SPINODAL DECOMPOSITION IN AGE HARDENING COPPER–TITANIUM ALLOYS*

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The early stages of spinodal decomposition in age hardening Cu–Ti alloys have been studied by electron microscopy. The alloys (1.55, 3.08 and 5.17 w/o Ti) decomposed on the quench from solutionizing temperatures into Ti enriched and Ti lean regions. Superlattice reflections, at $\frac{1}{5}\{420\}_m$ positions as well as $\frac{1}{2}\{210\}_m$ reflections were observed in the diffraction patterns of the as quenched 5.17 w/o Ti alloy. The alloys continued to decompose when aged at elevated temperatures. A sequence of microstructures was used to show that continuous phase separation, and hence spinodal decomposition, was the mechanism of decomposition. The metastable two phase structure which formed from the spinodal process was aligned and periodic from the start of the process. The Ti enriched phase was ordered, with the $D1a$(Ni$_4$Mo; 14/m) structure. Reversion experiments were performed to determine the position of the coherent metastable solvus. When aging treatments were performed near this solvus, heterogeneous nucleation of the metastable phase was observed.

DECOMPOSITION SPINODALE D'ALLIAGES CUIVRE–TITANE DURCIS PAR VIEILLISSEMENT

On a étudié en microscopie électronique les premiers stades de la décomposition spinodale des alliages Cu–Ti durcis par vieillissement. Les alliages (1,55, 3,08 et 5,17% Ti en poids) se décomposent par trempe à partir des températures de la solution solide en régions riches et en régions pauvres en titane. Des réflexions, aux positions $\frac{1}{5}\{420\}_m$ et $\frac{1}{2}\{210\}_m$, sont observées dans les diagrammes de diffraction de l'alliage à 5,17% en poids brut de trempe. Les alliages continuent de se décomposer si on les vieillit à hautes températures. Un série de micrographies montre que le mécanisme de la décomposition est une séparation continue des phases, et donc le processus de décomposition spinodale. La structure diphasique métastable qui se forme par le mécanisme de décomposition spinodale est alignée et périodique dès le début du processus. La phase riche en Ti était ordonnée, avec la structure $D1a$(Ni$_4$Mo; 14/m). Des expériences de réversion ont été faites pour déterminer la position du solvus cohérent métastable. Lorsque le vieillissement est fait au voisinage de ce solvus, on observe une germination hétérogène de la phase ordonnée métastable.

SPINODALE ENTMISCHUNG IN GEALTERTEN KUPFER–TITAN-LEGIERUNGEN

Die Anfangsstadien der spinodalen Entmischung in gealterten Cu–Ti-Legierungen wurden elektronenmikroskopisch untersucht. Die Legierungen (1,55, 3,08 und 5,17 w/o Ti) entmischen sich beim Abschrecken von der Lösungstemperatur in Ti-reiche und Ti-arme Bereiche. In den Beugungsbildern der abgeschreckten 5,17 w/o Ti-Legierung beobachtet man bei $\frac{1}{2}\{210\}_m$ und $\frac{1}{5}\{420\}_m$ Überstrukturreflexe. Die Legierungen entmischen sich weiter beim Altern bei höheren Temperaturen. Mit Hilfe einer Reihe verschiedener Mikrostrukturen wurde gezeigt, daß kontinuierliche Phasentrennung und somit spinodale Entmischung als Entmischungsmechanismus wirken. Die in diesem spinodalen Prozeß gebildete metastabile Zweiphasenstruktur ist von Prozeßbeginn an ausgerichtet und periodisch. Die Ti-reiche Phase ist geordnet und besitzt $D1a$(Ni$_4$Mo; 14/m)-Struktur. Mit Hilfe von Reversionsexperimenten wurde die Lage des kohärenten metastabilen Solvus bestimmt. Führt man in der Nähe dieses Solvus Alterungsbehandlungen durch, so beobachtet man eine heterogene Keimbildung der metastabilen Phase.

1. INTRODUCTION

Age hardening in alloys occurs as a consequence of the formation of precipitate phases. In many alloy systems, there is a succession of different precipitate phases at a given temperature and this succession may be different for different temperatures and alloy compositions. The ultimate crystal structure should be the equilibrium one. Some crystal structures in the succession may correspond to thermodynamically metastable phases and as a result may persist for some time. However, no precipitate morphology is ever carried to full metastable or stable equilibrium since all morphologies having more than one pre-cipitate particle are at least unstable with respect to coarsening. Thus, age hardening is a continuing sequence of dynamic processes which may be classified according to the dominant structures present and processes occurring.

We report herein results of a study of age hardening processes in copper base titanium alloys leading to the formation of a metastable precipitate phase with tetragonal symmetry. This phase is responsible for peak hardening and persists for long periods of time before and after.[1] The details of the steps by which this phase arises have been the subject of several studies with conflicting results.

Buckle and Manenc[1] were the first to show that copper titanium alloys belong to the class of 'sideband alloys.' They concluded that the copper titanium alloys decomposed in the following sequence.

(1) A so called pre-precipitation stage where the sidebands first became apparent by X-ray diffraction techniques. The resistivity of the specimen decreased during this stage, and the hardness increased.

Because the intensity and position of the sidebands were found to vary asymmetrically with time, they concluded that the sidebands arose from isolated complexes within the matrix.

(2) Formation of a metastable precipitate of tetragonal symmetry with $c/a = 0.980$, when indexed according to the original face-centered cubic lattice. No superlattice reflections were found. However, they only looked near the positions in reciprocal space corresponsing to the $\{100\}_m$ and $\{110\}_m$ planes of the supersaturated matrix, where we now know no superlattice reflections occur.

(3) Formation of the equilibrium Cu_3Ti phase. Cornie et al.[2] were the first to publish detailed electron microscopy results of the first stages of decomposition in Cu–Ti alloys. When aging occurs well below the metastable solvus, the second phase is aligned along the $\langle 100 \rangle$ directions, and is periodically spaced.[2,3] They showed that the "net matrix strain contrast . . . exhibited a primary displacement vector R, principally along $\langle 100 \rangle$." This is similar to the work of Thomas[4,5] and coworkers on the early stages of spinodal decomposition in Cu–Ni–Fe alloys. Cornie et al. concluded that the Cu–Ti alloy decomposed by the spinodal mechanism into two disordered f.c.c. phases. The Ti rich regions afterwards transform in situ to a disordered tetragonal transition phase. No superlattice reflections were reported.

