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DISCONTINUOUS COARSENING OF SPINODALLY DECOMPOSED Cu-Ni-Fe ALLOYS

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ABSTRACT

The coarsening behavior of two Cu-Ni-Fe alloys has been found to include a discontinuous reaction which originates at larger misorientation grain boundaries. Segments of these boundaries migrate at a rate depending on temperature and time and consume the semicoherent matrix spinodal, leaving behind larger irregularly shaped semicoherent particles in a cellular morphology. The combined influence of a dominant driving force (reduction in total interphase interfacial energy) and sluggish boundary migration rate promotes additional coarsening among the boundary-fed particles, wherein their effective interparticle spacing (λ_2) varies as $\lambda_2 = k_2 t^{0.7}$, compared to that of the matrix, $\lambda_1 = k_1 t^{0.34}$. In both cases the rate of coarsening is greater in the alloy of asymmetrical composition than in the symmetrical alloy. No satisfactory account of Cu-Ni-Fe discontinuous coarsening reaction kinetics can be made based upon current theories of thermally activated growth processes.

1. INTRODUCTION

Previous light optical metallography of overaged Cu-Ni-Fe alloys has revealed¹ the presence of a highly coarsened lamellar constituent at some grain boundary regions, suggestive of a cellular precipitation reaction. Evidence of preferential loss of coherency of the spinodal product in the vicinity of grain boundaries has also been reported.² The object of the present investigation was to characterize, using light optical and transmission electron microscopy, the nature of the grain boundary reaction (i.e. whether it is nucleation and/or growth controlled) with specific concern for its relationship with the previously existing spinodal product. An analysis of the kinetics of the coarsening reaction in these alloys after loss of coherency was also carried out.

2. EXPERIMENTAL PROCEDURE

The two alloys chosen for this study have compositions on a binary section through the Cu-Ni-Fe ternary which connects the Cu corner and the point $\text{Ni}_{0.7}\text{Fe}_{0.3}$ (see Fig. 1). The alloy compositions were determined by wet chemical analysis. They are (in atomic %):

Alloy A: 51.5 Cu - 33.5 Ni - 15 Fe

Alloy B: 69.3 Cu - 19.4 Ni - 11.1 Fe.

Both alloys were fabricated after the method of Livak and Thomas.⁴

Following their encapsulation in evacuated quartz tubing, samples were aged at 654°C, 748°C and 838°C for 10, 50, 100, 500 and 1000 hrs. and quenched by breaking the capsules under a solution of iced brine. Furnace temperature variation was $\pm 4^\circ$ over the entire aging period. An additional batch of specimens was cooled directly to the aging temperature (800°C and 840°C), held for 200 hours and 150 hours

respectively, and quenched.

Light optical metallographic specimens were etched in a solution of 10 g FeCl_3 , and 200 ml ethyl alcohol, diluted 50-95% with water to optimize phase contrast and minimize surface relief. The volume fraction (y) of the grain boundary constituent was determined by a systematic point count method⁵ using a 9-point square grid reticule at 500 $\times$. The maximum linear growth dimension (r) of the grain boundary product was also measured by means of a calibrated filar eyepiece.

Specimens for electron microscopy were jet polished in a nitric acid-methanol electrolyte. Difficulties encountered in this stage of the investigation included the low volume fraction of the grain boundary product and occasional preferential polishing of the Cu-rich phase, both of which required the preparation of an extremely large number of foils and the viewing of thicker foil regions.

The interparticle spacings or effective wavelengths (λ) of the coarsened spinodal alloys were obtained by direct measurement from enlarged micrographs, since the magnitude of λ was too large to be resolved in the reflections obtained by selected area diffraction.⁶ Selected area diffraction (S.A.D.) analysis was employed to establish the orientation relationships between the grain boundary product and contiguous grains. In a few cases, it was possible to determine the angle of misorientation across specific grain boundaries when suitable Kikuchi electron diffraction was encountered (e.g. three pairs of non-parallel Kikuchi lines⁷ or two spot-Kikuchi line pairs⁸).

