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ON THE PRODUCT PHASES OF THE CELLULAR TRANSFORMATION IN Cu-Ti AGE HARDENING ALLOYS

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Abstract

Cu-Ti alloys have significant high-strength and high-conductivity and may replace conventional Cu-Be alloys in numerous applications. However, overaging in these alloys is associated with the formation of a coarse lamellar microconstituent (cellular regions) which nucleates at the grain boundaries of the parent matrix phase. The growth of these cells consumes the metastable, fine-scale coherent/semicoherent phase mixtures leading to a rapid degradation of mechanical properties. It is therefore important to control the nucleation and growth of the cellular or “discontinuous” precipitation reaction, in order to optimize the physical properties of the Cu-Ti alloys. In this paper we investigate the identity and stability of the phases present in the cellular regions of the overaged alloys. We find that the β-Cu_4Ti (Au_4Zr) phase is present in the cellular regions at temperatures as low as 450 °C.

Introduction

The age hardening of copper-titanium alloys containing 1 – 6 atomic percent Ti has been investigated for nearly three quarters of a century [1-3]. Copper-titanium alloys are receiving a great deal of attention as ultra-high strength conductive materials for applications such as conductive springs and interconnections, potentially displacing the conventional copper-beryllium alloys. In a recent paper [4] we reviewed work regarding the decomposition of supersaturated Cu-Ti alloys and microstructural development during aging. In this paper we focus on the identity of the second phase that forms in the cellular regions during overaging of the decomposing Cu-Ti alloys.

A currently utilized phase diagram (see Figure 1) of the Cu-Ti system shows the terminal FCC Cu-rich solid solution (α) to be in equilibrium with either of two Cu_4Ti phases, designated as β-Cu_4Ti with the Au_4Zr structure and space group Pnma [5-7] and β′-Cu_4Ti with the $D1_a$ structure (Ni_4Mo) with the space group I 4/m [8,9]. For short aging times the alloy displays a three dimensionally modulated periodic structure characteristic of spinodal decomposition. The structure of the phase which eventually develops from such decomposition is $D1_a$. During extended aging at low or moderate temperatures a coarse lamellar microconstituent composed of a Cu_4Ti phase and the terminal FCC solid solution forms at the grain boundaries and consumes the fine-scale dispersion of coherent / semicoherent $D1_a$ particles. See Figure 2. Such a transformation lowers the strength of the alloys as well as lowering their fracture toughness.

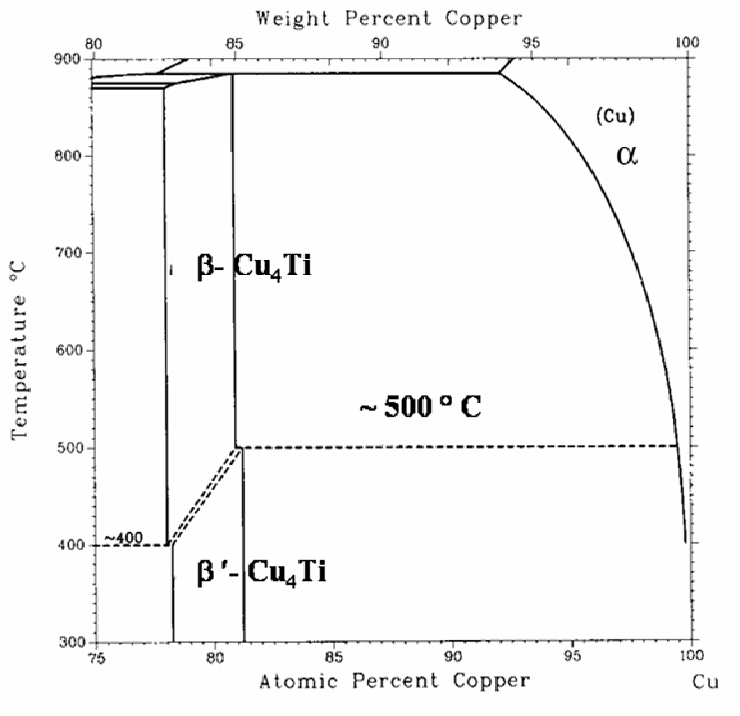


Figure 1. Detailed portion of diagram showing polymorphic transformation in Cu_4Ti phase [5].

The phase diagram of Figure 1 displays a polymorphic transformation of the Cu_4Ti phase. The tetragonal $D1_a$ phase is shown to be the stable phase below ~500°C and the orthorhombic Au_4Zr-type structure is shown to be the equilibrium high temperature phase. That the Cu_4Ti phase with the $D1_a$ structure is the stable low temperature phase is not unexpected since it is a ground state for FCC-based alloys [10]. Both the $D1_a$ and Au_4Zr phases derive from the stacking of essentially close-packed layers with different intralayer ordering. The $D1_a$ phase exhibits oblique ordering within the layers and these are stacked ABC… as its parent FCC structure. The Au_4Zr-structure shows a triangular-striped ordering and is a derivative of HCP stacking [11]. See Figure 3.

