Precipitation Kinetics in a Cu-4 mass\% Ti Alloy

Felipe Hernandez-Santiago\(^1\), Nicolas Cayetano-Castro\(^1\), Victor M. Lopez-Hirata\(^1\), Hector J. Dorantes-Rosales\(^1\) and Jose de Jesus Cruz-Rivera\(^2\)

\(^1\)Instituto Politecnico Nacional (ESIQIE), Apartado Postal 118-018, Mexico, D.F.07051
\(^2\)Facultad de Ingenieria-Instituto de Metalurgia UASLP, Sierra Leona 550, SLP, Mexico

The precipitation kinetics in a Cu-4 mass\% Ti alloy was studied using SEM, TEM, XRD and Vickers hardness. A Cu-4 mass\% Ti alloy was prepared, homogenized, solution treated and then aged at 673, 773 and 873 K for times between 0.6 to 720 ks. The XRD and TEM results indicated that the phase decomposition occurred by spinodal decomposition during the early stages of aging. The growth kinetics of composition modulation wavelength is very slow at the early stages of aging. The precipitation of metastable $\beta'$ (Cu$_3$Ti) preceded to that of the equilibrium phase $\beta$ phase (Cu$_4$Ti), which formed through cellular precipitation. The coarsening process of $\beta'$ phase followed the LSW theory for diffusion-controlled growth. The activation energy for this coarsening process was determined to be about 190 ± 10 kJ mol$^{-1}$. The discontinuous precipitation of $\beta$ phase has an activation energy of about 207 kJ mol$^{-1}$ and an exponent time of about one. The highest hardness and fastest transformation kinetics occurred at aging temperatures of 673 and 873 K, respectively.

(Received January 26, 2004; Accepted May 24, 2004)

Keywords: copper-titanium alloys, hardness, spinodal decomposition, precipitation, discontinuous precipitation, microstructure, growth kinetics

1. Introduction

Cu-Ti alloys are susceptible to age-hardening. Besides, this type of alloys has shown to be a possible substitute for expensive and toxic age-hardenable Cu-Be alloys. The precipitation process and strengthening in Cu-Ti alloys have been a subject of continuous studying.\(^1\)-\(^6\) The phase decomposition in the early stage of aging has been shown to take place via the mechanism of spinodal decomposition.\(^1\) A sharp increase in hardness has been reported to occur after the continuous nucleation and growth of fine, coherent and metastable (Cu$_4$Ti) $\beta'$ precipitates in aged Cu-Ti alloys.\(^6\) The decrease in hardness has been attributed to the cellular or discontinuous precipitation of stable (Cu$_4$Ti) $\beta$ phase during aging of Cu-Ti alloys. In spite of all the above results, there is insufficient information about the growth kinetics and its corresponding parameters for the different stages of the precipitation process in this type of alloys. Thus, the purpose of the present work was to carry out a study on precipitation kinetics from the early stages of precipitation to the coarsening process for an isothermally aged Cu-4 mass\% Ti alloy.

2. Experimental Procedure

A Cu-4 mass\% Ti alloy was prepared from the pure elements in an alumina crucible under an argon atmosphere using an electrical furnace. The alloy ingot was homogenized at 1223 K for 2592 ks. Samples of 20 mm × 10 mm × 5 mm were cut and solution treated at 1123 K for 3.6 ks in a tubular electrical furnace and then quenched in ice-water. The solution treated samples were aged at 673, 773 and 873 K for times from 0.6 to 720 ks in a tubular electrical furnace. The X-ray diffraction analysis of solution treated and aged samples were carried out with a diffractometer using Cu K$\alpha$ radiation. The aged samples were also observed with an SEM at 15 kV. The samples for transmission electron microscopy were prepared by the twin-jet electropolishing method at 213 K with an electrolyte composed of 25% nitric acid and 75% methanol in volume. The TEM observation of samples was pursued at 200 kV. The Vickers hardness of heat-treated samples was determined using a load of 0.98 N.

