High-strength age hardening copper–titanium alloys: redivivus

W.A. Soffa[a], D.E. Laughlin[b],*

[a]*Department of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, PA, USA*
[b]*Department of Materials Science and Engineering, Carnegie-Mellon University, Pittsburgh, PA 15213-3890, USA*

Abstract

In this review the decomposition of supersaturated Cu–Ti solid solutions and subsequent microstructural evolution are discussed in terms of modern views of precipitation from solid solution. This update is motivated by an anticipated emergence of these alloys as technologically significant high-strength, high-conductivity, precipitation hardened alloys over the next decade replacing conventional Cu–Be alloys in numerous applications. The decomposition of Cu–Ti alloys is shown to involve a complex interplay between clustering and ordering effects including a synergy between LRO and SRO similar to those observed in Ni_4Mo-type concentrated solutions. New perspectives regarding metastable and stable phase equilibria in the system are discussed including the polymorphic nature of the Cu_4Ti precipitate phase. The role of non-classical nucleation and spinodal decomposition in the initial breakdown of the supersaturated state is addressed within the context of a generalized nucleation theory. The fine-scale coherent/semicoherent two-phase mixtures which emerge coarsen according to a LSW coarsening law with an activation energy for the diffusion of Ti in Cu of approximately 50 kcal mol^{-1} in excellent agreement with reported values from diffusion studies in the Cu–Ti system. Overaging in Cu–Ti age hardening alloys is associated with the emergence of a coarse lamellar microconstituent which nucleates at the grain boundaries of the parent matrix phase and the growth of these cells consumes the metastable, fine-scale coherent/semicoherent phase mixtures leading to a rapid degradation of mechanical properties. The activation energy for the growth of the cellular microconstituent is less than half that for bulk diffusion indicating interfacial/boundary diffusion control. It is suggested that to enhance and optimize the mechanical properties of the precipitation hardened Cu–Ti alloys, alloying and thermo-mechanical processing strategies should focus on controlling the nucleation and growth of the cellular or "discontinuous" precipitation reaction.

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* Corresponding author. Tel.: +1-412-268-2706; fax: +44-412-268-7169.
E-mail address: d10p@andrew.cmu.edu (D.E. Laughlin).

Contents

1. Introduction

The age hardening of copper–titanium (Cu–Ti) alloys containing approximately 1–5 wt.% Ti ($\sim$1–6 at.% Ti) has been known since the 1930s. The mechanical and physical properties were found to be comparable to the widely used copper–beryllium (Cu–Be) alloys with better high temperature strength and superior stress relaxation behavior. The electrical conductivity of the aged alloys, however, falls somewhat below that of the Cu–Be alloys [1–4]. Cu–Ti alloys are now receiving a great deal of attention as ultra-high strength conductive materials for applications such as conductive springs, interconnections etc. essentially displacing the conventional Cu–Be alloy series. This move away from Cu–Be has been catalyzed to a large extent by the full recognition of serious health hazards associated with the Be-based metallurgy in production. It is likely that the precipitation hardened Cu–Ti alloys will rise to prominence as a commercial alternative in a myriad of applications over the next decade. This paper and a forthcoming companion paper are aimed at providing an update including recent work regarding the decomposition of supersaturated Cu–Ti alloys and microstructural development during aging along with a survey of the strengthening mechanism and deformation behavior of these high strength precipitation hardened alloys.

The early phase diagrams of the Cu–Ti system showed the terminal FCC Cu-rich solid solution (α) to be in equilibrium with a Cu_3Ti phase characterized by a space group Pnmm [5]. However, a Au_4Zr-type structure was reported and this orthorhombic phase Cu_4Ti exhibits the space group Pnma [6–8]. Work in the early 1970s by Hakkarainen [9] and Laughlin and Cahn [10] reported that a metastable coherent precipitate phase with the tetragonal $D1_a$ structure (Ni_4Mo-type; I 4/m) having the composition Cu_4Ti forms during aging below approximately 600–700 °C. This important finding was further verified in a comprehensive electron microscopy study of the microstructural behavior in a series of alloys containing 1–4 wt.%Ti by Datta and Soffa [11]. The resultant metastable, finely dispersed two-phase mixtures of $\alpha' + D1a$ which arise during aging produce highly aligned and quasi-periodic microstructures often called modulated structures. During prolonged aging at low or
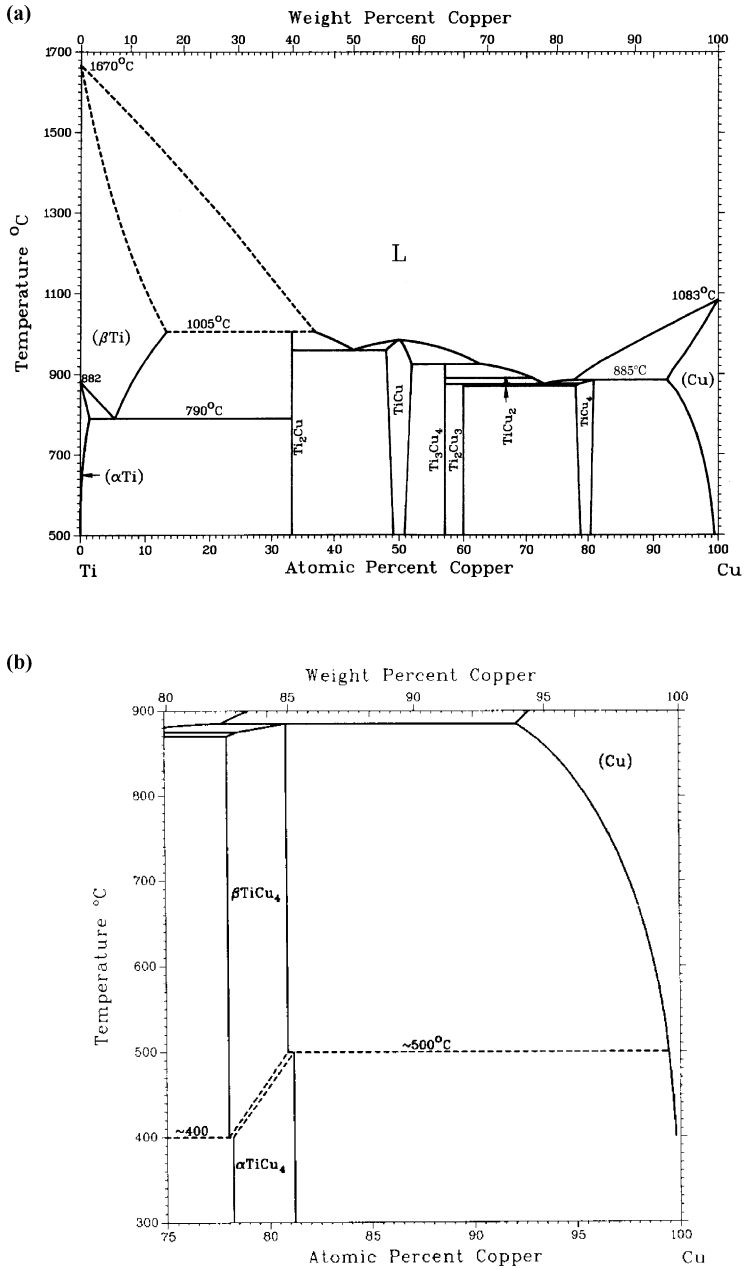
Fig. 1. Recent versions of the Cu–Ti phase diagram: (a) Cu₄Ti (orthorhombic; Pnma) shown as the equilibrium phase above 500 °C; (b) detailed portion of diagram showing polymorphic transformation in Cu₄Ti phase [8]; and (c) measured metastable D1ₐ solvus in Cu-rich region of the diagram [16].
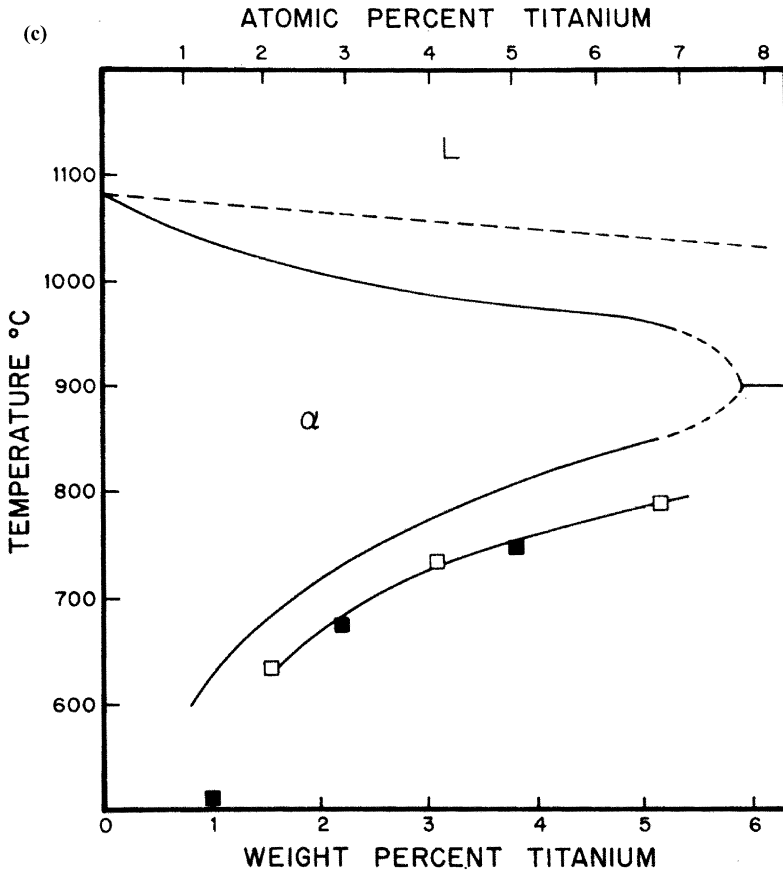
(c)

