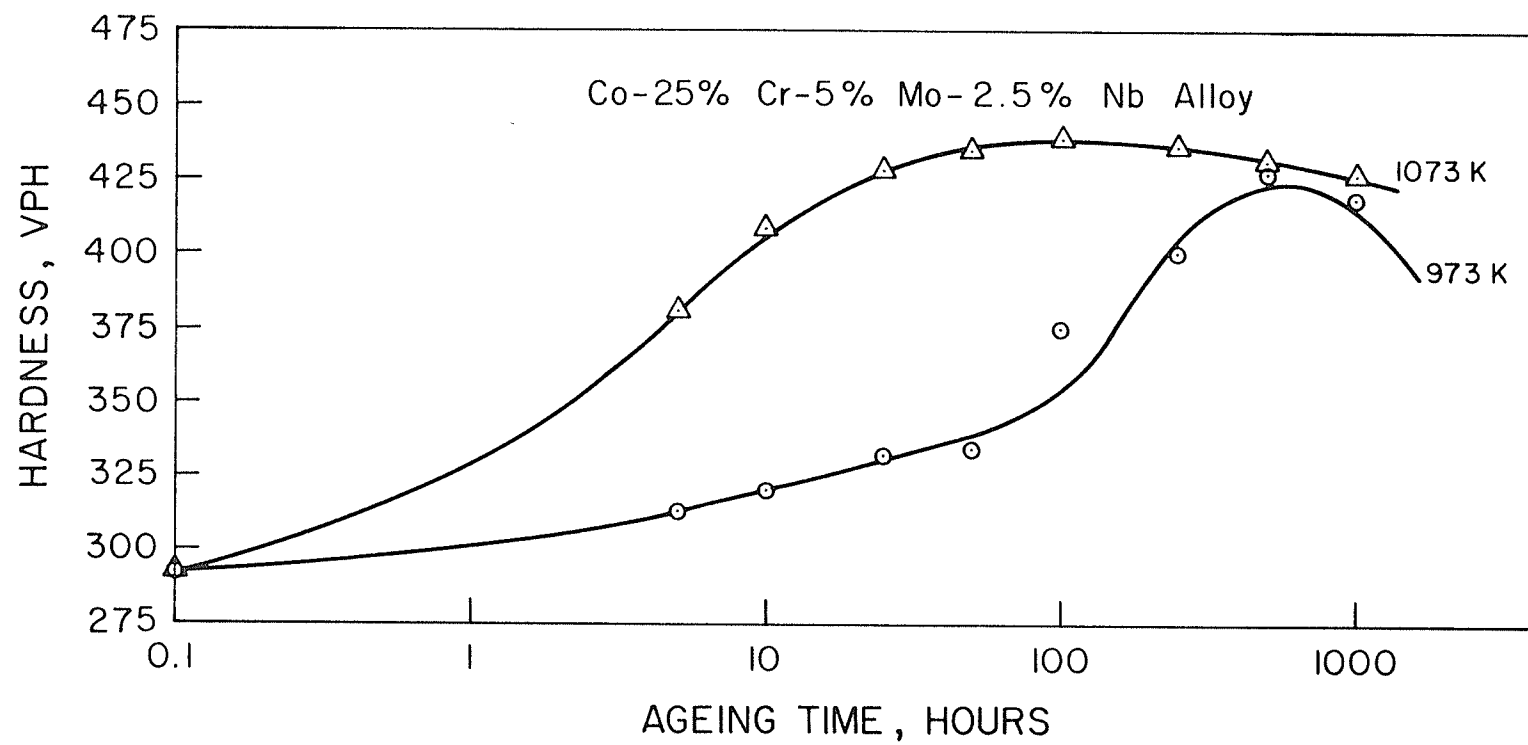


Figure 72

Figure 73: Optical microstructure of the Co-25% Cr-5% Mo-2.5% Nb alloy solution treated at 1473K. (110 x).

Figure 74: Optical microstructure of the Co-25% Cr-5% Mo-2.5% Nb alloy aged at 973K for 100 hours. (400 x).



