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STUDY OF PRECIPITATION IN NIOBIUM-NITROGEN ALLOYS

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TABLE OF CONTENTS

	Page
I. INTRODUCTION.....	1
II. EXPERIMENTAL PROCEDURE.....	10
III. RESULTS.....	12
IV. DISCUSSION OF RESULTS.....	30
V. SUMMARY.....	32
REFERENCES.....	33

I. INTRODUCTION

In recent years there has been considerable interest in refractory metal alloys because of their high temperature applications. Many of the physical and thermodynamic properties of the body-centered cubic metals such as niobium and tantalum containing interstitial solutes of carbon, oxygen, or nitrogen are presented in the literature. Study of the kinetics of precipitation in these systems has just begun.⁽¹⁾ The present work considers the niobium-nitrogen system and examines precipitate morphology and growth rates in order to derive a growth rate law and an activation energy. From these facts conclusions can be made about the precipitation mechanism. In this study optical and electron metallographic techniques were employed.

The basic theory of metal-gas reactions will first be reviewed, followed by specific work on the niobium-nitrogen system. In thermodynamic treatments, equilibrium between the metal and the gas is initially assumed. Cost, Gibala, and Wert⁽²⁾ made the following assumptions for describing the pressure-temperature-composition relations as a metal and a diatomic gas form a terminal solid solution:

- 1) The gas goes into solution atomically in the interstitial sites of the metal lattice, with Henry's law valid over the entire solubility range.

2) The solubility of the gas is so low that the activity of the solid solution is essentially that of the pure metal.

3) The partial molar heat of solution of the gas in the metal and the standard heat of formation of the MG phase are both constant with temperature.

4) The MG phase is of constant composition.

5) The gas is considered to be ideal.

With these assumptions the pressure-temperature-composition relationships for niobium-nitrogen were determined for alloys up to about ten atomic per cent nitrogen. The quantities determined include heat and entropy of solution of nitrogen gas in niobium, heat of solution of the nitride phase Nb_2N , heat of formation of the nitride, and its solubility as a function of temperature. These calculations have been reported by Cost and Wert⁽³⁾; Gebhardt, Fromm, and Jakob⁽⁴⁾; and de Lamotte, Huang, and Altstetter⁽⁵⁾. These thermodynamic properties for the Nb-N system are summarized in Table I.

In work done by de Lamotte, Huang, and Altstetter⁽⁶⁾ a precipitate was observed to grow inward from the sub-boundaries in addition to continuous precipitation within the subgrains. This sub-boundary precipitation effect, thought to be discontinuous precipitation, was not found in all specimens, but only under specific (but somewhat unknown) conditions of nitrogen concentration and cooling rate. Discontinuous precipitation is the nucleation and coupled growth of nitride and depleted matrix into supersaturated matrix.

TABLE I

Molar Thermodynamic Parameters of Nb-N

Heat of solution of 1/2 mole N_2 in solution	-42,000 cal
Entropy of solution of 1/2 mole N_2 in solution	-8 cal/°K
Heat of solution of nitride in solution	+21,000 cal
Heat of formation of nitride	-62,000 cal

In contrast to this, continuous precipitation occurs simultaneously throughout the entire specimen, although various localized regions may show greater rates than others. As isolated particles of precipitate are nucleated, the concentration of the solute in the surrounding matrix is depleted at further and further distances from the particle as it grows. This gives a change in linear dimension which increases with time parabolically. In discontinuous precipitation an interface separates the two-phase mixture of precipitate, β , and depleted matrix, α , from the supersaturated α . For discontinuous precipitation the product/parent interface moves linearly with time. In the Nb-N system the product constituent forms as a uniform shell at the sub-boundaries, and the reaction proceeds by the thickening of this layer.

Theories of discontinuous precipitation assume that a lamellar structure of precipitate, β , and a depleted α is formed (Figure 1). However, de Lamotte, Huang, and Altstetter observed that the product phase in the niobium-nitrogen system is not lamellar, but appears in optical micrographs to be a needle-like structure of β dispersed in α . Christian⁽⁷⁾ states that the nucleation of a discontinuous precipitate requires the formation of an incoherent boundary, and therefore nucleation is difficult in regions of undisturbed atom arrangement in the crystal. At a grain boundary an interface is already present, and thus the discontinuous mode of precipitation nearly always initiates at these regions.