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Fig. 1 (*continued*).

moderate aging temperatures a coarse lamellar microconstituent composed of the equilibrium phase and terminal solid solution (α) nucleates and grows consuming the fine-scale dispersion of coherent/semicoherent $D1_a$ particles. Fig. 1a–c shows recent versions of the equilibrium diagram as well as the measured metastable solvus of the $D1_a$ precipitate phase. The portion of the Cu–Ti equilibrium diagram in Fig. 1b indicates a polymorphic transformation of the Cu_4Ti phase; it suggests that the tetragonal $D1_a$ phase is the stable phase below $\sim$500 °C and that the orthorhombic Au_4Zr-type structure is the equilibrium high temperature phase. The existence of the $D1_a$ structure as the stable low temperature phase is not surprising since the $D1_a$ structure is a ground state for FCC-based alloys [12]. The orthorhombic Pnma structure (Au_4Zr-type) is presumably stabilized at higher temperatures by entropic effects. Both the $D1_a$ and Au_4Zr phases derive from the stacking of essentially close-packed layers with different intralayer ordering; the $D1_a$ exhibits the so-called oblique ordering within the layers and the Au_4Zr-structure shows a

triangular-striped ordering [13] (see Fig. 2). However, it should be noted that the hard sphere stacking sequence is different since the Au_4Zr structure is a derivative of HCP stacking as depicted in Fig. 3.

A fundamental interest was directed at the Cu–Ti age hardening alloys in the 1960s and 1970s when these alloys were recognized to be prototypical binary "side-band alloys" perhaps exhibiting spinodal decomposition [9–11,14–16]. The strong age hardening response also received new attention since these precipitation hard-
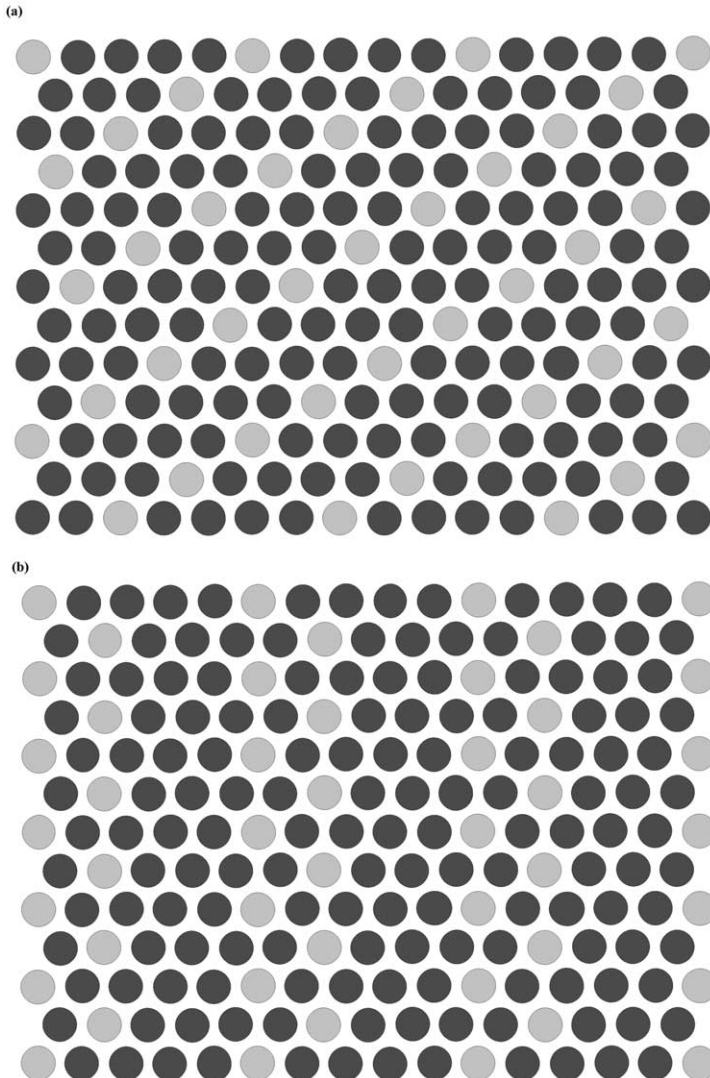