Figure 73

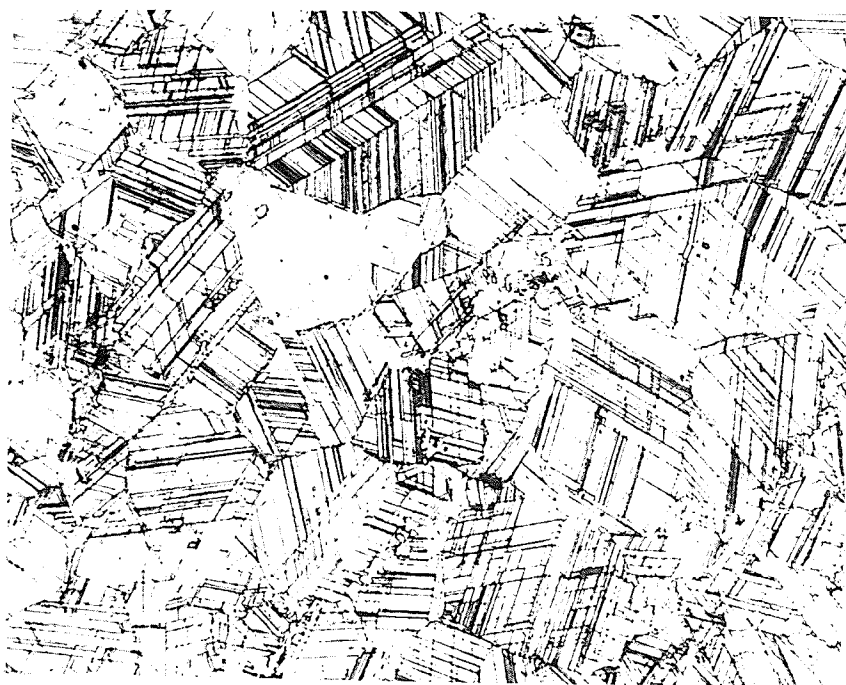


Figure 74

Figure 75: Carbon extraction replica of the Co-25% Cr-5% Mo-2.5% Nb alloy aged at 1073K for 50 hours. (18200 x).

Figure 76: Carbon extraction replica of the Co-25% Cr-5% Mo-2.5% Nb alloy aged at 1073K for 100 hours. (14000 x).

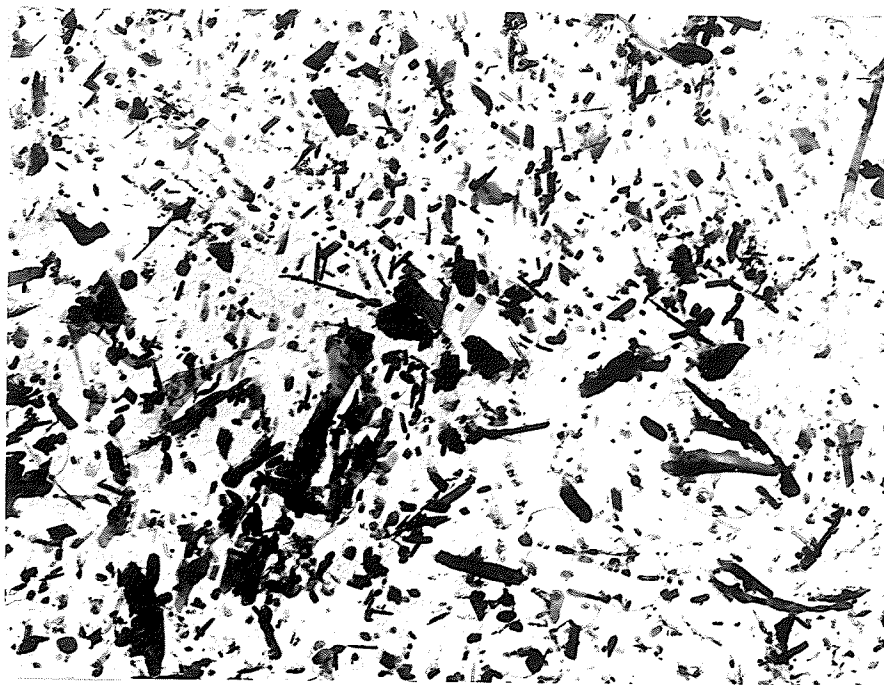


Figure 75



Figure 76

Figure 77: Ring pattern of the carbon extraction replica of the Co-25% Cr-5% Mo-2.5% Nb alloy aged at 973K for 100 hours.