Hakkarainen[3] also has reported that the transformation may occur by spinodal decomposition, particularly if the supersaturation is high, but he does not rule out nucleation and growth. He reported for the first time that the precipitate crystal structure becomes $D1a(14/m, Ni_4Mo)$ after some aging.

The electron microscopy work of Knights and Wilkes[6] confirms the general features reported by Cornie et al.[2] and Hakkarainen,[3] and they also found that the metastable phase became ordered but indexed it as $L1_2(Pm3m;\ Cu_3Au)$. However, we have shown[7] that this assignment is incorrect.

The $D1a$ structure is a crystallographic derivative of the f.c.c. (A1) structure. Such a phase can form continuously from the supersaturated solid solution of titanium in copper without losing coherency with the matrix, and could be an example of the formation of a tetragonal structure from a cubic one by means of a continuous transformation.

The prior literature thus suggests that here is a precipitation system in which an ordered precipitate might form by a spinodal mechanism. The theoretical aspects of such a process have recently been considered by Richards[8] in which he concluded that while both spinodal and ordering could occur in the same alloy

simultaneously, one process had to precede the other at least partially.

There exists considerable controversy in the literature on what criteria may be used to prove that spinodal decomposition has occurred in a given alloy.[9] The work of Ardell and Nicholson[10] showed that the presence of periodic and aligned two phase mixtures are not necessarily unique to the spinodal mechanism. The Ni–Al alloys they studied developed a periodic and aligned array of particles subsequent to apparent random nucleation.

If the exact position of the thermodynamically defined spinodal were known on the phase diagram, there would be no problem, since spinodal decomposition must occur when an alloy is held below it. Unfortunately, it is very difficult to determine accurately the spinodal of a system such as Cu–Ti. A direct calculation of the necessary thermodynamic functions from first principles is not feasible for any system that is not ideal, while extrapolation from known thermodynamic data may not be allowable when one of the phases which forms is ordered.[11] The root three rule, derived by Cook and Hilliard,[12] is a poor approximation, and the assumptions behind it have been called into question. Furthermore, it cannot be used in the Cu–Ti system because the shape of the metastable miscibility gap is not yet known past 6.5 a/o Ti. (see Section 3.2).

In order to overcome these shortcomings a new method for determining if spinodal decomposition has occurred was developed in this investigation. This method uses evidence obtained from a sequence of electron micrographs to prove that the system is decomposing spinodally (see Section 3.1).

2. EXPERIMENTAL PROCEDURES

2.1 Preparation of the alloys

Strips of three high purity copper–titanium alloys were provided by the Kennecott Copper Corporation. The alloys had been made by first vacuum induction melting the copper and holding the temperature at 1150°C. Additions of titanium were made after the furnace was back filled to $\frac{1}{3}$ atm of purified argon. The alloys were cast in 2.54 cm dia. calcia stabilized zirconium crucibles.

The as-cast samples were repeatedly cold-rolled and recrystallized (at 900°C in an argon atmosphere) until strips 0.3 mm thick were obtained.

Wet chemical analyses were performed on the alloys for titanium content, as well as spectrographic analyses for oxygen content. The alloys were found to be 1.55, 3.08 and 5.17 w/o Ti(2.07, 4.05 and

6.77 a/o). All alloys had less than 130 ppm (weight) of oxygen.

2.2 *Solution treatment*

Strips of the alloys (2.54 × 1.27 × 0.3 mm) were solution treated in a vertical tube rapid quench furnace in flowing argon at 900°C for 1 hr. This resulted in grain sizes of ASTM 1. The strips were suspended in the hot zone by a tube which was connected to a gas reservoir, at a pressure of 160 bar. The pressure could be released by a pair of electrically activated valves, forcing the strips down the furnace, through an aluminum foil membrane (25 μm) into a water quench bath. The estimated quenching rate was from 5000 to 10,000°C/sec.[13] The specimens were then stored in liquid nitrogen until aging.

2.3 *Aging treatments*

Discs 3 mm in dia. were punched from solution treated strips that were quenched into iced brine. For aging times up to 10 min three methods of subsequent heat treatment were used. For temperatures up to 550°C the discs were wrapped in 25 μm copper foil, placed in liquid salt for various times and quenched into iced brine. The 400°C time sequence was repeated by hot-quenching into the salt bath directly from the solution treating temperature. These specimens are shown in Fig. 4 and did not differ significantly from those obtained by the other method. Above 550°C the specimens were wrapped in 75 μm stainless steel foil and heat treated in liquid lead. Before immersion the foil package was dipped in oil and graphite powder to reduce the adherence of lead to the foil.

Specimens aged longer than 10 min were encapsulated in quartz with an argon atmosphere. Agings at temperatures less than 550°C were done in liquid salt while those above 550°C were done in furnaces. In all cases, the temperatures were monitored, and varied less than ± 5°C.

2.4 *Electron Microscopy*

(a) *Sample preparation.* The specimens were mechanically polished with 600 grit polishing paper. Care was taken to keep the samples well lubricated, and hence, cool. They were then thinned in a twin-jet electropolisher obtained from Fischione, Inc.,[14] using a $\frac{1}{3}$ nitric acid and $\frac{2}{3}$ methyl alcohol electrolyte at -50°C and with the cell voltage at about 15 V. The cathode was platinum.

(b) *Electron microscopy.* Two electron microscopes were used in the course of the investigation, a JEM-7

and a Siemens 101A. The JEM-7 was equipped with a tilt–rotate stage, with tilting capabilities of ± 30° and an electromagnetic beam deflection system for expediting dark field microscopy.