Fig. 2. (a) Oblique ordering of close-packed plane in Ni_4Mo-type ($D1_a$) structure; (b) triangular striped ordering in Au_4Zr-type structure (after Ref. [13]).

ening alloys were found to show extraordinary plastic flow behavior including profuse deformation twinning [17–20]. The occurrence of spinodal decomposition during the early stages of precipitation resulting in the formation of an ordered phase provoked new thinking regarding the interplay of clustering and ordering tendencies in solid solutions [11,21,22] similar to those articulated by Allen and Cahn [23] and Ino [24]. During the anticipated expanded commercialization of age hardened Cu–Ti alloys the nature of the cellular reaction or discontinuous precipitation mode will undoubtedly be a major focal point since the appearance of the cellular microconstituent leads to deleterious effects on mechanical properties [11,25]. Also, the influence of plastic deformation on the aging response will be of paramount importance in the thermomechanical processing of these materials in production [26].

As mentioned above, this first paper will address the current understanding of the precipitation sequence or decomposition path exhibited by supersaturated Cu–Ti solid solutions involving nucleation, growth and coarsening. Numerous experimental methods have been applied to elucidate the basic mechanisms controlling the formation of the characteristic periodic and aligned two-phase microstructures which arise during aging, including X-ray and neutron diffraction, electron microscopy and diffraction and atom probe field-ion microscopy (APFIM). The early stages of decomposition and the origin of the "sideband state" will be discussed along with the evolution of the microstructures during prolonged aging.
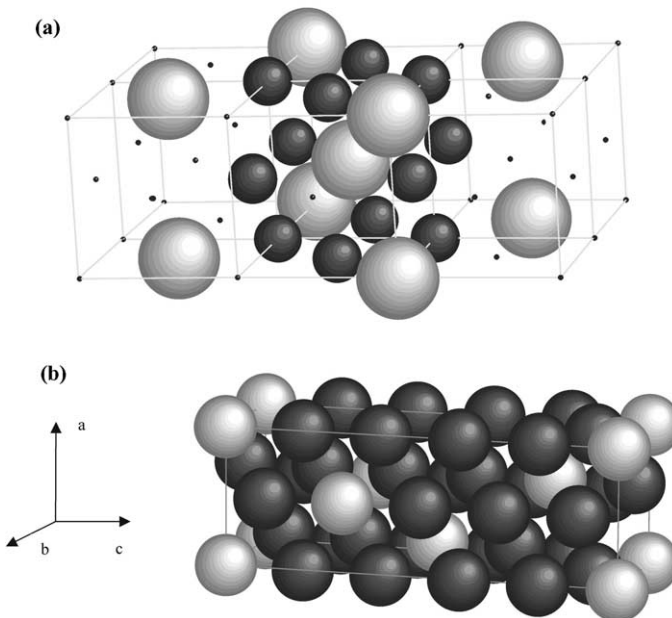

Fig. 3. (a) Schematic of the $D1_a$ structure showing the unit cell as a crystallographic derivative of the parent FCC structure; (b) schematic of the Au_4Zr-type structure revealing the orthorhombic cell and characteristic ABAB stacking (along the *b*-axis of the orthorhombic cell).

2. The early stages of decomposition

The decomposition of supersaturated Cu–Ti alloys containing 1–6 at.% titanium (Ti) embodies a complex interplay of clustering and ordering effects in solid solutions [21–24] as well as a subtle synergy between short range order (SRO) and long range order (LRO) [27,28]. In addition, the supersaturated Cu–Ti alloys exhibit well-known ''sideband'' phenomena in the diffraction patterns during the early stages of decomposition. As pointed out above, the precipitate phase of particular interest in the age hardening response of these high-strength alloys exhibits the $D1_a$ superstructure (Ni$_4$Mo-type; I4/m) and therefore is the focus of this discussion. A generalized Bragg–Williams description of the thermodynamics of the LRO Cu$_4$Ti/ $D1_a$ structure requires fourth-nearest neighbors to stabilize the structure as a non-degenerate ground state for FCC-based superstructures but third nearest-neighbor interactions will lead to the emergence of SRO and LRO structures from a disordered solid solution at low temperatures. The A_4B superstructure is favored in systems where the first nearest-neighbor interchange potential $V^{(1)}$ and second nearest-neighbor interchange potential $V^{(2)}$ are of the same sign when considering just the first and second nearest-neighbors in the structural energies of the various FCC-based superstructures [12,29].

Order–disorder effects have been studied extensively in Ni$_4$Mo-type ordering systems for stoichiometric and off-stoichiometric compositions including effects under irradiation [28,30]. The concentration wave approach depicted in Fig. 4 has proven very useful for describing the emergence of SRO and LRO in these systems [27,28,31]. Interestingly, the atomic arrangements in dilute (1–6 at.%) Cu–Ti alloys appear to be essentially consistent with the concentration /ordering wave stability analysis where the A_2B_2/AB related stoichiometries emerge. The short-range ordered A_2B_2 metastable configuration evolves rapidly through amplification of concentration waves having a wave vector $\langle 1/4 \ <420\rangle$ producing a modulation of the A and B atoms in solution along the {420} planes. This atomic rearrangement tends to produce a stacking sequence. AABBAA... and diffracted intensity in reciprocal space at positions $< 1\frac{1}{2}0 >$. This change in atomic configuration is associated with an ordering instability and is, therefore, thermodynamically and kinetically continuous. The LRO transition giving rise to the $D1_a$ phase is thermodynamically first order and produces superlattice reflections at 1/4 $\langle 420\rangle$. The $\langle 11/20\rangle$ positions are so-called ''special points'' in the k-space representation of the concentration wave description [27,28].

The age hardened Cu–Ti alloys are typically quenched from 800 to 900 °C to room temperature prior to aging. These dilute alloys characteristically exhibit diffuse scattering near the $\langle 11/40\rangle$ positions in reciprocal space in the as-quenched state and during the very early stages of aging in the range 350–550 °C. Further aging leads to a rapid decay of the $\langle 11/40\rangle$ SRO intensity and a concomitant appearance of LRO 1/5 $\langle 420\rangle$ superlattice reflections characteristic of the Cu$_4$Ti ($D1_a$) superstructure (see Fig. 5). Nesbitt and Laughlin [32] reported an apparent ''continuous'' transfer of intensity from the SRO $\langle 11/20\rangle$ positions to the $D1_a$ superlattice reflections (LRO) in a concentrated, off-stoichiometric Ni–Mo alloy. In real space this represents a

change in the atomic configuration from SRO toward a state of LRO. In the dilute Cu–Ti solid solutions the $D1_a$ ordering is accompanied by the emergence of discrete, coherent precipitates and the formation of a two-phase alloy [9–11,33].