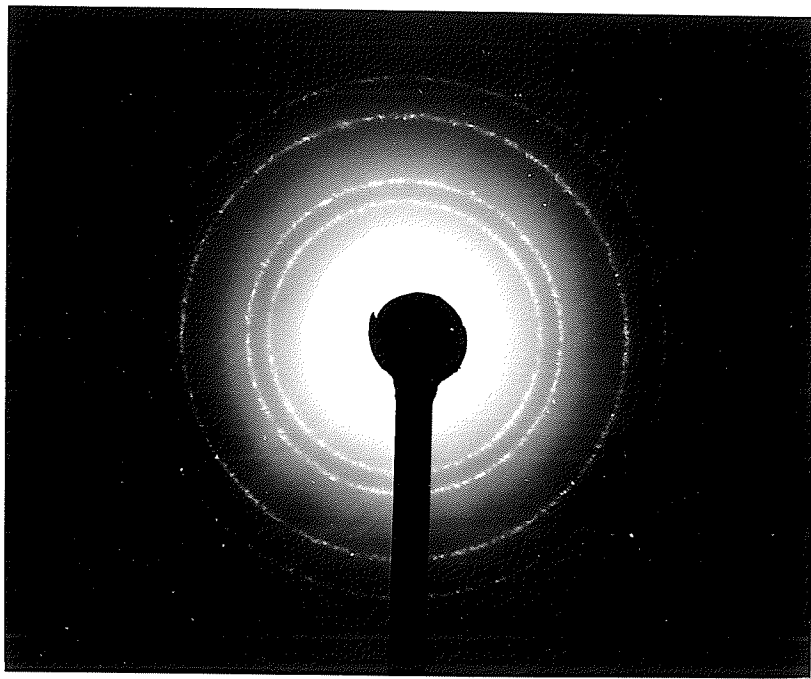


Figure 77

precipitates were combination of hcp $\text{Co}_3\text{Mo}^{(40)}$ ($a = 5.12 \text{ \AA}$ and $c = 4.11 \text{ \AA}$) and hexagonal (rhombohedral) $\text{Co}_7\text{Nb}_6^{(41)}$ ($a = 4.92 \text{ \AA}$, $c = 26.28 \text{ \AA}$) phases. The extracted precipitates can be seen in Figures 75 and 76. The precipitates are observed within the grains and also at the grain boundaries. One of the many ring patterns used for identification of second phase particles can be seen in Figure 77.

CHAPTER 5 DISCUSSION

In this chapter, the previously presented results are examined and discussed in the light of information available in the literature on the relevant alloys.

5.1 Co-25% Cr-4% Ti Alloy

The precipitates in the Co-25% Cr-4% Ti alloy are the γ' (Co_3Ti) phase which has an ordered fcc Li_2 (Au_3Al) type of structure whose lattice parameter was observed to be between $3.60 \text{ \AA}$ and $3.62 \text{ \AA}$ depending upon the ageing time and temperature. No change in the precipitate morphology was observed in the faulted regions of the matrix.

The Co_3Ti type of precipitates have been observed in Co-Ti⁽⁴²⁻⁴⁴⁾ and Co-Ni-Ti^(45,46) alloys. The studies of the decomposition of the supersaturated solid solutions during early stages of ageing of the cobalt-base alloys, revealed the formation of G.P. zones on (100) planes of the matrix in titanium enriched regions^(44,48). It was reported that the Co_3Ti precipitates formed from the coalescence of the randomly distributed Guinier complexes and not by spinodal decomposition⁽⁴⁶⁾. The nucleation of the γ' precipitates was modelled as follows, G.P. zones $\rightarrow \gamma'$ phase $\rightarrow$ stable phase⁽⁴⁶⁾. These considerations may suggest that the formation of the Co_3Ti precipitates which are observed on the (100) planes of the matrix in the present alloy might also follow a similar precipitation sequence.

According to Berezina and Chuistov⁽⁴²⁾, the Co_3Ti particles while precipitating from a Co-Ti solid solution are exposed to hydrostatic pressure. On their alloy, the mismatch between the lattice parameters of the matrix and the precipitates ($\frac{\Delta a}{a}$) was between 0.59% and 0.87% which is close to the misfit in the present Co-Cr-Ti alloy. The γ' (fcc) to η (hcp) phase transformation of the precipitates was not observed by the previous authors which is similar to the findings of the present investigation. Baker, Brandon and Nutting⁽⁴⁹⁾ reported that when the precipitates are exposed to hydrostatic pressure, stresses resulting from the applied pressure may be relieved by formation of rows of vacancies in the close-packed planes of the precipitates. Consequently, such rows of vacancies can give rise to stacking faults which can act as nucleus for the fcc $\rightarrow$ hcp phase transformation when the size of the precipitates exceeds certain critical values. Chung et al⁽⁵⁰⁾ have reported that in a Co-38% Ni-17% Cr-5% Ti alloy with a lattice mismatch of 1.3%, the strain due to hydrostatic compression of γ' - Ni_3Ti precipitates was relieved by condensation of vacancies on $\{111\}$ planes of the γ' precipitates, which resulted in the formation of intrinsic faults within the precipitate particles. Such faults led to the transformation of γ' to η - Ni_3Ti phase. It may be concluded that in the present Co-Cr-Ti alloy, the compressive stresses exerted on the γ' precipitates are not high enough to produce the γ' - η transformation since ($\frac{\Delta a}{a}$) misfit value is not of high magnitude. The density of stacking faults and/or transformation bands in the matrix does not seem to

increase significantly on ageing. This would also suggest a low level of tensile stresses present in the lattice due to the presence of coherent γ' precipitates.