The Siemens 101A was equipped with a double tilt stage, with tilting capabilities of ± 24° and an electromagnetic beam deflection system. The objective astigmatism could be corrected on each sample by observing the structure that exists at the edge of the foil at extremely high magnifications (4.0 million times with binoculars). When optimally stigmated, the structure is equiaxed. The line-to-line (lattice image) resolution on the Siemens 101A was found to be better than 2A (0.2 nm), when using the double tilt specimen holder.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Below, the experimental results on the formation of the metastable ordered phase are presented and discussed. The initial reaction is spinodal decomposition which begins during the quench from solutionizing temperatures and continues during the early stages of aging. The titanium-enriched clusters of the earliest observable stages of decomposition in the 5.17 w/o Ti alloy are shown to be partially ordered. However, no evidence of ordering was found in the as-quenched 3.08 w/o Ti alloys. The clusters undergo a complex ordering sequence, leading to the persistent metastable $D1a$ precipitate. The metastable coherent solvus for the $D1a$ phase was found by reversion experiments on three alloys. Heterogeneous nucleation is shown to occur when the alloy is aged near the metastable solvus.

3.1 *Spinodal decomposition*

(a) *As quenched alloys.* The microstructure observed by transmission electron microscopy of a 5.17 w/o Ti alloy in the as-quenched condition is shown in Fig. 1. The wavy contrast which is perpendicular to the operating **g** in Fig. 1(a) is similar to that which has been observed in other systems which decompose spinodally.[4,5] Figure 1(b) shows that a cross-hatch type microstructure is observed when the operating **g** is such that $\mathbf{g} \cdot \mathbf{R} \neq 0$ for two of the $\langle 100 \rangle$ displacement vectors associated with the composition modulations. The contrast arises from a phase displacement of the diffracted electrons caused by the net strain induced by the composition modulations.[5] No distinct particles could be observed this early in the transformation by high resolution electron microscopy techniques.

A selected area diffraction pattern of an as-quenched sample is shown in Fig. 2(a). Satellites are observed

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(a)
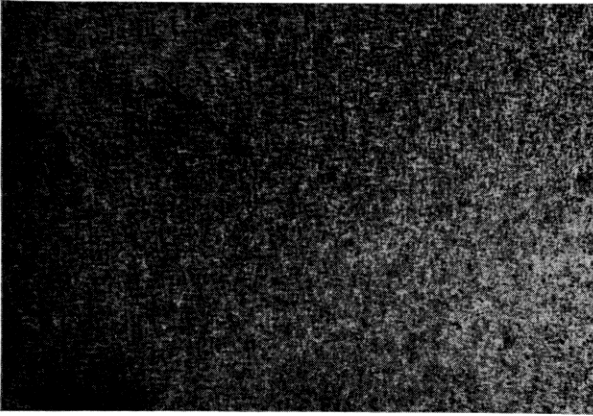
(b)

Fig. 1 (a). Bright field electron micrograph of a Cu–5.17 w/o Ti as-quenched specimen. **g** = (200), [011] foil normal. (b) Bright field electron micrograph with **g** = (11$\bar{1}$), [011] foil normal. Note how the contrast depends on the operating **g**.

along the [100]* direction around the (h00) fundamental diffraction spots. Sometimes the direct beam is observed to have satellites, but these are due to double diffraction as they can be made to disappear by tilting the sample slightly.[3]

The diffraction patterns for the as quenched 5.17 w/o Ti alloy also showed faint superlattice reflections at the $\frac{1}{2}\{210\}_m$, $\frac{1}{5}\{420\}_m$ and equivalent positions. (See Fig. 2(b); also shown schematically in Fig. 3.) Thus, for the 5.17 w/o Ti alloy the ordering reaction begins during the quench. On the other hand, no evidence of ordering could be found in the as-quenched 3.08 w/o Ti samples, although satellite reflections were prominent.[15] The alloys therefore apparently begin to decompose into Ti enriched and depleted regions before the ordering reaction occurs in the enriched regions.

(b) *The early stages of aging the 5.17 w/o Ti alloy: aging at 400°C—the microstructural sequence method.* The effect of short time agings at 400°C on the microstructure of the 5.17 w/o Ti alloy is shown in Fig. 4. The plane of the micrograph and operating **g** in each case are (011) and (200) respectively. Furthermore, s, the deviation parameter was slightly positive for all photographs. The wavelength of the modulations initially remains at about 55A (5.5 nm), as measured from the spacings of the satellites shown in each of the diffraction patterns. This can also be seen from the microstructures. However, aging for ten minutes resulted in an increase in the modulation wavelength to 65A (6.5 nm). This and further
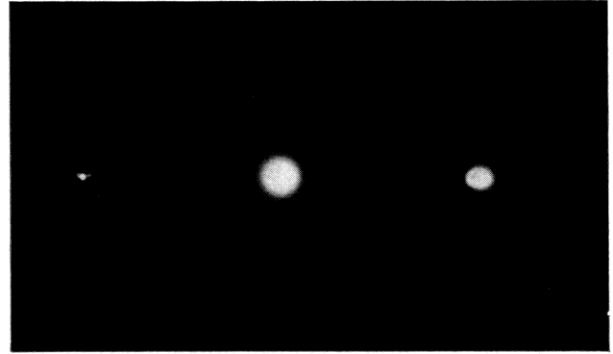
(a)
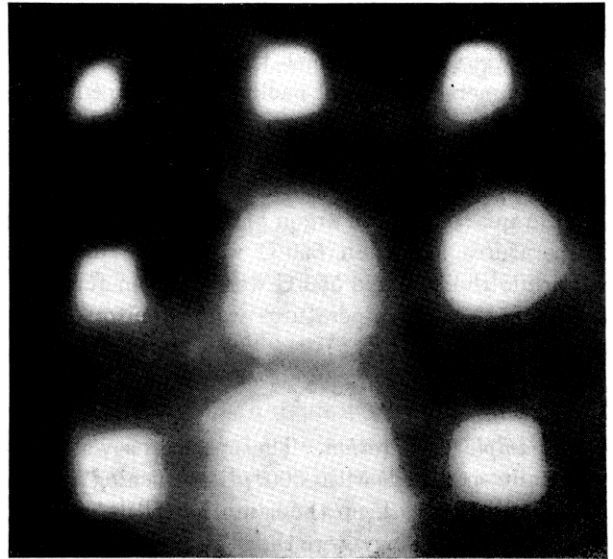
(b)