The early stages of decomposition of supersaturated solid solutions often give rise to the well-known "sideband" phenomena in X-ray, electron and neutron diffraction patterns as depicted in Fig. 6. These diffraction effects producing "satellite" reflections were first observed by Bradley [34] and analyzed by Daniel and Lipson [35] in their classic X-ray studies of precipitation in Cu–Ni–Fe alloys and interpreted in terms of a periodic or "wave-like" clustering of solute. Of course, this concept of precipitation deriving from a continuous amplification of concentration waves in a decomposing supersaturated solid solution found resonance with the concept of spinodal decomposition in the theoretical works of Hillert [36] and Cahn [37]. However, further analysis of the nature of these diffraction effects indicated that a quasi-periodic array of discrete particles surrounded by solute-depleted regions could account for specific aspects of the satellite reflections observed experimentally [38]. These modulated structures comprised of quasi-periodic arrays of second phase
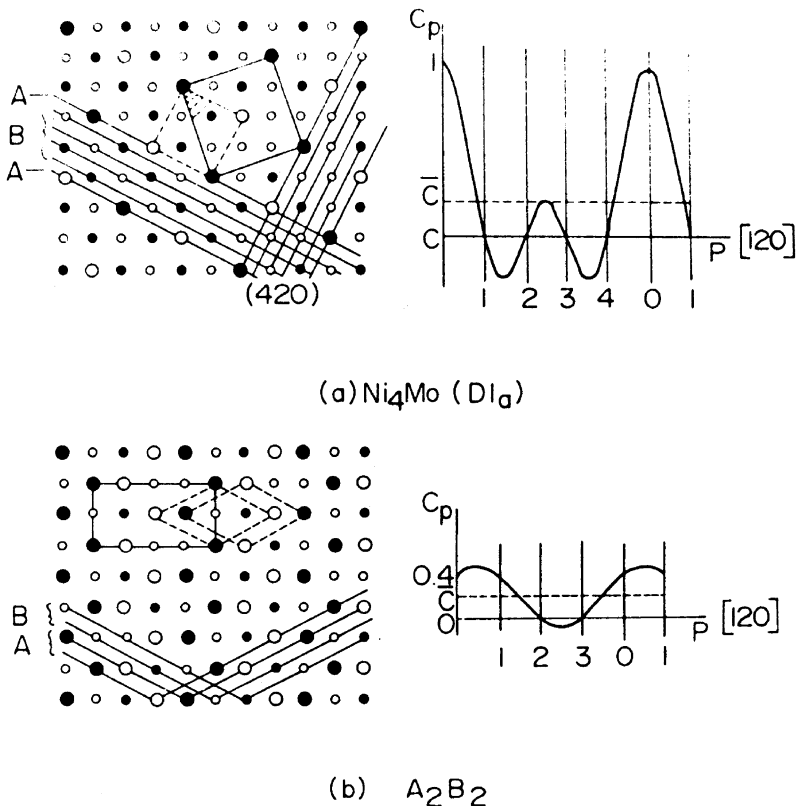

Fig. 4. (a) and (b) Concentration wave description of LRO and SRO in Ni$_4$Mo-type systems depicted as modulation of the atomic arrangement in {420} planes [30].

particles surrounded by solute-depleted regions can derive from nucleation or spinodal decomposition under the influence of short and long-range elastic interactions from the onset of precipitation. Indeed, the quasi-periodic strain contrast striations observed in electron microscopy studies of the early stages of decomposition shown in Fig. 7 are not conclusive evidence of "wave-like" precipitation but indicative of periodic elastic displacements in the transforming solid solution [39].

Borchers [40] recently studied the decomposition of Cu–0.9 at.% Ti solid solutions at 350 °C (623 K) using electron microscopy (TEM) and analyzed the energetics of nucleation aided by CALPHAD calculations of the approximate thermodynamics of the Cu–Ti system. The TEM studies revealed copious formation of nano-sized coherent ellipsoids or oblong particles from the onset of decomposition with an aspect ratio ca ∼1.5 in agreement with previous studies of dilute alloys [41,42]. These nanoscale prolate spheroids of the tetragonal Cu_4Ti ($D1_a$) phase tend to orient their c-axes along the $\langle 100 \rangle$ directions of the matrix and form quasi-periodic arrays or modulated structures aligned along the $\{100\}$ planes. The particle arrays appear to evolve through concomitant growth and coarsening under the influence of
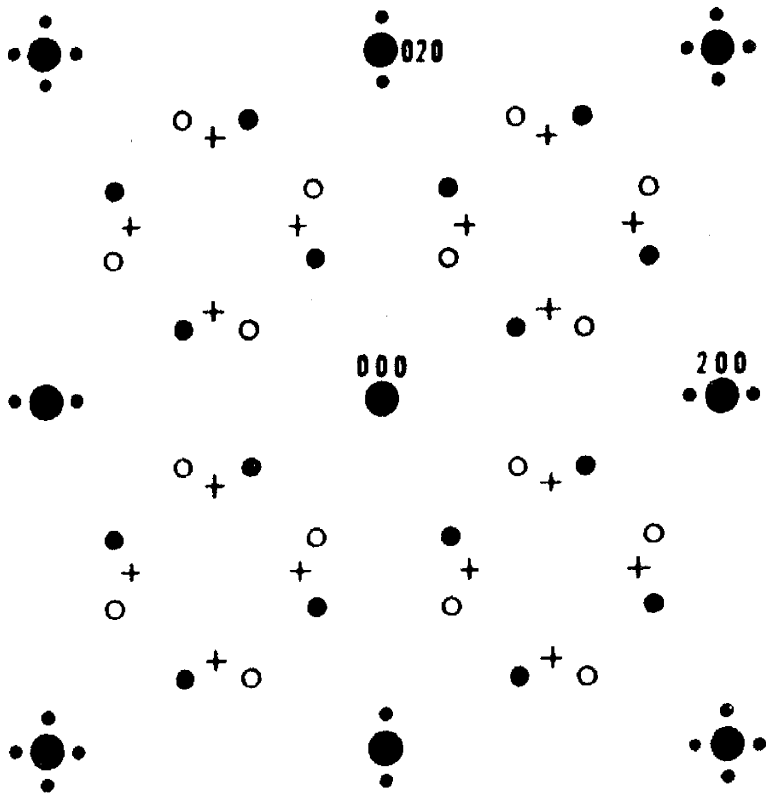