During the anticipated expanded commercialization of age hardening Cu-Ti alloys the nature of the cellular reaction or discontinuous precipitation mode will undoubtedly be a major focal point since, as mentioned above, the appearance of the cellular microconstituent leads to deleterious effects on mechanical properties [12,13]. Also, the influence of plastic deformation on the aging response will be of paramount importance in the thermomechanical processing of these materials in production [14].

In this paper we present the results of our initial investigations of the identity of the second phase Cu_4Ti in the cellular reaction in this alloy system. Future work will emphasize methods of controlling the cellular transformation.

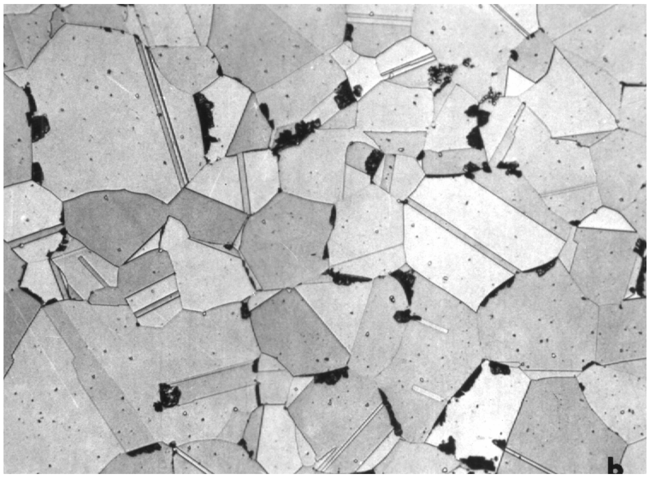


Figure 2. Optical micrograph revealing the cellular colonies emerging from the grain boundaries in an alloy ages 500 min at 500 °C.

Experimental Procedure

Samples of Cu-Ti alloys containing 3 w/0 Ti were cut to small cubes about 10 mm. in dimension. Each sample was solutionized at 800 °C for 1-2 hours in flowing argon and followed by a water quench. Isothermal aging temperatures ranging from 450°C to 525 °C were carried out in a salt bath with a temperature variation of about ± 2 °C.

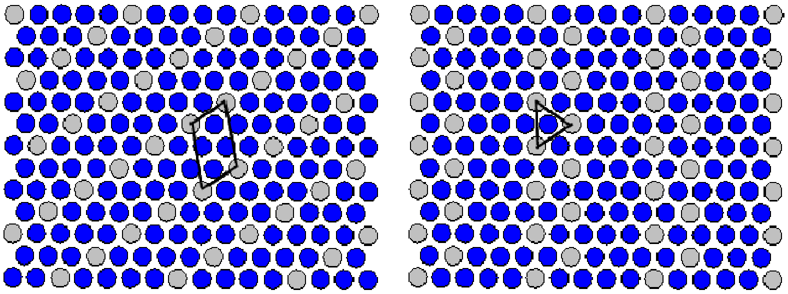


Figure 3. Oblique ordering (a) and triangular ordering (b) of the close packed planes of the D1a and Au_4Zr structures, respectively

Optical observations, X-ray analysis and hardness testing were performed on the aged samples. X-ray studies were carried out by Rigaku θ/θ, using Cu Kα radiation and a graphite monochromator. The target voltage was 35 kV and filament current was 25 mA. The scans were performed over the range of 2θ from 10 to 80°. Quantitative analysis was performed by optical microscopy and scanning electron microscopy (SEM). The accuracy of this method is within a few percent depending on the metallographic preparation.

Thin foils for transmission electron microscopy (TEM) were prepared by mechanical grinding, followed by double-jet electro-polishing. Methanol-33 vol.% Nitric acid (HNO_3) was used as the electrolyte and the electro-polishing was done at –50 °C to –30 °C. A JEOL 2000 EX operated at 200 kV equipped with a double tilt holder with tilting capabilities of ± 40° was used for the microstructure investigation.

Results and Discussion

We were interested in determining the validity of the phase diagram proposed by Brun et al. [5]. In particular we wanted to ascertain if the invariant temperature at 500 °C shown in Figure 1 was an accurate depiction of the phase equilibria between the β′ and β-Cu_4Ti phases.