Fig. 2 (a). Selected area diffraction pattern of an as-quenched Cu–5.17 w/o Ti alloy. (b) An electron diffraction pattern of a Cu–5.17 w/o Ti as-quenched specimen. The pattern was overexposed with respect to the matrix reflections to detect the faint superlattice reflections at and near all equivalent $\frac{1}{2}\{2\bar{1}0\}_m$. See Fig. 3.
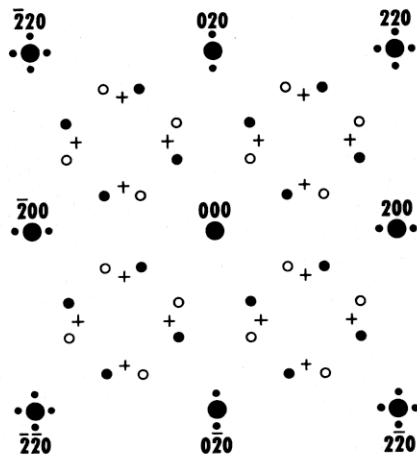
FIG. 3. Schematic of the [001] diffraction patterns shown in Fig. 2. Positions of the satellite spots are not to scale. The open and filled circles represent the superlattice reflections of two variants of the $D1a$ structure at all equivalent $\frac{1}{5}\{420\}_m$, and the crosses are at all equivalent $\frac{1}{5}\{210\}_m$ positions.

coarsening appeared to follow the well known $\Lambda^3 - \Lambda_0{}^3 = kt$ law,[15] where Λ_0 and Λ are the initial and current spacing at time t and k is a temperature dependent constant.

All three micrographs in Fig. 4 were taken with identical diffraction conditions, and the wavelength of the modulation is the same in each photograph, yet the strain constant shown in Fig. 4(c) is stronger than that shown in 4(b), which is likewise stronger than that shown in 4(a). The strain contrast of the microstructure shown in each micrograph represents the maximum attainable for the given aging treatment. Any slight deviation in the diffracting conditions would decrease the contrast. This enhancement of maximum observed strain contrast at constant wavelength must be due to an increase in the average amplitude of the modulations present within the sample. Put in other terms, the Ti enriched regions are increasing in Ti composition. But an increase in Ti content at constant modulation wavelength implies that uphill diffusion is taking place. In a binary, this can only happen when the alloy is being aged within the spinodal. Thus, the increase in strain contrast observed at constant wavelength during aging at 400°C satisfies the thermodynamic conditions sufficient to prove unambiguously that the reaction is taking place spinodally.
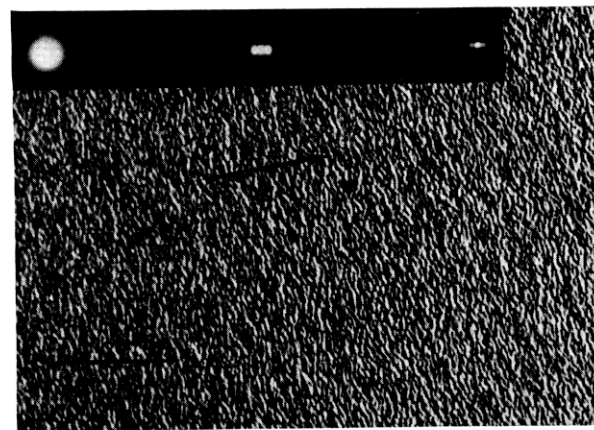
This technique, which we call the microstructural sequence method, uses microstructural observations to show that the diffusion coefficient ($\tilde{D}$) is negative. However, any experiment that shows that $\tilde{D}$ is negative in a binary is sufficient to prove that the spinodal has been crossed. For example, Rundman
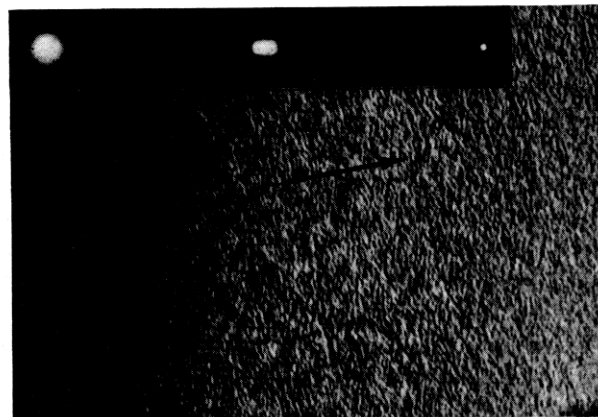
(a)
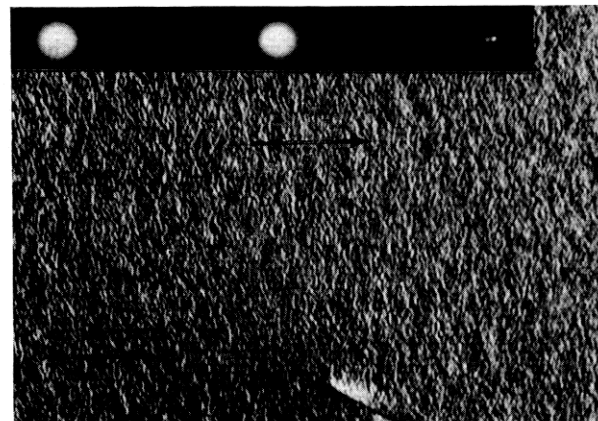
(b)

(c)

FIG. 4. Electron micrographs of the 5.17 w/o Ti alloy aged at 400°C for various times. In all cases $g = (200)$, [011] foil normal. The (000), (200) and (400) reflections are included at the top of each micrograph. Note the constant spacing of the satellites flanking the (400) reflection. (a) 10 sec; (b) 1 min; (c) 5 min.

and Hilliard[16] have used small angle X-ray scattering data to show that $\tilde{D}$ was negative in an Al–22 a/o Zn alloy, and prove that the alloy decomposed spinodally.

Caution must be observed, however, in the use of the microstructural sequence method. The strain contrast must be associated with compositional modulations, that is, the technique must prove that phase separation has occurred. This is clearly the case in Cu–Ti, as evidenced by the observation of $\langle 100 \rangle^*$ satellites in reciprocal space. However, the $\langle 110 \rangle$ tweed[17] observed in many systems is not associated with compositional modulations in the $\langle 110 \rangle$ directions, and therefore cannot be used to demonstrate that phase separation has occurred.