Fig. 5. Schematic of (001) reciprocal lattice section showing "satellite" reflections and positions of $D1_a$ superlattice spots (LRO) (● ○) as well as locations of SRO diffuse scattering (+). The $D1_a$ reflections represent two variants within the parent FCC matrix [10].
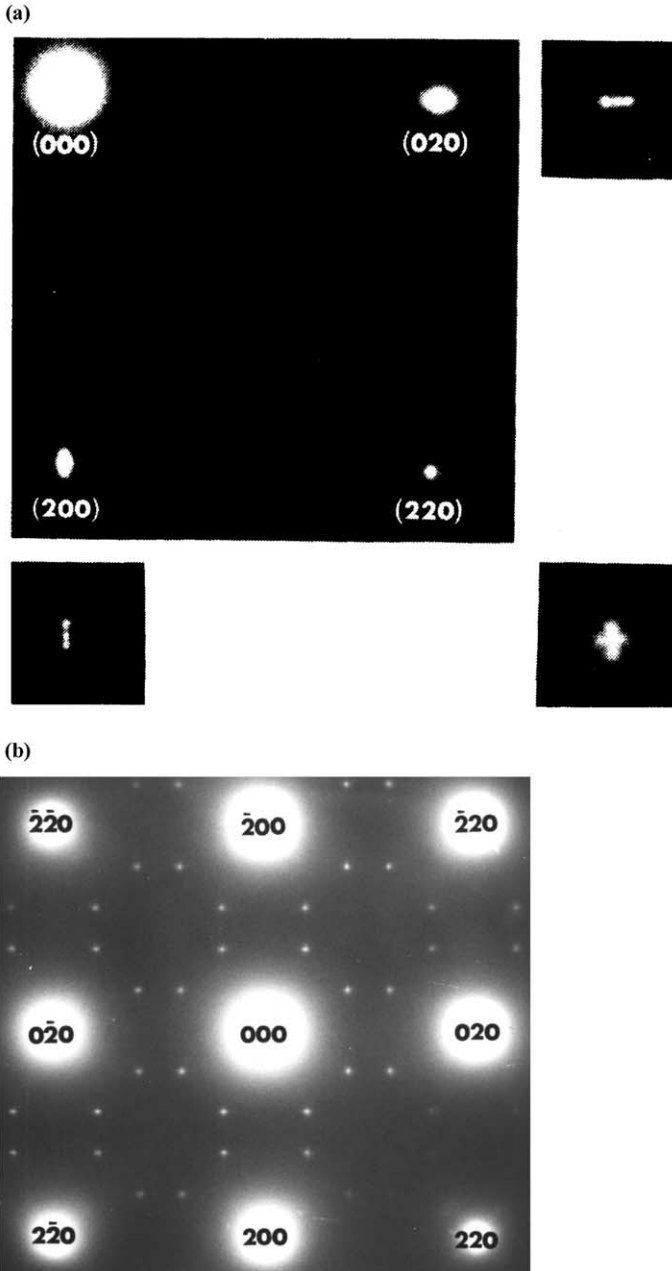
Fig. 6. (a) (001) electron diffraction pattern clearly showing "sidebands" or "satellites" flanking matrix reflections associated with clustering in a decomposing Cu–Ti solid solution [11]; (b) (001) electron diffraction pattern showing D1$_a$ superlattice reflections associated with two variants of the D1$_a$ precipitate phase in a Cu–Ti alloy [11].

elastic interaction from the very earliest stages of decomposition. An analysis using classical nucleation theory indicates a nucleation barrier $\Delta G^* \sim k_B T$ for an estimated interfacial free energy $\sigma \sim 30$ ergs cm^{-2} including an Eshelby analysis of the strain energy. Therefore, Borchers suggests that the supersaturation at 350 °C essentially precludes classical nucleation as the initial step in the decomposition of the alloy and contends that the precipitation behavior is best interpreted in terms of a "catastrophic" nucleation or "non-classical" nucleation phenomenon [43,44].

Regarding whether Cu–Ti alloys at high supersaturations represent "spinodal alloys" will be addressed briefly. The basic concept of spinodal decomposition is said to date back to Gibbs and van der Waals but entered the fields of physical metallurgy and materials science through the works of Hillert [36], Cahn [45] and Hilliard [46]. This alternative to classical nucleation from a supersaturated solid solution is rooted in the notion of a well-defined free energy–composition curve defining non-equilibrium states in the two-phase field of the system. The free energy functional exhibits a double-well and regions of positive and negative curvature $\left(\partial^2 f/\partial c^2\right)$ defining metastable and unstable states of the solution. The region of negative curvature is determined by the so-called "chemical spinodes" where $\frac{\partial^2 f}{\partial c^2} = 0$. Within these spinodal points (coherent spinodes if the solution energetics are modified by elastic energy) the classic theory of spinodal decomposition [46] suggests that the system is unstable to long wavelength fluctuations of rather low amplitude which can grow spontaneously to produce a two-phase mixture through continuous phase separation. This concept of continuous amplification of concentration waves (Fourier components of the atomic configuration) is now the stuff of standard textbooks and identifies a process different from classical nucleation of a second phase whereby high amplitude fluctuations of critical size r^* initiate the decomposition of the supersaturated state. The artificial singularity at the "spinodal points" can be smeared out kinetically by the non-classical nucleation behavior analyzed by Cahn
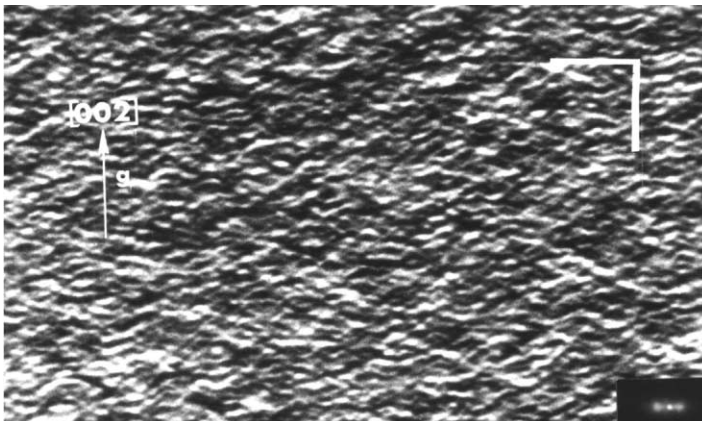

Fig. 7. Periodic strain contrast striations along ⟨002⟩ matrix directions characteristic of early stages of decomposition in Cu–Ti alloys; two-beam bright-field electron micrograph, $g = [002]$.

and Hilliard [43] and Binder [47] within the context of a generalized nucleation theory.

At high supersaturations coherent phase separation or precipitation in solid solutions is generally not described energetically or kinetically by the basic tenets of classical nucleation theory. Essentially a spectrum of fluctuations of varying amplitude and spatial profile emerges spontaneously and evolves producing a two-phase mixture. The work of formation of these fluctuations approaches the order of k_bT and they form copiously throughout the system leading to spontaneous phase separation, in effect, there is a ''big bang'' or ''catastrophic'' nucleation of the new phase. The concept of a well-defined critical nucleus or fluctuation loses its classical meaning replaced by a spectrum of decomposition paths leading to phase separation. The diffusion process governing the time-evolution of the phase separation is essentially a generalized non-linear version of the well-known Cahn–Hilliard equation. Because of the long wavelength of the critical modes of Cahn–Hilliard just inside the ''spinodal region'' fluctuations of finite amplitude and smaller spatial extent costing energy of the order of k_bT will form faster and dominate the kinetics of decomposition. When the barrier height of the fluctuation trajectories becomes $\sim k_bT$ and the spatial extent of the typical critical fluctuations reaches the correlation length, the system is intrinsically unstable in accord with the Cahn–Hilliard theory. Thus, the behavior of the supersaturated state is characterized by a gradual transition from classical nucleation through a stochastic non-classical nucleation behavior to global instability. This generalized nucleation theory delineates a regime at high supersaturations where the processes of nucleation, growth and coarsening can occur concomitantly giving rise to fine-scale two-phase mixtures [47,48].