The superlattice reflections due to ordered γ' precipitates were observed to be very weak. The change in volume fraction of the precipitates at different ageing temperatures did not seem to influence the above characteristic of the precipitates. It was reported that the x-ray diffraction analysis of the γ' precipitates extracted from a Co-7.45% Ti alloy did not reveal any reflections in Fe, Cr, Co and Cu radiations⁽⁴²⁾. Berezina et al attributed high intensity of the reflection of the γ' precipitates in the diffraction pattern of Co-7.8% W-9.6% Ti alloy⁽²⁸⁾ to the presence of W in the Co_3W phase. It may be concluded that the very weak reflections resulting from the ordered Co_3Ti precipitates on the (100) planes of the matrix is in agreement with the behaviour of the Co_3Ti precipitates previously observed by the above authors.

The stacking faults and twins observed in the solution treated and aged specimens are in the same planar orientations as the fcc matrix. The existence of stacking faults in cobalt-base alloys is attributed to the presence of alloying elements which promote the formation of stacking faults by decreasing the stacking fault energy (SFE). This is related to the capacity of the alloying elements to raise or lower the fcc $\rightarrow$ hcp transformation temperature. The stacking faults can act as nucleation sites for the fcc $\rightarrow$ hcp phase transformation.

The presence of stacking faults in fcc matrix suggests the beginning of fcc to hcp transformation during cooling from the solution treatment temperature. It is known that the fcc $\rightarrow$ hcp phase transformation of pure cobalt upon cooling proceeds by shear and the crystallographic relation is as follows⁽¹⁾

$$\{111\}_{\gamma} // \{0001\}_{\epsilon} \text{ and } \langle 110 \rangle_{\gamma} // \langle 1120 \rangle_{\epsilon} .$$

It seems that Ti is not one of the elements which stabilizes the hcp phase. The matrix of the specimens aged at 973K and 1073K is still of fcc structure, with a similar amount of stacking faults as observed in the solution treated specimens. The above behaviour suggests that the $\epsilon \rightarrow \gamma$ phase transformation in this alloy occurs below 973K.

5.2 Coarsening of The γ' Precipitates

Although the original LSW theory is applicable to spherical particles dispersed in a liquid matrix, it has been used for coarsening studies of spherical and non-spherical particles in solid matrices. In the present investigation, the average particle size of the Co_3Ti precipitates, being proportional to $t^{.336}$, $t^{.334}$, $t^{.312}$ respectively at 973K, 1023K, 1073K ageing temperatures, satisfies the average particle size should be proportional to $t^{1/3}$ criterion of the diffusion controlled coarsening process.

An activation energy of 425.1 kJ/mole is calculated for the coarsening of the γ' (Co_3Ti) precipitates in the Co-Cr-Ti matrix. The activation energy for self diffusion of Co is 273.6 kJ/mole in the temperature range of 1045K - 1321K⁽⁵¹⁾. The value of the activation energy for self diffusion of Cr in the temperature range of 1301K to 1821K is 308.4 kJ/mole⁽⁵²⁾. For growth of the Co_2Ti phase in the Co-CoTi and Co_3Ti - CoTi diffusion couples, the activation energies of 292.9 kJ/mole and 289.2 kJ/mole, respectively, were calculated⁽⁵³⁾. In the same investigation, the activation energy for the growth of Co in Co-CoTi couples was computed to be 362.4 kJ/mole⁽⁵³⁾. Diffusion data for the diffusion of Ti in Co-Cr-Ti alloy is not available, however, the activation energy of 425.1 kJ/mole calculated in this investigation is higher than reported above. Two factors could lead to a high value of activation energy 1) The assumption that the interfacial energy σ is independent of ageing temperatures may not be valid. For example, if the value of σ increases with temperatures, it can increase the value of the rate constant k . Consequently, the value of the computed activation energy Q will also be higher. 2) If the chemical composition of the γ' precipitates is of $\text{Co}_3(\text{Ti}, \text{Cr})$ type, the diffusion of Cr in Co-Cr matrix will also influence the value of the activation energy Q .

As can be seen from Figure 39, there are considerable deviations between experimental and theoretical particle size distributions. One of the differences is that the experimental particle size distributions are much broader than the theoretical ones, i.e., the

cut-off values are greater than $\rho = 1.5$. Other factors which are not in agreement with the theoretical distribution are the values and position of maxima. It is, however, observed that the distribution of γ' particle sizes after various ageing times is independent of the distribution at the onset of the coarsening process (Figure 39). This is in agreement with the prediction of the LSW theory.

Deviations from theoretical distribution has been examined by Ardell in terms of precipitate-matrix misfit in nickel base alloys⁽⁵⁴⁾. According to Ardell, the elastic strain due to the particle-matrix mismatch not only affects the shape of the precipitates but it can also lead to elastic interactions between the γ' precipitates themselves which influences their distribution. Eshelby⁽⁵⁵⁾ has evaluated such elastic interactions between the inclusions in a matrix. The interaction energy between two spherical particles is proportional to $(\frac{1}{R^6})$, where R is the distance between the centers of the two particles when $R \gg r_0$ (r_0 = radius of the largest particle). For particles which are closer to each other, the elastic interaction has a higher value with respect to the case when they are farther apart. For all the cases, the interaction energy is also proportional to the square of the dilations of the particles.