The theory of spinodal decomposition in elastically anistropic cubic systems predicts periodicity and alignment of modulations early in the transformation.[18] Since the only system which has been shown to produce periodicity and alignment without spinodal decomposition did so late in the transformation process[10] (during coarsening[19]), we can conclude that periodicity and alignment from the start of a transformation is a strong indication of spinodal decomposition.

The microstructures shown in Fig. 4 are precisely those predicted by theory. Furthermore, as can be seen from the micrographs, coarsening has not yet begun. This evidence confirms that the alloy is decomposing by the spinodal mechanism.

We suggest that the microstructural sequence method is a direct and simple method of proving whether or not spinodal decomposition is occurring. It suffices by itself, and should be easy to use in those systems in which it is possible to quench the single phase alloy and prevent the decomposition from going too far. The Cu–Ti system meets this criterion up to and including the 5.17 w/o alloy. All that is needed is to demonstrate an isothermal time sequence in which the modulations increase in composition difference at constant spacing.

Figure 5 is the electron diffraction pattern for the 5.17 w/o Ti alloy aged for 10 sec at 400°C (Fig. 4a). It was overexposed to detect the presence of faint superlattice reflections. The superlattice reflections are more intense than those in the as quenched sample (Fig. 2b) but still were not visible on the screen of the microscope. The schematic shown in Fig. 3 describes the indexing of the superlattice reflections.

The $\frac{1}{5}\{420\}_m$ reflections can be indexed as the $D1a$ structure (Ni$_4$Mo; $14/m$). The $\frac{1}{2}\{210\}_m$ reflections could be due to the presence of a phase with the symmetry of the $L1_0$, $m = 1$ (14_1amd) structure.
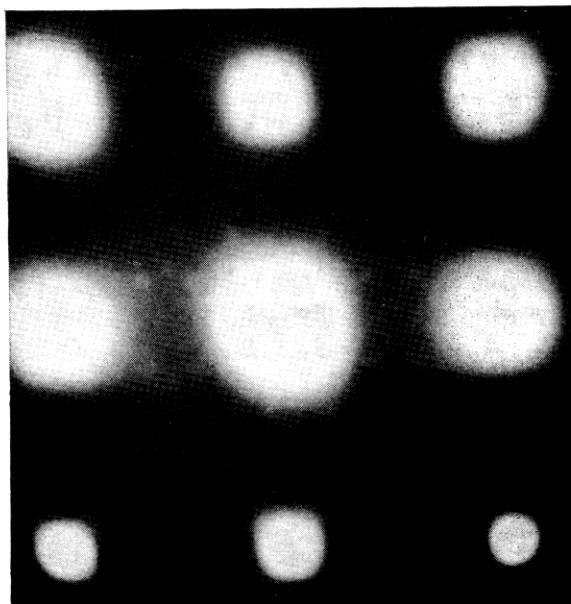

FIG. 5. Electron diffraction pattern of a 5.17 w/o Ti alloy aged at 400°C for 10 sec. Compare with Fig. 3.

Both structures are derivatives of f.c.c. and have the expected orientation relationships and all the expected variants. The $L1_0$, $m = 1$ reflections occur early and disappear, while the $D1a$ reflections grow in intensity. After 10 min at 400°C the $\frac{1}{2}\{210\}_m$ reflections disappear, indicating that the titanium rich particles belong now unambiguously to the $D1a$ phase.

It appears then, that spinodal decomposition occurs first, followed by and concomitant with the ordering reactions.

Aging at 450°C

The rate of decomposition greatly increased when the alloy was aged at 450°C. Figure 6(a) shows the microstructure of the 5.17 w/o Ti alloy which was aged for 15 sec at 450°C. The strain contrast is nearly uniform throughout the photograph, indicating that the spinodal reaction is nearly complete. The diffraction pattern (Fig. 6b) displays only the $\frac{1}{5}\{420\}_m$ type superlattice reflections, which correspond to the $D1a$ structure.

Extra reflections can be seen in the diffraction pattern (Fig. 6b) along the $\langle 110 \rangle^*$ directions. These are also present in Fig. 5. They can be indexed as the $\{110\}$ and $\{220\}$ reflections from Cu$_2$O. This oxide is present epitaxially on the surface of the thin films, so it is not surprising that long exposure diffraction patterns would reveal the faint reflections.

(c) *Summary*. The copper–titanium alloys begin to spinodally decompose during the quench into two
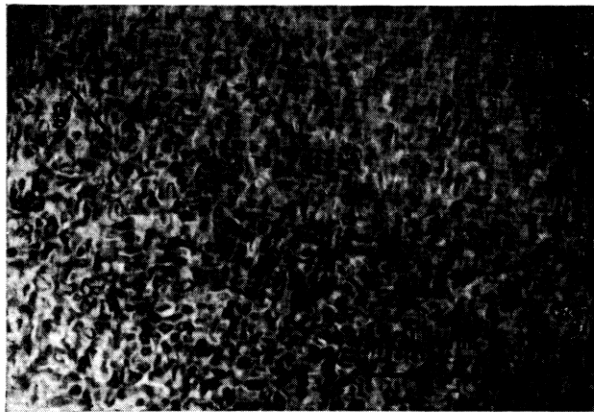
(a)
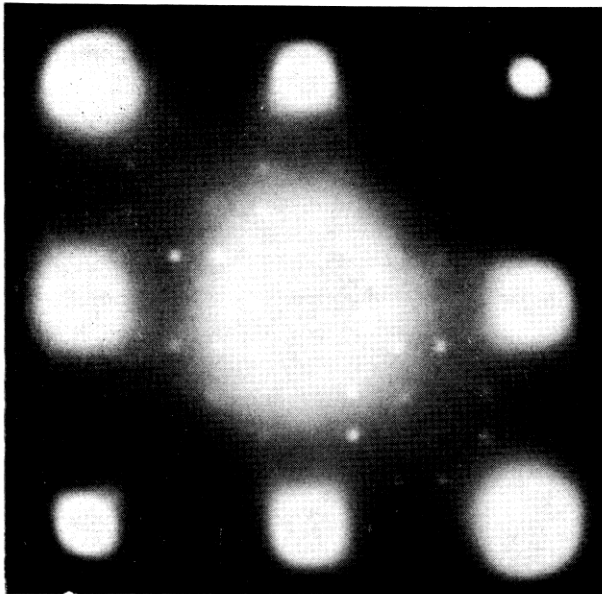
(b)