FIGURE 1. Schematic Diagram of Lamellar Precipitates.

supersaturated α

$\cdot x_0$

The unusual occurrence of the discontinuous precipitation from an interstitial solid solution is attributed to the following effects by de Lamotte, Huang, and Altstetter (6):

1) In niobium the body-centered cubic structure is stable over a wide temperature range. The nitrogen solubility is very high at high temperatures and quite low at room temperatures so that large supersaturations are possible.

2) Heterogeneous nucleation is very much easier than homogeneous nucleation, and there is an immediate supply of sub-boundaries and isolated dislocations on which precipitate can nucleate.

The general kinetic theory of discontinuous precipitation has been reported by Turnbull (8). He noted that cellular precipitation was quite similar to the formation of pearlite nodules in the decomposition of austenite. The Zener theory (9) for pearlite growth was the starting point for the development of cellular growth theory. Zener assumed that the rate of growth of pearlite was determined by diffusion of solute atoms parallel to the advancing interface. Zener derived the following expression, in accordance with Figure 1, for the growth rate:

$$G = \frac{X_0 - X_e}{X_0} \frac{2D}{l}$$

where X_0 = mole fraction of solute in alloy

X_e = mole fraction of solute in α at $\alpha/\alpha + \beta$ phase
boundary

D = volume diffusion coefficient

l = interlamellar spacing

$J/2$ = flux of carbon necessary to deplete the ferrite of its initial carbon content.

Work in lead-tin system by Turnbull and Treafis⁽¹⁰⁾ indicated precipitation rates much greater than those predicted by assuming volume diffusion. Turnbull concluded that the solute must be drained by boundary diffusion and gave the following expression for growth rate:

$$G = \frac{X_0 - X_e}{X_0} \frac{D_B \lambda}{l^2}$$

where λ = boundary thickness

D_B = diffusion coefficient in the cell boundary.

This expression was compatible with experimental results in the lead-tin system. He also stated that nucleation as well as growth is enhanced by orders of magnitude in imperfect crystals.

The Turnbull theory was later modified by Cahn⁽¹¹⁾ who developed a model based on the assumption that the discontinuous precipitation reaction is controlled by boundary mobility and that it was not necessary that the diffusion be rapid enough to completely deplete the product matrix phase to its equilibrium solute content, X_e . Thus, the driving force for the boundary motion in the transformation of a unit volume of supersaturated solution is:

$$\Delta F = P\Delta F_0 + (2\sigma V)/S$$

where ΔF_0 is the free energy change for the formation of one mole of product into the equilibrium product phases; σ is

the surface free energy; S is the interlamellar spacing. P , a disposable parameter, represents the fraction of ΔF_0 realized by the reaction due to non-equilibrium distribution of solute in the product.

Aaronson and Clark⁽¹²⁾ modified these theories to account for homogeneous, continuous precipitation ahead of the advancing cell boundary. Such precipitation further decreases the driving force for cell boundary migration.

II. EXPERIMENTAL PROCEDURE

Niobium rod produced by the Wah Chang Corporation* was swaged to wire 0.037 inch in diameter. Twenty-inch lengths of wire were outgassed by Joule heating at a temperature of 2100° C until a dynamic vacuum less than 5×10^{-6} Torr was maintained for at least one hour. Ultimate vacuums of 10^{-7} Torr were usually obtained. Internal friction versus temperature was determined using a torsion pendulum at frequencies close to 1 cps. From the peak heights the nitrogen content(13) was less than 0.005 w/o and the oxygen content was not detectable (less than 3 ppm) in the specimens outgassed by this procedure.