Foil examination was performed on Siemens Elmiskop IA and Philips EM 301 electron microscopes (the latter equipped with a high angle tilt

stage), both operated at 100 kV. High voltage electron microscopy (Hitachi, 650 kV) was also employed in order to exploit its particular advantages⁹ in accurate selected area microdiffraction and penetration of foil areas not affected by preferential polishing.

3. RESULTS

3.1 Morphology

The grain boundary reaction product is visible in light optical micrographs only at substantial stages of development, and appears typically as shown in Figure 2 (alloy A, aged 500 hours at (a) 654°C (b) 748°C and (c) 838°C). Particle size and shape variations are visible among different cellular enclosures in (a) and within the same cellular constituent in (b). The extremely coarse structure evident at the grain boundaries in (c) is particularly interesting. Here the matrix particles have dimensions comparable to the cellular "lamellae" of the same alloy aged at lower temperatures (c.f. Figure 2(b)).

A significant increase in resolution of morphological detail is achieved with transmission electron microscopy (T.E.M.) and diffraction. For example, Figure 3 illustrates that both matrix and boundary particles are semicoherent. Detailed contrast analysis of the interfacial dislocations within the grain boundary product reveal that they have $\vec{b} = \frac{a}{2} 110$. This Burgers vector is identical to that found for interfacial dislocations in the matrix.¹⁰ Matrix particles located ahead of the reaction front are also seen in Figure 3 under kinematical diffraction conditions. They appear to extend continuously up to the boundary with no evidence of a denuded or "precipitate free" zone.

By combining both imaging and SAD modes it is found¹¹ that the grain boundary reaction product has the same crystallographic orientation as the grain from which it has grown. A second, although less conclusive, indication of this relationship is the appearance of the images when a single strong reflection is excited in the grain boundary vicinity, as in Figure 3. The cellular constituent and parent grain in these micrographs exhibit identical image characteristics. Hence the grain boundary reaction product is not completely enclosed by a structural discontinuity; a grain boundary is located only at the leading edge of the cell. Selected area diffraction analysis also reveals no apparent distinction in shape, intensity or position of spots arising from matrix and cellular particles, indicating that the large particles at the boundary are not heterogeneously nucleated in a discontinuous precipitation process, but rather form as the result of a migration of select grain boundaries.

Further evidence of boundary migration is presented in the composite micrograph of Figure 4. The region of the lower "border" of the large cell (shown at upper left of the figure) is illustrated in detail for two operating $\bar{g}$'s (particle "A" is marked for identification). It is seen that in fact there is no grain boundary located at this edge of the cell, but a transition in particle size due to the passage of the boundary is clearly evident. An equal density of misfit dislocations at the interfaces of both matrix and boundary particles is also illustrated.

Attempts at correlating the tendency for boundary migration with angle of grain misorientation remain inconclusive due to the relatively few number of quantitative measurements obtained. It is generally

observed, however, that low angle boundaries appear to be unaffected by the grain boundary reaction, and that the maximum measured angle of misorientation for a stationary boundary is $\sim 5.2^\circ$ in this study. Coherent twin boundaries are also stable with respect to migration of the type described above, although some irregularity of the boundary plane occurs in well-coarsened structures.¹¹

3.2 Reaction Kinetics

The temperature and time dependence of y and r are shown in Figure 5. In all cases the rate of growth (G) of the grain boundary constituent, given by the slope of the curves is slightly greater for the asymmetrical (B) than the symmetrical alloy (A). The pronounced curvature of these graphs indicates that the grain boundary reaction is subject to a time-dependent driving force and/or activation energy over all temperatures for both alloys. The temperature dependence of the growth rate follows a behavior typical¹⁵ of cellular precipitation reactions. G initially increases with temperature, peaks at a maximum value, and then decreases to zero as the solvent temperature is approached. From a plot of the instantaneous values of $\frac{dr}{dt}$ at constant time against the reciprocal absolute aging temperatures, an activation energy for boundary migration of order 20 kcal/mole is suggested for the initial stages of the lower temperature reaction. This value then steadily decreases as the reaction proceeds.