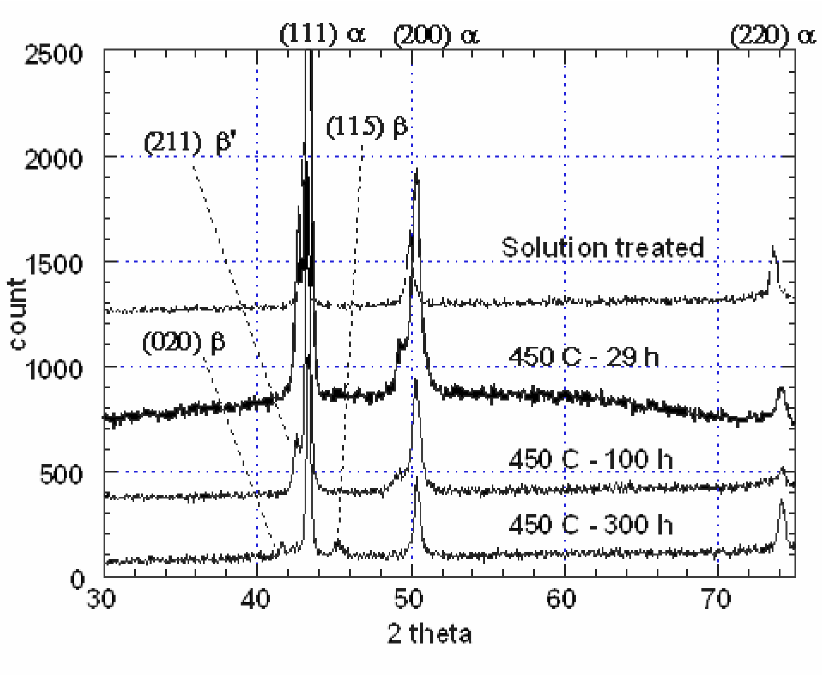


Figure 4. X-ray patterns of several aged samples indicating the presence of either the β or β′ phase.

Table 1 summarizes the results of our x-ray diffraction studies of the aging of Cu-3w/0 Ti alloy. Figure 4 displays some of the diffraction patterns. From these it can be seen that the β-Cu_4Ti phase (the high temperature Au_4Zr) was found to be present at long time aging for all the temperatures we studied. The β Au_4Zr phase can be seen to replace the $D1_a$ phase, though by x-ray diffraction it was not possible to determine if the $D1_a$ phase was present as a coherent mixture throughout the grains or if it was also present in the cellular regions.

Table 1. The specific Cu$_4$Ti phase (β or β′) present after various aging times and temperatures.

Temp (°C) Time (hour)	450	460	475	490	510	525
1	N/A	S.S.[a]	β′ [b]	β′	β′	β′
2	N/A	N/A	N/A	N/A	β′	β′
5	β′	N/A	N/A	β′	β′	N/A
10	β′	N/A	β′	β′	β′ / β	β [c]
25	β′	β′	β′	β′ / β	β	
50	β′	β′ / β	N/A	β′ / β		
100	β′	β′ / β	β	β		
300	β					