The nitrogen alloys were made in a well-outgassed Sieverts apparatus. Nitrogen of 99.975% purity was introduced first into a calibrated volume, where its temperature and pressure were measured, then it was released into the specimen chamber while the niobium wire was at 1800°C. The nitrogen was allowed to equilibrate for 20 minutes. Specimens were then directly subjected to an aging treatment by reducing the heating current to predetermined values and holding at temperatures from 300° C to 650° C for varying lengths of time. The specimens were then

*Lot Analyses in wt. pct.: O, 0.0093; N, 0.0048; H, 0.0003; C, 0.0043; W, 0.021; Ta, 0.058; Zr, 0.027; Ti, 0.004; Hf, 0.008; Fe, 0.005; others, less than 0.096.

cooled from the aging temperature to room temperature by introducing helium gas into the specimen chamber as the specimen current was turned off. For several specimens the temperature-time history was recorded on a chart recorder by employing a 0.010 inch tungsten-rhenium (W-5Re, W-26Re) thermocouple spot-welded onto the specimen. Cooling from 1800° C to 415° C was 96% complete in 80 seconds. After aging, helium quenching the specimen from 415° C to room temperature took less than 20 seconds. To insure that a build up of gaseous contaminants did not affect the calibration of the thermocouple wires, 2 - 3 inches of the thermocouple wires nearest the specimen was replaced after each use.

Sections of the niobium-nitrogen wires were mounted, ground longitudinally, vibropolished, and etched in equal parts of nitric acid, hydrofluoric acid, and water. The metallographic examination of the specimens revealed a discontinuous mode of precipitation at subgrain boundaries. Precipitate growth distances were measured with a calibrated filar eyepiece. An average value⁽¹⁴⁾ of one-half the growth distance for each specific aging time and temperature was recorded. For each specimen the average was taken over 15 measurements, each accurate to 0.5 micron. Electron micrographs were made to investigate the microstructure in further detail. Surface replicas were made using a collodian film, which was stripped with tape and shadowed with chromium.

III. RESULTS

The alloys in this work were all 0.2 w/o N in Nb (1.3 a/o N). Aging temperatures were 300°, 415°, 570°, and 650° C. for various times ranging from 3 minutes to 120 minutes. This alloy becomes unstable with respect to Nb₂N precipitate at temperatures below 1230° C. Results from these specimens were obtained by 1) optical light microscopy and 2) electron microscopy.

OPTICAL LIGHT MICROSCOPY

Typical microstructures at a series of aging times at 415° C are shown in Figures 2a, b, c. The numerical results for all four temperatures are summarized in Table II and are presented graphically in Figure 3. The curves of Figure 3 yield linear growth rates for each temperature. These rates are tabulated in Table III and are plotted versus reciprocal absolute temperature in Figure 4. According to the Arrhenius equation, the slope of this line may be used to calculate an activation energy for the process. The activation energy obtained was 5.6 kcal/mole. Although the activation energy is quite low, the linear growth rate suggests that the established theories for discontinuous precipitation may be applicable in this system.

FIGURE 2a. 0.2 w/o N specimen aged at 415° C for 20 minutes. 250X.

FIGURE 2b. 0.2 w/o N specimen aged at 415° C for 90 minutes. 250X.

FIGURE 2c. 0.2 w/o N specimen aged at 415°C for 120 minutes. 250X.

TABLE II

Temperature - Time - Growth Distance Data
(0.2 w/o N, cooled to aging temperature from 1800° C.)

Aging Temperature (Degrees C.)	Aging Time (Minutes)	(Growth Distance)/2 (Microns)
300	10	1.74
	20	1.64
	30	1.90
	45	2.12
415	20	1.00
	60	2.23
	80	2.66
	90	3.29
	100	1.96
	120	7.90
570	5	1.49
	15	6.50
	30	3.80
	60	6.70
	120	11.06
650	3	1.37
	10	6.40
	20	7.89
	40	10.04
	60	7.30

FIGURE 3. Growth Distance versus Aging
Time for Temperatures Investigated.

TABLE III
Growth Rates

Aging Temperature (Degrees C.)	Growth Rate (10^{-8} cm/sec)
300	3.2
415	5.4
570	14.0
650	20.3

FIGURE 4. Logarithm of Growth Rate
versus Reciprocal Temperature.

ELECTRON MICROSCOPY

The surface replicas revealed numerous qualitative characteristics of the precipitation that were not evident from light microscopy, as follows:

1) None of the specimens were characterized by well defined interfaces typical of cellular precipitation.

2) Several micrographs clearly indicated a precipitation process occurring within the matrix (Figures 5a, b, c). These particles appear first as platelets (Figure 5a), but at later times they take a simple dendritic form with very rounded branches (Figure 5c).