The results of a quantitative T.E.M. study of the relative coarsening behavior of matrix and boundary particles at a single temperature (654°C) are presented in Figure 6. The effective interparticle spacings (λ_1) characteristic of the matrix closely obey the empirical relationship

$$\lambda_1 = k_1 t^{0.34} \quad (1)$$

for both alloys A and B, where

$$k_1^B > k_1^A \quad (2)$$

The values of the interparticle spacings in the boundary region (λ_2) are also time dependent, and in spite of a relatively large scatter, their averages fit the kinetic description

$$\lambda_2 = k_2 t^{0.7} \quad (3)$$

for both alloys, where again

$$k_2^B > k_2^A \quad (4)$$

4. DISCUSSION

4.1 Nature of the Grain Boundary Reaction

4.1.1 "Discontinuous Coarsening"

In response to the aging treatments employed in this study the Cu-Ni-Fe spinodal product assumes for the most part a coarsened "particle" morphology rather than the characteristic composition "modulations" identified by their respective wavelengths. At this advanced stage in the aging sequence the outstanding morphological distinction between particles comprising the matrix and cellular constituent is their relative size. On this basis alone, the boundary migration process displays traits of a coarsening phenomenon.

At the 654°C and 748°C aging temperatures, both the alloys investigated lie within the spinodal. Butler and Thomas⁶ have shown that the symmetrical alloy reaches equilibrium by a spinodal mode within 1 hour at 625°C, while Livak and Thomas⁴ determined that this condition is attained in an asymmetrical alloy after 10 hours at 625°C. Hence, since spinodal decomposition will have relaxed all supersaturation (i.e. the

alloys will have reached their equilibrium tie-line compositions) within a 10 hour upper limit, the chemical component of the driving force for any further growth, including the grain boundary reaction, should be effectively zero. The compositions of particles on either side of the reaction front are identical, and the failure of selected area diffraction analysis to reveal any differences between matrix and boundary particles supports this conclusion.

The images (Figures 3 and 4) of both particle types are also similar, and significantly, the particles are found to possess the same state of coherency. This observation further verifies the absence of any chemical driving force derived from a change in particle coherency. Also, since the strain fields associated with the semicoherent matrix particles are localized at their interfaces,¹³ the boundary migration process receives no impetus from the reduction of long range matrix coherency strains. The occurrence of a grain boundary reaction after 10 hours aging time (in this case, continuing up to 1000 hours) must therefore necessarily result from the dominance of the interfacial energy component of the driving force for further growth. Hence, by the displacement of those grain boundaries comprising the reaction fronts, the overall interfacial energy at two phase boundaries is reduced in a coarsening process which favors the growth of the large boundary structures at the expense of the smaller matrix particles.

The discontinuous nature of the grain boundary coarsening reaction in Cu-Ni-Fe has its origin in the difference in particle sizes produced by passage of a suitable reaction front. Its primary distinction from the more familiar discontinuous reactions¹⁴ is the absence of a nucleation event. In this respect, the Cu-Ni-Fe reaction is set apart

as "discontinuous growth," or, with specific reference to the driving force for the reaction, "discontinuous coarsening." Similar reactions have been reported in a number of eutectoid and discontinuous precipitation systems, and the term "discontinuous coarsening" was first applied by Livingston and Cahn¹⁵ to describe the related phenomena.

4.1.2 Role of Grain Boundaries

The selectivity of grain boundaries which enter into the coarsening reaction would appear to be based on those observed properties which characterize discontinuous coarsening: (1) a high grain boundary diffusivity (D_B), and (2) a potentially high grain boundary mobility. The results of the present study suggest that augmented solute diffusion along specific grain boundary regions where D_B is high leads to preferential coarsening of the spinodal product. At about the time the matrix spinodal loses coherency, these boundary particles are sufficiently large to sense the presence of smaller matrix particles and proceed to coarsen in cooperation with the assisting mobile grain boundary. The reaction then assumes a "cellular" morphology. The absence of a denuded zone ahead of the boundary emphasizes the necessity of boundary migration in providing sufficient solute for the discontinuous coarsening reaction. Preliminary results on grain misorientation⁸ correlations also indicate that the Cu-Ni-Fe discontinuous coarsening reaction ceases at a lower threshold value of θ , but more empirical data is required to quantitatively predict the misorientation of the favored boundaries.