FIG. 6 (a). Electron micrograph of a Cu–5.17 w/o Ti specimen aged for 15 sec at 450°C. $g = (\bar{2}20)$, [001] foil normal. (b) Diffraction pattern of area shown in (a).

regions; one titanium enriched and the other titanium depleted. The regions are periodically spaced and are aligned along the elastically soft $\langle 100 \rangle$ directions. The titanium rich regions then order. At the beginning of the ordering reaction both $\frac{1}{5}\{420\}_m$ and $\frac{1}{2}\{210\}_m$ superlattice reflections are observable. With further aging, the spinodal and ordering processes occur together. Near the completion of the spinodal reaction the $\frac{1}{2}\{210\}_m$ superlattice reflections disappear, leaving only the $\frac{1}{5}\{420\}_m$ reflections.

3.2 The metastable D1a solvus

The solvus for the metastable D1a phase which develops from the spinodal reaction was found by determining the reversion temperatures of a coarsened

dispersion of this phase. Samples of the three alloys were solution treated, quenched and aged at 450°C for 100 min and cooled. In each case this resulted in microstructures similar to that of Fig. 7. The particles are rod shaped and are still coherent with the matrix.

The samples were then heated to various temperatures for 1 min by immersion in a lead bath. They were examined in the electron microscope to determine if the metastable phase had reverted. After a lowest temperature was found where the phase reverted, reversion was attempted 10°C below it. This time the sample was immersed for 10 min in the lead. In all cases, this failed to revert the second phase. The reversion reaction is extremely rapid just above the solvus, while the coarsening of the particles continues just below the solvus. The reversion temperatures for the 1.55, 3.08 and 5.17 w/o Ti alloys were found to be within 10°C below 640, 735 and 790°C respectively.

Examples of the microstructures of the samples heated just above and just below their reversion temperature are shown in Fig. 8. Figure 8(a) shows the coarsened second phase which resulted when the 3.08 w/o Ti alloy, which had been aged 100 min at 450°C, was heated for 1 min at 720°C. Figure 8(b) shows that all the coherent particles dissolved when heated at 735°C for 1 min. The few remaining particles are incoherent, as evidenced by the dislocations that are observed surrounding them. Thus, while 735°C is above the coherent metastable solvus, it is below the incoherent solvus. The position of the incoherent metastable solvus has been estimated to lie approximately 35°C above the coherent metastable solvus in the region near 3 w/o Ti content.[15]
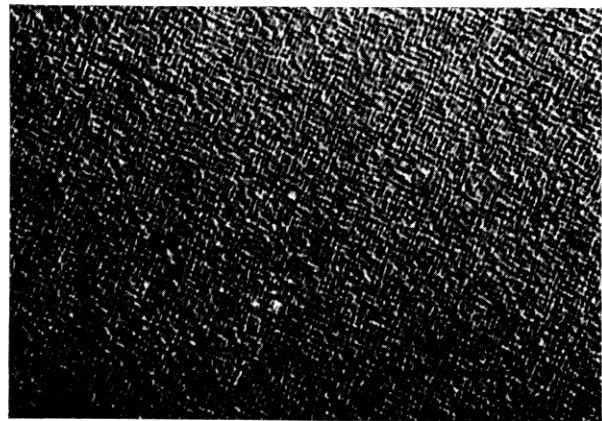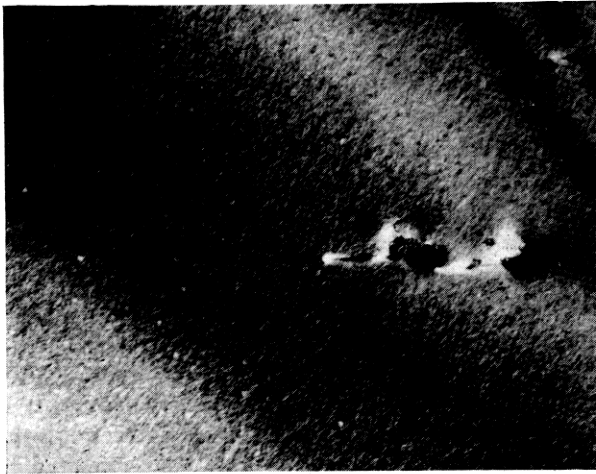

FIG. 7. Electron micrograph of a Cu–5.17 w/o Ti alloy aged for 100 min at 450°C. $g = (200)$, foil normal [001].

(a)

(b)

FIG. 8. Electron micrographs of Cu–3.08 w/o Ti alloys.
(a) Cu–3.08 w/o Ti alloy aged at 450°C for 100 min,
then at 720°C for 1 min. $g = (220)$, foil normal [001].
(b) Cu–3.08 w/o Ti alloy aged at 450°C for 100 min,
then at 735°C for 1 min. $g = (200)$, foil normal [001].

The wavy structure in the background of Fig. 8(b)
is due to composition modulations that were intro-
duced when the reverted sample was quenched through
the spinodal from its reversion temperature. The
alloy aged at 720°C did not show these modulations
because most of the Ti was associated with the
coarsened $D1a$ phase.

Figure 9 shows the copper rich section of the Cu–Ti
phase diagram. The solubility of titanium in copper
was determined by Saarivirta and Cannon.[20] The
reversion temperatures of the three alloys studied
in this investigation,[15,21] as well as those of three
other alloys determined in the independent work of
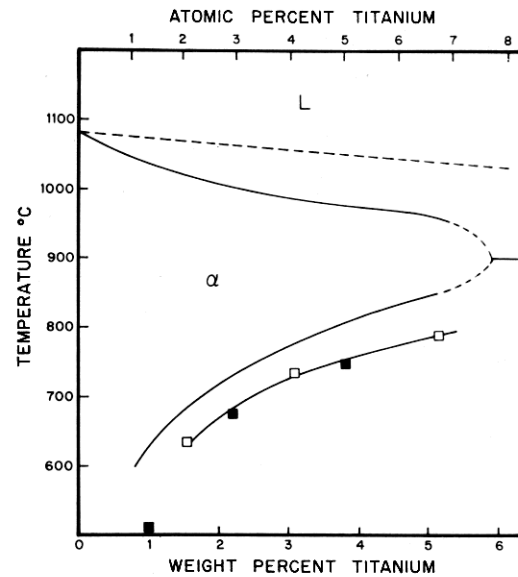Hakkarainen,[3] are plotted on the diagram.