Furthermore, it should be pointed out that the free energy curve which is central to the conventional discussions of metastability and instability in supersaturated solutions is not so-well defined upon closer examination. The curve must be a so-called ''coarse-grained'' free energy functional which depends fundamentally on thermodynamic constraints. In systems with significant short-range interactions, there is essentially no unique way to define a double-well free energy relevant to fluctuation behavior and thermodynamic stability [47]. For example, even if the disordered state is used as an initial reference state, atomic rearrangements within the non-equilibrium solution occurring on various length scales producing non-random configurations cause the effective region of negative curvature to move toward the common tangent and the spinodes toward the points of tangency. This was discussed in the spirit of Kikuchi's cluster variation method (CVM) by Liu and Loh in the 1970s [48]. This behavior is expected to be significant in metallic and ceramic systems. The utility of the standard stability analysis in terms of a relatively well-defined free energy–composition curve is most applicable in systems dominated by long-range interactions such as in certain phase separating polymer solutions [47,49].

Finally, most precipitation systems of practical importance including the Cu–Ti system involve the precipitation of ordered phases within a disordered parent solution. As a result, there can be a complex interplay of the ordering and clustering as noted in Section 1. It is expected that ordering prior to phase separation might

influence the thermodynamic stability of the supersaturated state and therefore the decomposition path. Importantly, even though a unique scheme of free energy–composition curves cannot be rigorously constructed, approximate free energy curve topologies can be used to qualitatively capture a spectrum of behavior exhibited by precipitation systems [21,22]. The diffusional processes governing the atomic rearrangement are still described by the local diffusion potentials which derive from the local solution energetics, i.e. $\left(\partial^2 f/\partial c^2\right)$.

The experimental results of various studies of the decomposition of Cu–Ti alloys at high supersaturations suggest that the system does display non-classical nucleation behavior and perhaps spinodal decomposition in the formation of the coherent $Cu_4Ti(D1_a)$ precipitate phase. The quasi-periodic and aligned microstructures which evolve clearly derive from decomposition generally involving concomitant nucleation, growth and coarsening or spinodal decomposition under the influence of elastic strain energy in an anisotropic matrix [49].

3. Later stages of aging: coarsening and cellular precipitation

During prolonged aging at high supersaturation fine-scale, quasi-periodic arrays of coherent/semi-coherent $D1_a$ particles emerge giving rise to a pronounced particle hardening. The variation of salient mechanical properties is shown as a function of aging time at 400 and 500 °C in Fig. 8 for polycrystalline specimens of a Cu–4 wt.% Ti alloy. The microstructure near peak hardness generally consists of prolate spheroids or block-like rods aligned along the $<100>$ matrix directions with aspect ratios ca ~1.5–3. The crystallographic misfit in the plane normal to the axis of the rods (c-axis of the b.c.t. cell) is ~2.0% while the misfit along the c-axis is approximately an order of magnitude less. Thus, the prolate spheroidal or block-like rods of
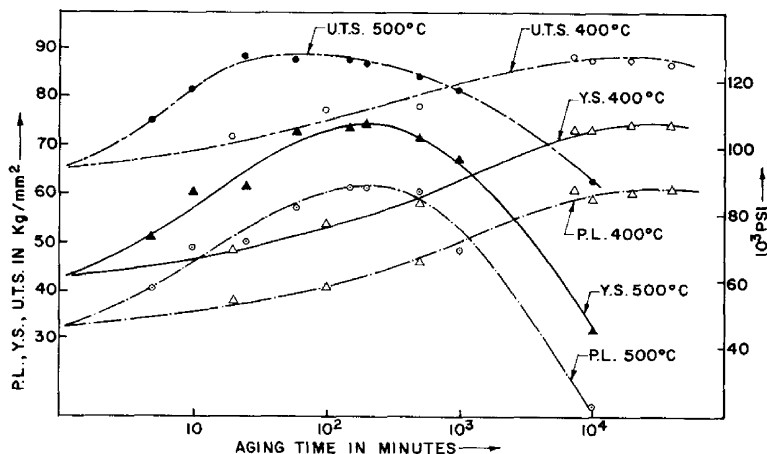

Fig. 8. Variation of the Proportional Limit (P.L.), Yield Strength (Y.S.) and Ultimate Tensile Strength (U.T.S.) for a Cu–4 wt.%Ti alloy with aging time at 400 and 500 °C [11].
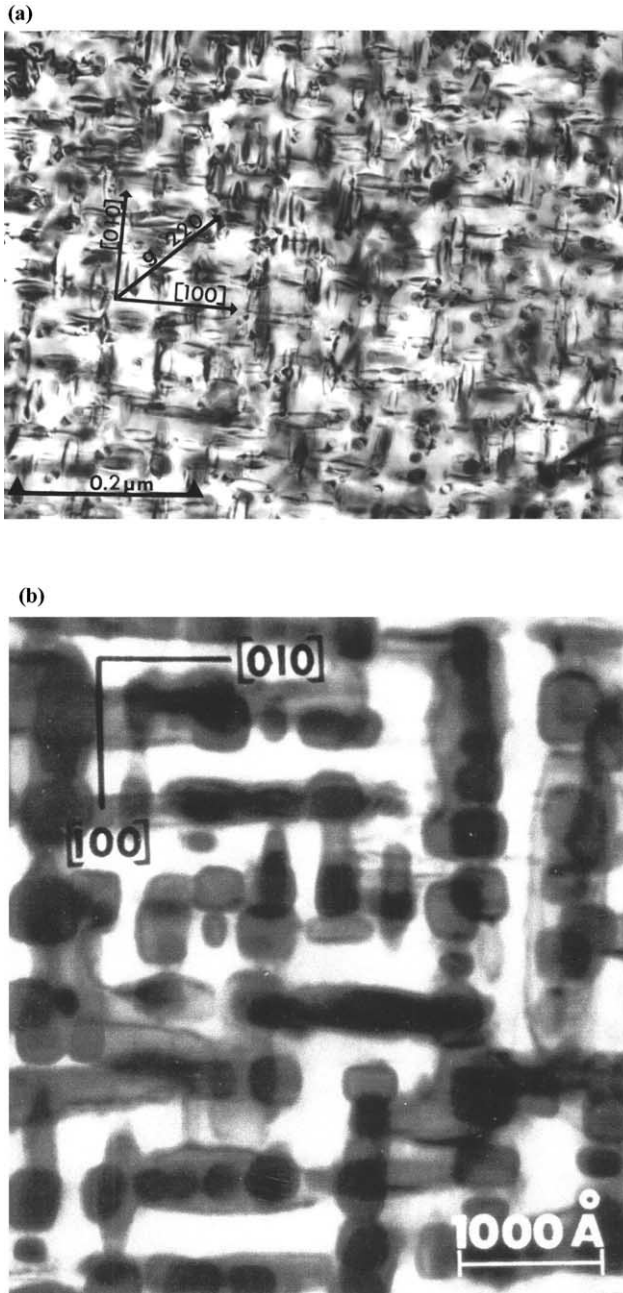
Fig. 9. Typical microstructures revealed by electron microscopy of age hardened Cu–Ti alloys aged near peak hardness: (a) Cu–1 wt.%Ti alloy aged 100 min at 500 °C [41]; and (b) Cu–4 wt.%Ti alloy aged 2000 min at 500 °C [42].