4.2 Coarsening Kinetics

4.2.1 Matrix Particle Coarsening

The empirical growth kinetics determined in this study for the semicoherent spinodal product are consistent with the theories of Lifshitz and Slyozov¹⁶ and Wagner¹⁷ on the diffusion controlled coarsening of spherical particles in an isotropic medium. A $t^{1/3}$ behavior has also been reported previously^{4,6} for coarsening of the coherent Cu-Ni-Fe spinodal over a range of temperatures, the activation energy for which is identified⁶ with the activation energy for volume diffusion. It is found by comparison with these earlier results that the empirical rate constant (k_1) increases after coherency is lost, a behavior which Butler and Thomas⁶ speculated might exist due to a modification of particle interfacial energy as a result of the misfit dislocation structure.

In a theoretical description of the coarsening of spinodal alloys Cahn¹⁸ concluded that, at least during the early stages of particle coarsening, asymmetrical alloys will tend to coarsen more rapidly than symmetrical alloys. The observation that $k_1^B > k_1^A$ in the present study verifies that this behavior persists even at the latter stages of aging.

4.2.2 Boundary Particle Coarsening

The data presented in Fig. 6 indicates that as a result of boundary migration, particles in the vicinity of a mobile high angle grain boundary undergo (1) a discontinuous change in particle size with respect to the "matrix", and (2) a continuous coarsening process in conjunction with other boundary-fed particles, the kinetics of which follow a $t^{0.7}$ rate law. No theories currently known to the authors treat

specifically this phenomenon, which is complicated by two distinguishing features.

The first of these features is the interconnectivity of the high angle grain boundaries forming the reaction fronts and the semicoherent particle interfaces which they border. As a result, the entire cellular structure in the Cu-Ni-Fe grain boundary reaction is potentially susceptible to very rapid solute redistribution. The second feature is the mobility of the reaction front. At the earliest stages of growth of the cellular constituent, an activation energy of ~20 kcal/mole is suggested from the boundary migration data. After the addition of 10 kcal/mole indicated by Hillert at al³ to account for the temperature dependence of the free energy change, the resultant is roughly 45% of the 66 kcal/mole activation energy for volume diffusion.¹⁹ This figure is within the range anticipated for grain boundary diffusion control, and indicates that initially the boundary is free to move as rapidly as permitted by solute diffusion along its interface. Subsequent reduction in the magnitude of this value is a measure of the increasing difficulty of boundary motion and therefore an effective change in rate controlling mechanism at the onset of the reaction.

A quantitative model of discontinuous coarsening by Livingston and Cahn¹⁵ predicts a variation in boundary velocity as $\lambda_2^{-2} \lambda_1^{-1}$. Although there is rough agreement with this result in Figures 5 and 6, it breaks down appreciably at longer aging times. Based upon the characteristics of other discontinuous reactions,^{17,18} a constant boundary migration rate at a given temperature produces a constant interparticle spacing within the cellular constituent. It therefore

follows that the coarsening of the Cu-Ni-Fe cellular constituent is related to the progressively decreasing boundary migration rate observed in these alloys (see Fig. 5(b)). Furthermore, if the migrating boundary is subject to "pinning" effects, their origin is not clear. Some irregularities in the reaction front are arrowed in Figure 3; however, the retarding influence of this surface tension effect should decrease as the reaction proceeds, since there will be fewer boundary cusps with larger particle size.

On the basis of Fig. 2(c), the driving force for the Cu-Ni-Fe discontinuous coarsening reaction remains unaltered throughout the aging process. This micrograph demonstrates, based upon the relative size of the "matrix" particles (c.f. Fig. 2(b)), that sufficient driving force exists even to initiate a "secondary" grain boundary reaction, should the first go to completion. A comparison of Figs. 5(a) and (b) furthermore shows that in some instances (e.g. alloy B aged at 748°C) boundary migration has ceased at a specific value of maximum displacement, while the volume fraction of the discontinuously coarsened material increases. The above findings together suggest a time dependent activation energy for boundary migration rather than a time dependent driving force for the coarsening reaction. Hence the $t^{0.7}$ coarsening kinetics of the grain boundary constituent appear to be associated with the migration characteristics of the high angle grain boundary forming the reaction front. The inability to specify

exactly the rate controlling mechanism is a result of the complexity of the reaction and the difficulties of obtaining the experimental data.