In the present alloy system the value of $\frac{\Delta a}{a}$ is between 0.6% and 1.0% and the precipitates are relatively close to each other, i.e., the energy of elastic interactions is considerably high.

Figure 78: Carbon extraction replica of the Co-25% Cr-4% Ti alloy aged at 1023K for 250 hours. The arrows indicate the coalescence of the growing γ' precipitates. (67000 x).

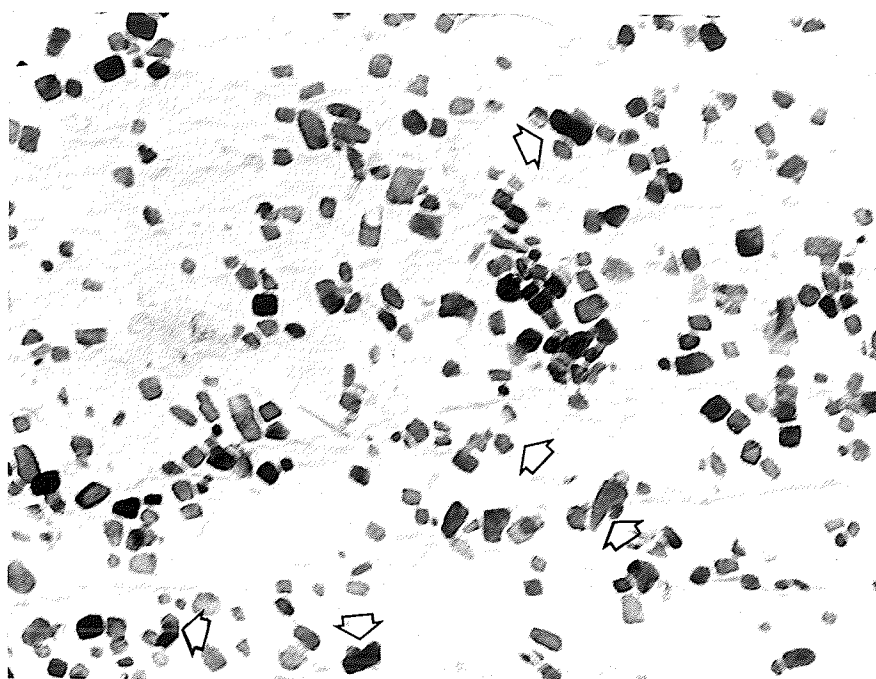


Figure 78

Therefore, the observed broad particle size distribution can be attributed to the elastic interaction between the particles. It is also observed that very often, growing particles coalesce together, as shown by the arrows in Figure 78. This would suggest that the "encounter" mechanism as proposed by Davies et al⁽¹⁷⁾, and discussed in Chapter 2, could also be operating in this system causing a broader distribution in particle size.

5.3 Co-Cr-Mo Alloys

It is known that the addition of alloying elements can have two different effects on the cobalt-base alloys. They can either enlarge or decrease the γ (or α) fcc phase (Figure 79) by raising or lowering the A_s ($\epsilon \rightarrow \alpha$ transformation upon heating) and the M_s ($\alpha \rightarrow \epsilon$ transformation upon cooling) temperatures⁽¹⁾.

Mo decreases the SFE of the cobalt-base alloys⁽²⁾ and it is also an hcp phase stabilizer. As can be seen from the Co-Cr-Mo ternary phase diagram (Figure 80), the matrix is fcc at 1473K for both the alloys. The initial stage of the fcc $\rightarrow$ hcp phase transformation can be seen by high density of stacking faults in the solution treated samples (Figures 58-61). When specimens were aged at 973K, the amount of transformation bands increased (Figures 44, 48, 49), suggesting the transformation of fcc to hcp phase since the ageing temperature 973K is below the A_s temperature⁽⁵⁷⁾. At 1073K, however, the optical structure showed a reduced amount of transformation bands (Figures 45, 46, 50) but the presence of hexagonal phase was established by

Figure 79: Two possibilities for the effects of alloying additions on the cobalt alloy phase diagrams, [1].

Type I : constricted α -field

Type II: enlarged α -field

Figure 80: Co-Cr-Mo ternary diagram at 1473K, [56].