FIG. 9. The copper rich side of the copper–titanium phase
diagram. The equilibrium solvus was determined by
Saarivirta and Cannon. The line through the squares is
the coherent solvus for the metastable $D1a$ phase. Tem-
peratures marked by filled squares were determined by
Hakkarainen. Those marked by open squares were
determined in this investigation.

3.3 Nucleation

The alloys were aged at temperatures very near
the metastable solvus in an attempt to find nuclea-
tion. Two types of aging sequences were used. In
the first one, the alloys were solution treated at 900°C
and quenched to room temperature. They were then
immersed in a lead bath, which was at a temperature
10°C below the metastable solvus for 10 sec and
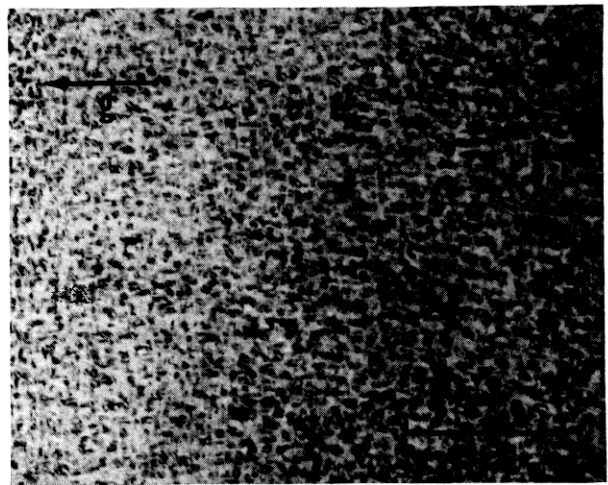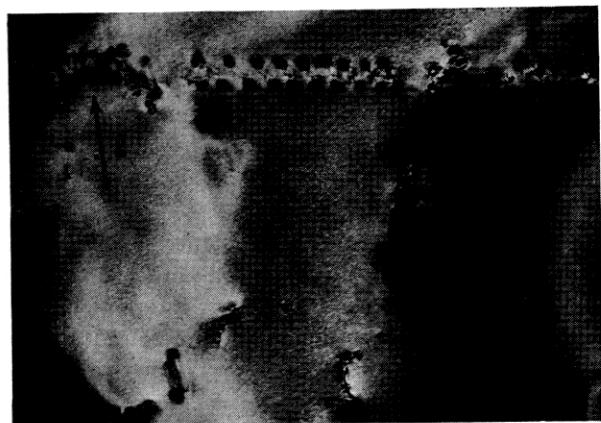quenched to room temperature. The microstructure

FIG. 10. Electron micrograph of a Cu–3.08 w/o Ti alloy
that was solution treated at 900°C, quenched to room
temperature, and up quenched to 725°C for 10 sec. $g =$
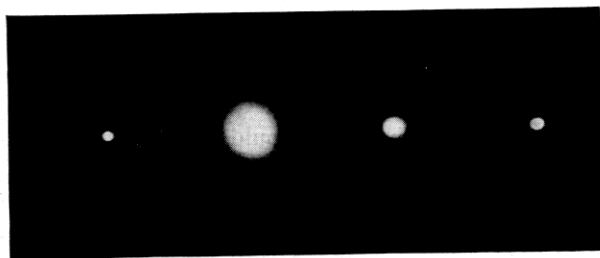(2$\bar{2}$0), foil normal [112].

of the 3.08 w/o Ti alloy treated in this manner is shown in Fig. 10. The aging temperature was 725°C.

In the second aging sequence, the alloys were also also treated at 900°C and quenched to room temperature. They were then immersed in a lead bath which was at a temperature 15–20°C above the metastable solvus of the alloy for two minutes. Then they were transferred directly to another lead bath at the aging temperature for 10 sec before being quenched to room temperature. The microstructure and the diffraction pattern of the 3.08 w/o Ti alloy that was cooled from 750 to 725°C and held for 10 sec is shown in Fig. 11.

The differences in the microstructures are apparent. The sample that was heated to the aging temperature has the typical microstructure of the coarsened spinodal products. The other sample shows heterogeneous nucleation at dislocations, a mottled structure in the background, and diffuse satellites in the diffraction pattern.

(a)

(b)

FIG. 11. Electron micrograph and diffraction pattern of a Cu–3.08 w/o Ti alloy that was quenched from above the metastable solvus directly to the aging temperature of 725°C for 10 sec, then quenched to room temperature. (a) g = (200), foil normal [013]. Notice heterogeneous nucleation at dislocations and mottled structure in background. (b) electron diffraction pattern of area shown in (a). Notice the diffuse satellites around the ($\bar{2}$00) reflection

These results can be explained by postulating that 725°C is above the coherent spinodal. The sample that was cooled to the aging temperature from above the metastable solvus (Fig. 11) did not pass through the spinodal until after the aging. The metastable phase formed by heterogeneous nucleation at dislocations. Then, during the quench from 725°C the alloy passed through the spinodal. Evidence of this can be seen in Fig. 11. The mottling in the microstructure perpendicular to the operating g, and the diffuse satellites in the diffraction pattern both point toward the interpretation that weak periodic modulations exist throughout the microstructure.

The sample that was heated from room temperature has the coarsened spinodal microstructure (Fig. 10). Apparently, the spinodal structure which formed on the quench from the solutionizing temperature coarsened while the sample was heating up to 725°C in the lead bath. The coarsening progressed far enough, such that the second phase did not dissolve when heated above the coherent spinodal.

The large volume of particles present indicates that equilibrium was not reached in the 10 sec in the lead bath. Aging at a temperature so near the metastable solvus should produce a much smaller volume fraction of particles (see Fig. 8a). Ten seconds is adequate for the specimens to reach the temperature of the lead bath, but not for diffusional equilibration.