5. SUMMARY AND CONSLUSIONS

As a result of this investigation of two Cu-Ni-Fe alloys during coarsening, the following characteristics have been discerned:

1. Certain grain boundary regions of relatively large grain misorientation promote enhanced growth of the decomposition products which they border.
2. After loss of coherency of the matrix spinodal, a number of these boundary segments migrate, and, in the role of reaction fronts, leave behind large irregularly shaped semicoherent particles with the appearance of a cellular morphology.
3. The rate of boundary migration (G) initially suggests grain boundary diffusion control (654°C), but decreases progressively with aging time. G undergoes an increase, peaks at a maximum, then decreases to zero as the temperature is increased to the solvus value.
4. The driving force for the grain boundary reaction is the reduction in overall interphase interfacial energy, hence it is appropriately a "discontinuous coarsening" reaction.

5. The effective interparticle spacings (λ_1) of the semicoherent matrix spinodal product (654°C) vary with time according to the empirical rate law

$$\lambda_1 = k_1 t^{0.34}$$

The asymmetrical alloy (B) coarsens at a more rapid rate than the symmetrical alloy (A) and the magnitude of the rate constants for both alloys is greater than that observed² for the coherent spinodal product.

6. Within the cellular constituent, the effective interparticle spacing (λ_2) of the discontinuously coarsened (654°C) particles obey a kinetic law of the form

$$\lambda_2 = k_2 t^{0.7}$$

where again the rate constant (k_2) of the asymmetrical alloy is greater than that of the symmetrical alloy.

7. The growth kinetics of the discontinuously coarsened particles are not suitably explained in currently available theory, and the rate controlling mechanism for the reaction is tentatively associated with boundary migration.

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FIGURE CAPTIONS

- Fig. 1. Cu-Ni_{0.7}Fe_{0.3} quasi-binary section studied in this research, with the indicated solubility limit, spinodal, and alloy compositions. The position of the chemical spinodal is that calculated in reference 7, and is very near to the experimentally determined curve, which has its extremum at ~53% Cu.⁷
- Fig. 2. Light optical micrographs of alloy A aged for 500 hrs at (a) 654°C, (b) 748°C and (c) 838°C. The radically coarsened matrix particles shown in (c) have dimensions comparable to the cellular lamellae in (b). Note also the extremely coarse boundary structure in (c).
- Fig. 3. Transmission electron micrograph of alloy A aged 1000 hrs at 654°C. The grain boundary constituent has the appearance of cellular growth in the direction of the arrow indicating the operating reflection. Note also the appearance of cusps at the (arrowed) positions of the boundary particle interphase interfaces, [110] zone, B.F.
- Fig. 4. T.E.M. evidence that the cellular reaction is the result of grain boundary migration. The lower "border" of the cell at the upper left is shown at two reflection conditions (see particle "A" for identification) to have no boundary structure at all. Boundary migration has caused a discontinuous increase in particle size, where both matrix and boundary particles have identical interfacial dislocation structures. Alloy B, aged 500 hrs at 748°C, B.F., [110] zone.

Fig. 5. Summary of the light optical metallographic data on (a) the volume fraction (y) of discontinuously coarsened material and (b) the maximum boundary displacement (r) during the discontinuous reaction in alloys A and B at 654°C, 748°C, and 838°C.

Fig. 6. Plot of the interparticle spacing of matrix (λ_1) and boundary (λ_2) particles as a function of aging time at 654°C for (a) alloy A and (b) alloy B.

XBL 747-6725

Fig. 1.

-19-

(XBB 746-4112)

Fig. 2.

Fig. 3.

(XBB 746-4114)

Fig. 4.

XBL 747-6797

Fig. 5(a).

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XBL747-6796

Fig. 5(b).

XBL 747-6728

Fig. 6(a).

XBL 747-6 729

Fig. 6(b).

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