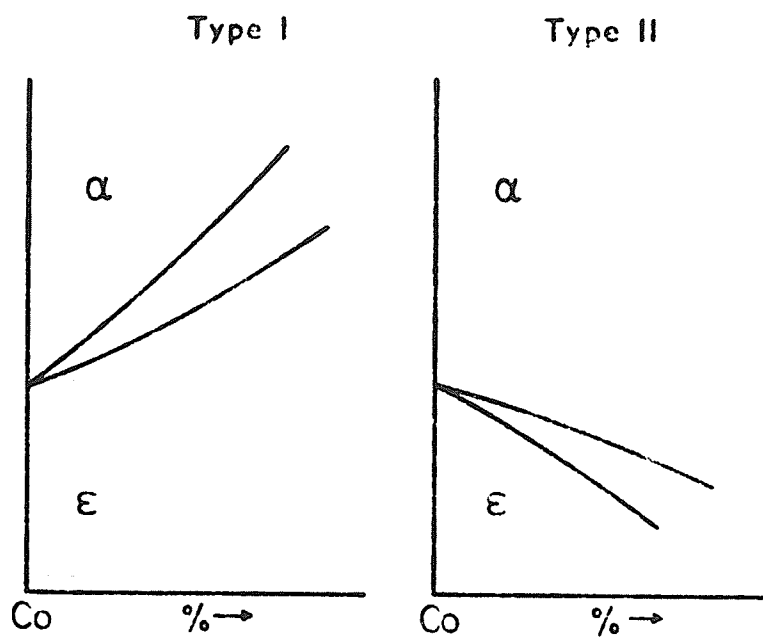


Figure 79

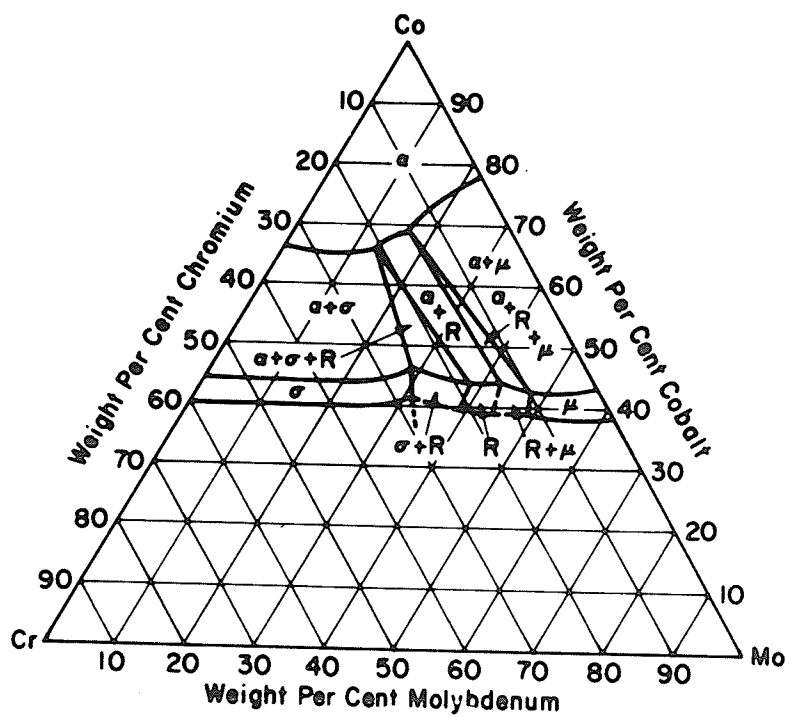


Figure 80

electron diffraction patterns (Figures 69, 71). Since this temperature is also below the fcc to hcp transformation temperature⁽⁵⁷⁾, a large number of grains have fully transformed from fcc to hcp phase and small islands observed in a few grains (Figures 45, 46, 50) could be of fcc structure. That is to say a much greater amount of hcp phase seems to be present in specimens aged at 1073K than in these that were aged at 973K.

As it was reported in Chapter 4, the peak strength attained at 973K is not higher than that obtained by ageing at 1073K. This behaviour can be explained qualitatively by considering the strengthening mechanisms which may be operating in the aged specimens. The presence of both, the precipitate particles and also of the hcp phase in the matrix affects the strength of the specific alloys⁽⁵⁸⁾. It is known that the degree of supersaturation at 973K is higher than that of 1073K which should suggest a higher amount of precipitate particles at 973K. However, since the amount of Mo which is present in the solid solution at 1073K is higher than that of 973K, the amount of hcp phase should be higher at 1073K with respect to 973K as discovered earlier. The combined effects of the second phase particles and of the hcp ϵ phase can be considered as the source of the observed higher peak strength at 1073K.