[a] Cu-3w/0 Ti solid solution

[b] Low temperature β′-Cu$_4$Ti with D1$_a$ structure

[c] High temperature β -Cu$_4$Ti with Au$_4$Zr structure

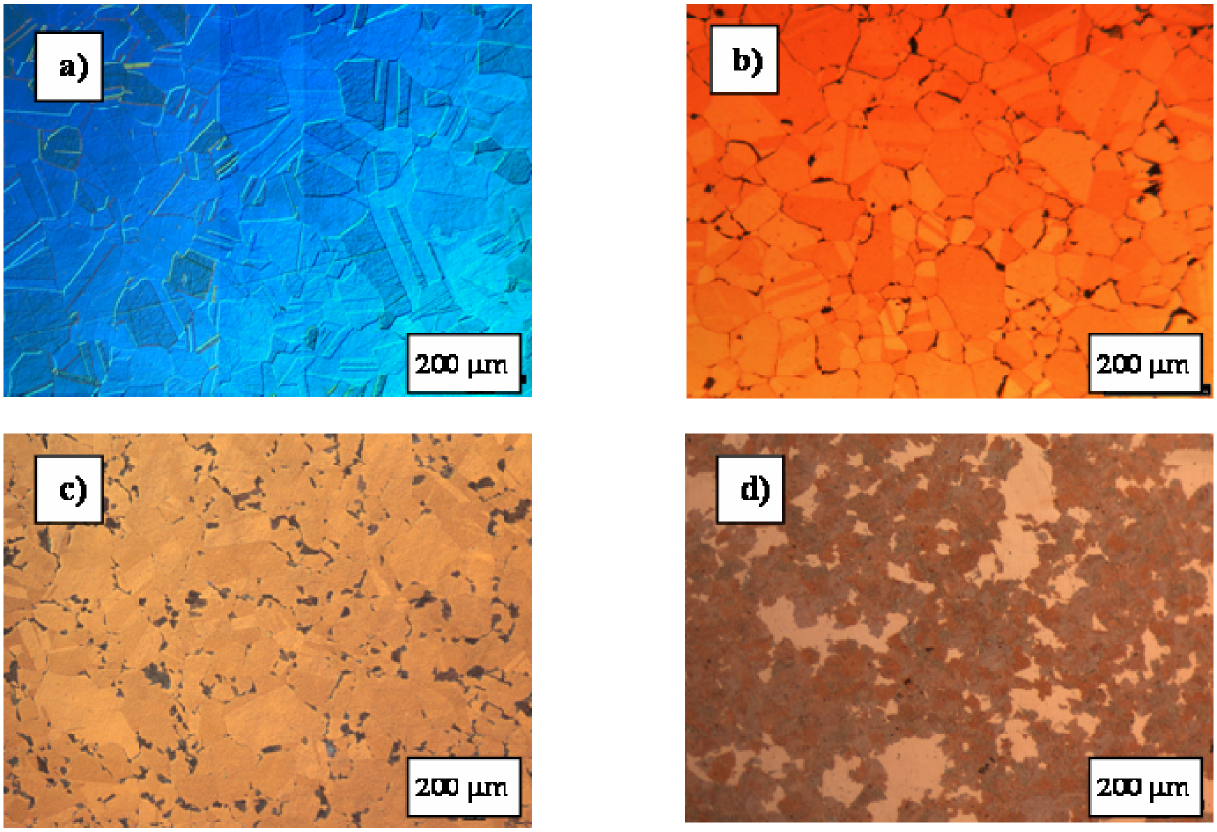
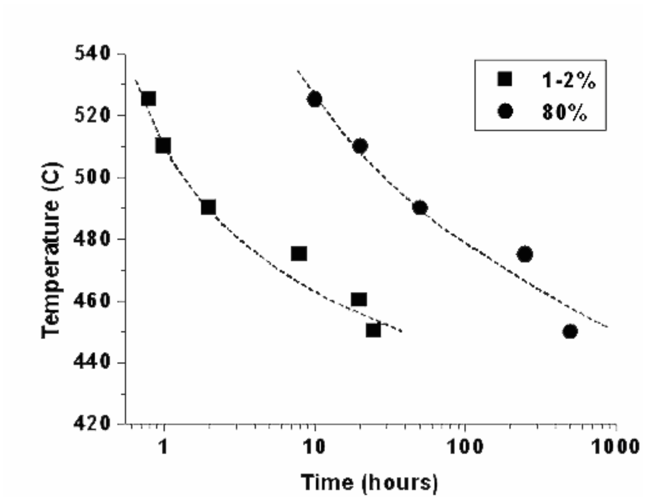


Figure 5. Optical micrographs of Cu 3w/0 Ti alloys: a) solution treated, b) 450 °C 29 h, c) 450 °C 100 h, d) 450 °C 300 h

Preliminary data on the kinetics of the cellular precipitation were obtained by quantitative metallographic analyses. As shown in Figure 5 the amount of cellular precipitation increases with aging time at 450°C. The TTT diagram of the cellular precipitation was constructed as presented in Figure 6. It is obvious that the TTT diagram in the range of temperature studied is the portion below the "nose" of the normal TTT curve. More results of the kinetics studies for this alloy will be presented in a future paper.



TEM Results

As seen earlier from the X-ray results, at temperatures below 500°C for a short period of aging only the low temperature β′-Cu_4Ti phase along with the FCC-Cu are present. However, by optical microscopy, we have shown that cellular precipitation has already occurred. On the other hand the X-ray diffraction shows that at temperature greater than 500°C, the metastable low temperature β′-Cu_4Ti was also present in the sample. In order to determine the specific structure of the phases present in the colonies, TEM was performed.

β′-Cu_4Ti (D1a) Phase In The Cellular Precipitation Colony. The TEM results of the Cu-3w/0 Ti alloy samples aged below 500°C for a short period (1h at 475°C followed by 1h at 500°C) are shown in Figure 7. The electron diffraction pattern of the bright field image of the cellular colony shown in Figure 7 b) reveals that there are two sets of electron diffraction patterns superimposed on each other. The more intense spots correspond to both FCC-Cu with the [211] zone axis and the fundamental reflections of the β′- Cu_4Ti with the [111] zone axis. The less intense spots are superlattice reflections of the β′. The fact that the $D1_a$ phase forms within the cellular regions is noteworthy.