the D1$_a$ phase are elongated along the direction of "good fit" or minimum "misfit". Fig. 9a and b shows typical microstructures in the vicinity of peak hardness in a Cu– 1 wt.% Ti alloy and Cu–4 wt.% Ti alloy. The coarsening of these two-phase mixtures follows a $\lambda^3 - \lambda_0^3 = kt$ kinetic law from the early stages of aging where λ is the "wavelength" of the modulated structure (quasi-periodic array of precipitates) and k is a rate constant. The rate constant $k \sim CD/T$ according to the classic LSW theory for diffusion-controlled coarsening [50,51] where C is the metastable equilibrium concentration of solute in the matrix at the β′(D1$_a$) solvus and D is the diffusion coefficient describing the migration of titanium (Ti) in copper (Cu). Using the data of Hakkarainen [9] and Laughlin and Cahn [10] and an Arrhenius plot of ln $\frac{k_B T}{C}$ vs. $\frac{1}{T}$ yields an experimental activation energy of approximately 50 kcal mol^{-1} for the coarsening process [11]. This is in excellent agreement with the activation energy for diffusion of titanium (Ti) in copper (Cu) reported by Iijima, Hashino, and Hirano [52] in their study of the interdiffusion coefficients in Cu–Ti alloys using the standard Miatano analysis of diffusion couples of pure Cu and dilute Cu–Ti alloys. In this study a value of $Q \sim 47$ kcal mol^{-1} is calculated and a Kirkendall marker movement slightly toward the Ti-rich side is shown indicating that the titanium atoms diffuse faster than the copper atoms in dilute Cu–Ti alloys. Earlier studies of the kinetic behavior using electrical resistivity or the development of mechanical properties typically reported values of $Q \sim 42$–54 kcal mol^{-1} for the volume diffusion of titanium atoms in copper [53].

Although loss of coherency and a transition from particle shear to an Orowan-type by-pass mechanism have been observed in the age hardening Cu–Ti alloys [41,42], overaging appears to be related more directly to the onset of cellular
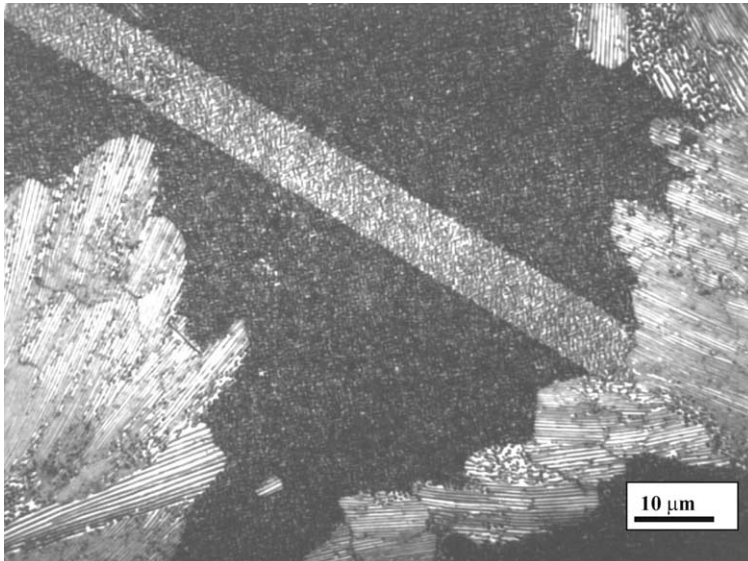

Fig. 10. Cellular microconstituent growing into the coherent/semicoherent two-phase mixture near peak hardness in a Cu–4 wt.%Ti alloy aged for 1000 min at 600 °C.
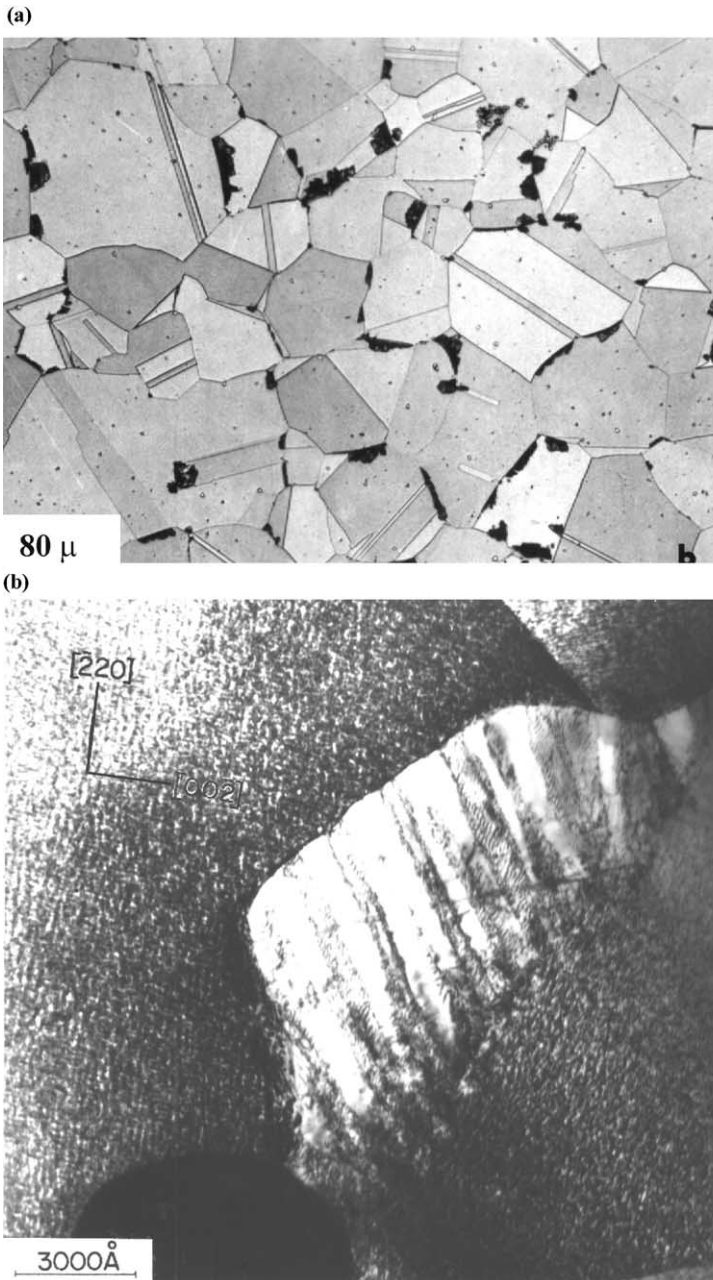
(a)