The same type of aging treatments were done at 700°C. In this case, the cooled samples did not show heterogeneous nucleation. The microstructure was similar to that of Fig. 10, implying that it underwent spinodal decomposition and subsequent coarsening. It can therefore be concluded that 700°C is below the spinodal for the 3 w/o alloy and that the spinodal lies between 700 and 725°C.

This is very close to the metastable solvus or miscibility gap. The root three rule is not obeyed in this system. This has also been observed in other spinodal systems.[22] No quantitative value can be found from this work because of the uncertainty of the shape of the miscibility gap. The recent theoretical work of Gaunt and Baker[23] suggests a critical index of 1.2.

This can also explain a peculiar observation of Knights and Wilkes.[6] Figure 1 of their paper shows two strikingly different microstructures for a 1 w/o Ti alloy that was aged at 500°C. One is similar to the microstructure that occurs in the copper cobalt alloy (homogeneous nucleation) while the other is the so-called typical spinodal microstructure. Hakkarainen[3] has shown that the metastable solvus lies

between 505 and 515°C for this composition. We conclude that 500°C is very near the coherent spinodal, and that the different microstructures arise from possible slight variations in composition or aging temperature.

3.4 Summarizing discussion

By means of the microstructural sequence method, we have shown that copper titanium alloys decompose by the spinodal mechanism. This is not surprising, since the resulting microstructures are precisely those expected for a system which has undergone spinodal decomposition. We believe that the technique developed here proves beyond question that spinodal decomposition has occurred.

The logic of the method is based on two premises. The first one is thermodynamic:

(1) A binary alloy at temperature T is within the spinodal if and only if the interdiffusional coefficient $\tilde{D}$ is negative. This is so because $\tilde{D}$ is equal to the diffusional mobility M, times the second derivative of the free energy with respect to composition, $\partial^2 f/\partial c^2$. Since M is always positive,[24] $\tilde{D}$ takes the sign of $\partial^2 f/\partial c^2$.

The second premise relates electron microscopy observations to the sign of $\tilde{D}$:

(2) In a binary alloy, $\tilde{D} < 0$ if and only if continuous phase separation is occurring at constant wavelength.

From these premises, it may be said that spinodal decomposition is occurring in a binary if and only if continuous phase separation is occurring at constant wavelength.

In this investigation continuous phase separation was observed by the continuous increase in strain contrast (at contrast wavelength) that resulted when the alloy was heated at 400°C for increasing times. The strain contrast was associated with the composition modulations that existed within the crystal. The continuous increase in strain contrast wavelength implies that the amplitude of the modulations increased, which further implies that continuous phase separation, or uphill diffusion, had occurred. For a binary system, this implies that the alloy decomposed within the spinodal.

This investigation also has shown that the metastable phase which is responsible for the improvement in mechanical properties is ordered, with the structure $D1a$. The ordering reaction begins very early in the transformation process, probably after some critical amount of titanium content is reached in the titanium rich regions. This system is thus an example of one in which both clustering and ordering occur.[8]

Reflections that may arise from a quite different ordered phase ($L1_0$, $m = 1$; $14_1/amd$) appear early, and then disappear, leaving only the superlattice reflections of the metastable $D1a$ phase. These $\frac{1}{2}\{210\}_m$ reflections have been seen in other systems in which the $D1a$ structure forms,[25] and have been variously attributed to local order[26,27] or antiphasing within existing microdomains that have the $D0_{22}$ (Ti_3Al; $14/mmm$) structure.[25,28] Das et al.[25] rule out the possibility that the $\frac{1}{2}\{210\}_m$'s arise from the $L1_0$, $m = 1$ structure on two grounds: firstly, the necessity of large composition fluctuations to produce the stoichiometric $L1_0$, $m = 1$ structure, and secondly on the basis of calculations by Clapp that the most enhanced cluster in a similar system (Ni–10 a/o W) was found to be "the $D0_{22}$ type." The first of these need not mitigate against the existence of the $L1_0$, $m = 1$ structure, as the composition of the phase need not be stoichiometric. All that is needed to produce the $\frac{1}{2}\{210\}_m$ reflections is a phase with the symmetry elements of the $L1_0$, $m = 1$ structure.

The $L1_0$, $m = 1$ structure is attractive because it does not give rise to the $\{210\}_m$ or $\{100\}_m$ reflections that the $D0_{22}$ structure does. Thus, there is no need to postulate planar faults in the extremely small clusters of atoms. These peculiar special extinctions for the $L1_0$, $m = 1$ structure (which for f.c.c. indexing leads to superlattice reflections for $n + k = 2n + 1$; $l = n + \frac{1}{2}$)[29] arise from its glide planes.

The structure is an expected one in f.c.c. systems that have first and second neighbor interaction energies positive, with second neighbor energies less than half as strong as first.[30] These systems would also have $D1a$ and $D0_{22}$ as possible phases. As a metastable sequence, it is somewhat anomalous, in that the symmetry elements of the $D1a$ are not a subset of those of the $L1_0$, $m = 1$. In terms of stacking sequences of $\{420\}_m$ f.c.c. planes $L1_0$, $m = 1$ has a periodicity of four, arranged as Ti Cu Cu Ti Ti Cu Cu Ti Ti ... while $D1a$ has periodicity five arranged as Ti Cu Cu Cu Cu Ti Cu Cu Cu Cu Ti .... The transition from one to the other should then involve streaking between the $\frac{1}{2}\{210\}_m$ reflections and the $\frac{1}{5}\{420\}_m$ reflections. This has been observed in Ni_4Mo alloys.[27]

Furthermore, the $L1_0$, $m = 1$ structure is the expected first structure if ordering occurs continuously by the growth of a single $\frac{1}{2}\{210\}$ wave. All other structures of this family require at least two waves and either can form only by nucleation or by a sequence of continuous ordering steps in which single waves are involved.[31]

Of course, structures attributed to very small clusters are not always unambiguous. At the present,

it is best to leave open the origin of the $\frac{1}{2}\{210\}_m$ reflections until more work is done on suitable alloys.

Finally, when aging is done very near the metastable solvus, it has been shown that heterogeneous nucleation occurs. This is of course consistent with the finding that the spinodal reaction is responsible for the homogeneous transformation which occurs at larger undercoolings.

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