Another feature which was noticed in Chapter 4 was that the elongation of the aged specimens was higher than that of the solution

treated ones. This behaviour can be explained as follows. The hcp phase is present both, in the solution treated and aged specimens. The plastic deformation during the tensile tests at room temperature may increase the amount of hcp phase for all the alloys, if the M_d temperature (lowest temperature fcc $\rightarrow$ hcp transformation can proceed by plastic transformation) lies just above the room temperature. This is due to the presence of Mo in the solid solutions^(1, 59). The amount of Mo in solid solution is higher for the solution treated specimens than for the aged ones. This may lead to a larger amount of fcc hcp phase transformation in the solution treated specimens as compared to those which were aged. Also, the presence of stacking faults, which are known to block slip in the cobalt-base alloys⁽⁶⁰⁾, may additionally decrease the ductility of the solution treated samples. Since, these faults were not detected in the aged specimens, their elongation properties are not affected. Consequently, the presence of stacking faults and high amounts of Mo in the solid solutions of the samples quenched from 1473K can lead to lower elongation properties compared to those aged at 973K and 1073K. Also, it is observed that, in the aged specimens, lower ductility is detected in specimens which have higher strength, as is generally the case.

CHAPTER 6 CONCLUSIONS

From the results presented in Chapter 4, and discussed in Chapter 5, the following conclusions can be deduced.

6.1 Co-25% Cr-4% Ti Alloy

1. The precipitates are the ordered fcc Co_3Ti phase which form on the {100} planes of the fcc matrix.
2. Up to 1000 hour of ageing the particles maintained their cuboid shape and cubic structure. The matrix also remained cubic and did not transform to the hexagonal, ϵ phase.
3. The lattice misfit between γ - γ' phases varies between 0.6% and 1.0% depending upon the ageing time and temperature.
4. The coarsening of the γ' precipitates obeys the criterion of the diffusion controlled coarsening of particles.
5. The application of the LSW theory to the growth kinetics of the Co_3Ti precipitates leads to particle size distributions which deviate considerably from theoretical predictions. These variances between theoretical and experimental particle size distributions can be considered to be resulting from the elastic interactions and the encounters between the growing γ' precipitates.

6.2 Co-Cr-Mo Alloys

1. The mechanical properties of the two alloys exhibit similar characteristics in terms of their hardness behaviour. The increase in Mo content is observed to improve the strength.
2. The strengthening mechanisms are attributed to the presence of the precipitate particles and also of the hcp ϵ phase.
3. The precipitation in both the alloys is a combination of hcp Co_3Mo and rhombohedral Co_7Mo_6 phases.
4. For both the alloys, the matrix of the solution treated and aged specimens consists of fcc and hcp phases, while the amount of hcp phase increases by ageing.

REFERENCES

- 1) A. Giamei, J. Burma and E.J. Freise, *Cobalt*, 39, (1968), p. 88.
- 2) C.T. Sims, *J. Met*, 21, (December 1969), p. 27
- 3) G.P. Sabol and R. Stickler, *Phys. stat sol.*, 35, (1969), p. 11.
- 4) P.S. Kotval, *Metallogr*, 1, (1969), p. 251.
- 5) P. Viatour, J.M. Drapier and D. Coutsouradis, *Cobalt* 3, (1973), p.67.
- 5a) F.R. Morral, *J. of Materials*, 1, No. 2, (1966), p. 384.
- 6) A. Kelly and R.B. Nicholson, *Prog in Mat. Sci.*, 10, (1963), p. 277.
- 7) M. Volmer and A. Weber, *Z Phys. Chem*, 119, (1925), p. 277.
- 8) R. Becker and W. Doring, *Ann. Phys.*, 24, (1935), p. 719.
- 9) R.E. Reed-Hill, *Physical Metallurgy Principles*, 2nd edition, D. Van Nostrand Company, (1973), p. 370.
- 10) J.W. Martin, *Micromechanisms in Particle-Hardened Alloys*, Cambridge University Press, (1980), p. 10.
- 11) J.W. Cahn, *Acta Met.* 5, (1957), p. 169.
- 12) P.J. Clemm and J.C. Fisher, *Acta Met*, 3, (1955), p. 70.
- 13) J.W. Christian, *The Theory of Transformation in Metals and Alloys*, 2nd edition, Pergamon Press, (1975), p. 452.
- 14) C. Wagner, *Z. Elektrochem*, 65, (1961), p. 581.
- 15) J.M. Lifshitz and V.V. Slyozov, *J. Physics Chem. Solids*, 19, (1961), p. 35.
- 16) A.J. Ardell, *Acta Met*, 20, (1972), p. 61.
- 17) C.K.L. Davies, P. Nash, R.N. Stevens, *Acta Met*, 28, (1980), p. 179.
- 18) C.P. Sullivan, J.D. Varin and M.J. Donachie Jr., *Metals Eng. Quart*, 9, No. 2, (1969), p. 16.
- 19) M.J. Wouds and T.R. Cass, *Cobalt*, 42, (1969), p. 3.