3) The parallel columns of precipitate particles projecting from the subgrain boundary had a constant spacing between them (Figures 6, 7). The columns appeared to consist of a succession of platelets.

4) There was evidence of a denuded zone surrounding the precipitation at subgrain boundaries (Figures 5b, 6). In addition Figure 6 shows a depleted region between the matrix and the tips of the precipitate columns.

5) Some precipitates at the subgrain boundaries appear to grow in preferential directions (Figures 5a, 8a, b).

FIGURE 5a. 0.2 w/o N specimen aged at 415° C for 60 minutes. 7500X.

FIGURE 5b. 0.2 w/o N specimen aged at 415° C for 90 minutes. 7500X

FIGURE 5c. 0.2 w/o N specimen aged at 415° C for 100 minutes. 15,000X.

FIGURE 6. 0.2 w/o N specimen aged at 415°C for 90 minutes. 10,000X.

FIGURE 7. 0.2 w/o N specimen aged at 415° C for 90 minutes. 15,000X.

FIGURE 8a. 0.2 w/o N specimen aged at 650°C for 15 minutes. 7500X.

FIGURE 8b. 0.2 w/o N specimen aged at 300° C for 45 minutes. 7500X.

IV. DISCUSSION OF RESULTS

The electron microscopic results seem to contradict the hypothesis that the decomposition is a simple discontinuous precipitation. In the present system there are four factors which are believed to be deviations from the simple process:

- 1) The product phase is not lamellar.
- 2) A fine precipitate is present in the matrix.
- 3) There is a zone denuded of precipitate between columns of sub-boundary precipitate and the precipitates in the subgrain interior.
- 4) The activation energy is far below that for bulk diffusion of nitrogen.

It is suggested that a considerable amount of precipitation occurred during the 80 second quench to the aging temperature. During aging the precipitates at the subgrain boundaries grew inward by a modified coarsening process. That is, these heterogeneously nucleated particles grew at the expense of the finer particles within the subgrains. This process is similar to, but not exactly what is referred to as coarsening or Ostwald ripening⁽¹⁵⁾, which is a growth of large particles distributed homogeneously. A cube root of time dependence is predicted⁽¹⁶⁾. A model which is more compatible with the present observations is based on the assumptions, 1) that precipitation is essentially complete by the time the aging

temperature is reached, and 2) that the finer matrix precipitate is dissolved as the nitrogen diffuses across the denuded zone to the larger subgrain boundary precipitates. As in Ostwald ripening, the completion of precipitation means that the volume fraction of precipitate is constant, so that the amount of precipitate removed from the subgrain interior is equal to the amount gained at the subgrain boundary. This maintains a fixed width of the denuded zone. Therefore, with a constant diffusion distance from the smaller to larger precipitates, the thickening rate of the sub-boundary layer will be constant.

This discontinuous coarsening model can be considered as a combination of a discontinuous precipitation process and a simple coarsening process. Aaronson and Clark⁽¹²⁾ observed in Al-Ag alloys initial linear growth of lamellae cells into a matrix in which continuous precipitation had occurred.

The activation energy reported in this work does not distinguish clearly the mechanism involved in this precipitation process. An activation energy for pearlite calculated from linear growth rates by Frye⁽¹⁷⁾ was found to be only slightly less than the accepted value for carbon diffusion in austenite. He attributed this to diffusion along an interface. In the present work the fact that the value obtained is much less than the commonly reported value⁽²⁾ of activation energy for nitrogen diffusion in niobium of 34,920 cal/mole can mean that other factors influence the growth besides the volume diffusion of nitrogen.

V. SUMMARY

This work is summarized as follows:

- 1) Linear growth rates of precipitate thickening at subgrain boundaries were experimentally determined.
- 2) From an Arrhenius equation, the growth rates yielded an activation energy of 5.6 kcal/mole, which is less than the accepted value reported for bulk diffusion of nitrogen in niobium. This is interpreted to mean that the simple discontinuous precipitation theory does not apply.
- 3) Results from electron microscopy suggested a coarsening process initiating at the subgrain boundary precipitates.
- 4) A discontinuous coarsening model is proposed. In this model the sub-boundary precipitates thicken by diffusion of dissolved nitrogen from the matrix, across a denuded region, to the larger subgrain boundary precipitates.

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