(b)

Fig. 11. (a) Optical micrograph revealing cellular colonies emerging from the grain boundaries in a Cu–4 wt.%Ti alloy aged 500 min at 500 °C. This cellular microconstituent has initiated the overaging process; (b) cellular colony in an aged hardened Cu–3 wt.%Ti alloy emerging from a grain boundary and consuming the fine dispersion of $\alpha' + D1_a$ (10,000 min at 375 °C).

precipitation which gives rise to a coarse lamellar microconstituent originating primarily at the grain boundaries of the parent solid solution [42]. The details of the deformation behavior will be discussed in a forthcoming companion paper as mentioned in Section 1. Fig. 10 shows the cellular product growing into the metastable coherent/semicoherent two-phase mixture of the depleted matrix (α') and the tetragonal $\beta'(D1_a)$ phase. The evolution of the cellular product is shown in a Cu–4 wt.% Ti alloy aged at 500 °C beyond peak hardness. The yield strength of an alloy aged at 500 °C for 1000 min drops approximately 10% compared to peak strength; however, the ductility is less than 50% that of the alloy at maximum strength [11]. Kinetic studies of the growth of the cellular colonies typically indicate an activation energy for the discontinuous reaction $Q \sim 20$ kcal mol^{-1} [53], well-below the value for volume diffusion of titanium in copper. Clearly, this is indicative of boundary diffusion as the rate controlling mechanism governing the evolution of the cellular microconstituent and consumption of the fine-scale phase mixtures which give rise to the marked age hardening response.

Studies of the cellular or discontinuous precipitation reaction giving rise to the equilibrium precipitate have clearly established that the genesis of the lamellar microconstituent derives from grain boundary precipitation. Fig. 11a and b reveals the early stages of assembly of cellular colonies in association with heterogeneous nucleation of the equilibrium phase at the grain boundaries of the matrix. Fig. 11b shows the early stage migration of a cellular colony and the consumption of the fine-scale metastable coherent/semicoherent two-phase mixture $\alpha' + D1_a$. Several
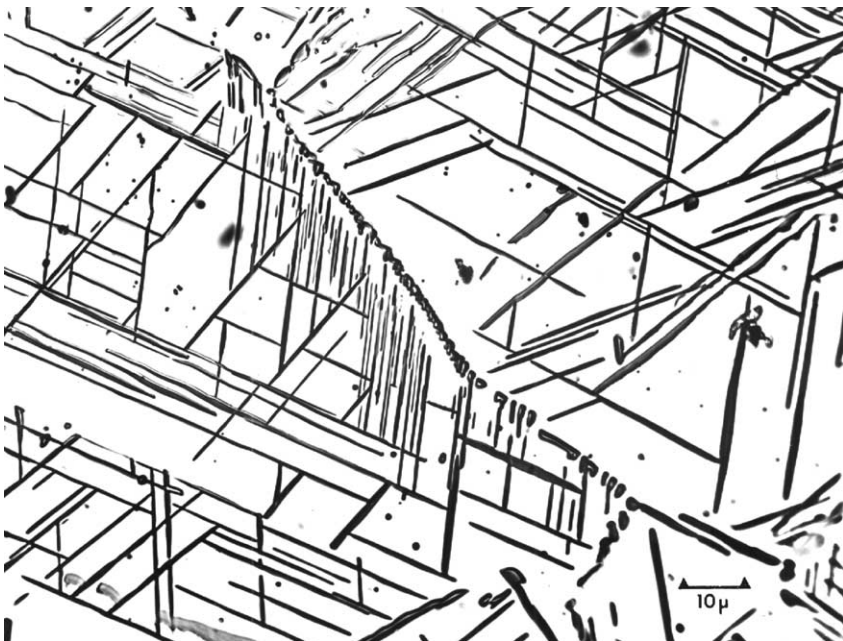

Fig. 12. Widmanstätten precipitation in a Cu–3 wt.%Ti alloy aged 10 h at 730 °C.

mechanisms have been proposed over the years for the genesis of the cellular colonies [54] and evidence for virtually all of these models has been observed in Cu–Ti alloys including direct evidence of the "pucker" mechanism of Tu and Turnbull [6,55]. Fonda and Shiftlet [56,57] have recently characterized the interfaces and crystallography of the cellular colonies forming at relatively high temperatures. At the higher aging temperatures a classic Widmanstätten morphology forms giving rise to a coarse microstructure comprised of α and the equilibrium phase β (see Fig. 12). Ecob et al. [6] have suggested that the Widmanstätten plates in the vicinity of the grain boundaries can catalyze the formation of cellular colonies at the higher aging temperatures.

Clearly to suppress the emergence of the cellular microconstituent heterogeneous nucleation of the equilibrium phase at the grain boundaries and the interaction of the grain boundaries with these particles must be elucidated and controlled. One obvious approach is to systematically add ternary and quaternary alloying elements which can influence the nucleation and growth processes and boundary migration involved in the genesis of the cellular colonies. This "grain boundary engineering" was successful in the classic Cu–Be alloy series using cobalt (Co) additions [58] and has recently been applied to the age hardening Cu–Ti alloys with some promising results [59].

4. Conclusions

1. The equilibrium phase in the age hardening Cu–Ti alloys has been reported to have the composition Cu_4Ti and may exhibit a polymorphic transformation. The high temperature phase is the Au_4Zr type orthorhombic phase with the space group Pnma and the low temperature polymorph is the tetragonal $D1_a$ phase.

2. The equilibrium phase in the Cu–Ti system generally forms by classic Widmanstätten or cellular precipitation. The cellular or "discontinuous" precipitation reaction plays a central role in the overaging of these high-strength alloys. The growth kinetics of the cellular microconstituent are governed by an activation energy of less than half the activation energy for lattice diffusion of Ti in Cu.

3. The formation of fine-scale coherent/semicoherent $D1_a$ (Cu_4Ti) precipitates at high supersaturation imparts to these age hardened alloys strength levels comparable to Cu–Be alloys. The quasi-periodic arrays of $D1_a$ particles or modulated structures coarsen according to a generalized LSW kinetic law with an activation energy of ~ 50 kcal mol^{-1} in agreement with reported values for the activation energy of Ti in Cu.

4. The early stages of decomposition of supersaturated Cu–Ti alloys involves a complex interplay of ordering and clustering effects in solution. The formation of the coherent two-phase mixtures almost certainly involves non-classical nucleation or spinodal decomposition within the context of a generalized nucleation theory and clear definition of the spinodal process.

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