- 20) P. A. Beaven, P.R. Swann, D.R.F. West, J. Mater. Sci, 14, (1979), p. 354.
- 21) J.M. Drapier, P. Viatour, D. Coutsouradis, Cobalt, 52, (1971), p. 147.
- 22) C.T. Sims, The Superalloys, (Edited by C.T.Sims, W.C. Hagel), Wiley-Interscience, (1972), p. 155.
- 23) E.W. Ross, J.Met., 19, (December 1967), p. 12.
- 24) N.T. Wagenheim, Cobalt, 48, (1970), p. 129.
- 25) V. Biss, G.N. Kirby, and D.L. Sponseller, Met. Trans. 7A, (1976), p. 1251.
- 26) C. Hammond and J. Nutting, Metal Sci, 11, (1977), p. 474.
- 27) P. Viatour, J.M. Drapier, D. Coutsouradis, L. Habraken, Cobalt, 51, (1971), p. 67.
- 28) A.L. Berezina, L.P. Gun'ko and K.V. Chuistov, Fiz Metal. Metalloved, 34, No. 6, (1972), p. 1213.
- 29) Yu. K. Nazarov, G. I. Terrebito and A.D. Korotayev, Fiz Metal. Metalloved, 37, No. 1, (1970), p. 163.
- 30) J.H. Davidson, Revue de metallurgie, (Decembre 1974), p. 943.
- 31) J.M. Drapier, J.L. de Brower and D. Coutsouradis, Cobalt, 27, (1965), p. 59.
- 32) J.M. Drapier and D. Coutsouradis, Cobalt, 39, (1968), p. 63.
- 33) D. Coutsouradis, Journees du Cobalt, Brussels, (1964), p. 168.
- 34) B.J. Pearcey, R. Jackson and B.B. Argent, J. Inst. Metals, 91, (1962), p. 257.
- 35) M.C. Chaturvedi and D.W. Chung, J. Inst. Metals, 101, (1973), p. 253.
- 36) D.W. Chung and M.C. Chaturvedi, Metallogr, 8, (1975), p. 329.
- 37) Owen H. Kriege and J.M. Baris, Trans ASM, 62, (1969), p. 195.
- 38) ASTM Powder Diffraction File, No. 23-938.

- 39) A.J. Ardell and R.B. Nicholson, J. Physics Chem Solids, 27, (1966), p. 1793.
- 40) W.B. Pearson, Lattice Spacings and Structures of Metals and Alloys, Pergamon Press, (1964), p. 511.
- 41) ASTM Powder Diffraction File, No. 18-417.
- 42) A.L. Berezina and K.V. Chuistov, Fiz. Metal Metalloved, 27, No. 2, (1969), p. 370.
- 43) R.W. Fountain and W. Forgeng, Trans. AIME, 215, (1959), p. 998.
- 44) R.W. Fountain, G.M. Faulring and W. Forgeng, Trans. AIME, 221, (1961), p. 747.
- 45) O.V. Tsinenko, A.N. Tyumentsev, L.S. Bushnev and A.D. Korotayev, Fiz. Metal Metalloved, 32, No. 4, (1971), p. 758.
- 46) A.D. Korotayev, Yu. K. Nazarov, G.I. Terebilo, Fiz. Metal Metalloved, 22, No. 3, (1966), p. 404.
- 47) A.L. Berezina and K.V. Chuistov, Fiz Metal. Metalloved, 29, No. 4, (1970), p. 834.
- 48) O. Ye. Tkachenko and K.V. Chuistov, Fiz. Metal. Metalloved, 29, No. 4, (1970), p. 834.
- 49) R.G. Baker, D.G. Brandon and J. Nutting, J. Phil Mag, 4, (1959), p. 1339.
- 50) D.W. Chung and M. Chaturvedi, Metal Sc. J, 6, (1972), p. 134.
- 51) K.I. Hirano, R.P. Agarwala, B.L. Averbach and M. Cohen, J. Appl. Phys, 33, (1962), p. 3049.
- 52) J. Askill and D.H. Tomlin, Phil Mag, 11, (1965), p. 467.
- 53) P.J.M. Van der Straten, G.F. Bastin, F.J.J. Van Loo, G.D. Rieck. Z. Metallkde, 67, H. 3, (1976), p. 152.
- 54) A.J. Ardell, Met Trans, 1, (1970), p. 525.
- 55) A.J. Ardell and R.B. Nicholson, Acta Met, 14, (1966), p. 1295.
- 56) S. Rideout, W.D. Manly, E.L. Kamen, B.S. Lement and P.A. Beck, J of Metals, 3, (1951), p. 872.

- 57) E.E. Fletcher and A.R. Elsea, J. Met, 3, (1951), p. 897.
- 58) A.H. Graham and J.L. Youngblood, Met. Trans, 1, (1970), p. 423.
- 59) F.R. Morral, L. Habraken, D. Coutsouradis, J.M. Drapier and M. Urbain, Metals Eng Quart, 9, No. 2, (1969), p. 1.
- 60) J.B. Vander Sande, J.R. Coke, and J. Wulff, Met Trans, 7A, (1976), p. 389.