3. Results and Discussion

3.1 Spinodal decomposition

Figure 1 shows the X-ray diffraction (XRD) patterns for samples solution treated and aged at 873 K for different times. The XRD pattern of solution treated sample shows only the diffraction peaks corresponding to an fcc solid solution. No sidebands were detected on 200 diffraction peak. The XRD pattern of sample, aged for 0.6 ks, shows the diffraction peaks corresponding to an fcc phase and the presence of sidebands near 200 diffraction peak. The diffraction peaks corresponding to the equilibrium $\beta$ (Cu$_4$Ti) phase were detected for samples aged since 1.8 ks. Its presence seems to be related to the discontinuous precip-
solution decomposed into a mixture of copper-rich and titanium-rich regions. Sidebands were analyzed with the Daniel-Lipson equation\(^8\) to determine the wavelength of composition modulation, \(\lambda\). The variation of wavelength with aging time for 673 K is shown in Fig. 3. The time exponent was determined to be about 0.1 for short agings. A time exponent of about 1/3 was observed at later times. A similar behavior has been reported to occur in different spinodally-decomposed alloys.\(^8\) That is, the slower kinetics of modulation wavelength has been associated with a cluster coagulation mechanism.\(^9\) The faster kinetics corresponds to the coarsening stage and is in agreement with the exponent of 1/3, predicted by the Lifshitz-Slyozov-Wagner (LSW) theory for diffusion-controlled coarsening.\(^7\)

A sequence of BF-TEM microstructure evolution of samples solution treated and aged at 673 K for different times is shown in Figs. 4(a)–(g). The TEM micrograph of solution treated sample shows no precipitation at all, Fig. 4(a). The corresponding electron diffraction pattern shows only the spots characteristic of an fcc crystalline structure. This means that the quenching rate was fast enough to suppress the phase decomposition during the quench. The microstructure of sample, aged for 18 ks, consisted of a modulated structure with sidebands flanking the 200 reflections, Fig. 4(b). This fact confirms that the phase decomposition takes place via spinodal decomposition.\(^7\)

### 3.2 \(\beta^\prime\) and \(\beta\) precipitations

After prolonged agings, the sample microstructures were composed of a periodic array of coherent cuboids aligned on the elastically soft (100) matrix directions, Figs. 4(c–g). Superlattice reflections were observed in the corresponding electron diffraction pattern, Fig. 4(f). These have been identified\(^2\) to match with a Ni\(_3\)Mo-type structure. This suggests that the cuboid particles correspond to the metastable \(\beta^\prime\) (Cu\(_4\)Ti) phase.\(^5,6\) The \(\beta^\prime\) phase has been reported\(^4\) to be formed from a spinodal decomposition mechanism involving clustering and ordering. The stable \(\beta\) phase was present in the lamellar structure, nucleated on grain boundaries due to the cellular precipitation, \(\alpha \rightarrow \alpha + \beta\).\(^4-6\)

The Ostwald ripening of \(\beta^\prime\) precipitates was analyzed using the BF-TEM micrographs.
The morphology of $\beta'$ precipitates changed from cuboids to block-like rods elongated on $\langle 100 \rangle$ matrix directions during coarsening. The facets of these precipitates are flat. This suggests that the interface between precipitates and matrix is coherent or semicoherent. The plot of $r^3 - r_0^3$ vs. aging time for $\beta'$ precipitates is shown in Fig. 5. An Arrhenius plot of $\ln k$ vs. $1/T$ yields an activation energy of about $190 \pm 10$ kJ mol$^{-1}$. This value agrees fairly well with the activation energy of 198-206 kJ mol$^{-1}$ determined for the diffusion of Ti in Cu. This fact confirmed that the coarsening process of $\beta'$ precipitates occurred by a diffusion-controlled growth mechanism.

Figure 6 shows the SEM micrographs for the Cu-4 mass%Ti alloy aged at 673, 773 and 873 K for different times. The transformation fraction increased with aging time and temperature. The fastest and slowest kinetics of discontinuous precipitation took place at 873 and 673 K, respectively. The cellular precipitation started from grain boundaries and its morphology was flat at the early stages and changed to an irregular shape at the end of process. It is important to mention that the discontinuous precipitation of $\beta'$ phase and the precipitation and coarsening of $\beta'$ phase took place simultaneously and in a competitive manner. The analysis of the variation of transformation fraction, $f$, with aging time was carried out using the Johnson-Mehl-Avrami equation. A time exponent $n$ was determined to be about 1 from the plot of $\ln(\ln(1/(1-f)))$ vs. $\ln t$, Fig. 7. This value is in agreement with exponents calculated using data of discontinuous precipitation in Cu-Ti alloys. Besides, the activation energy for the discontinuous precipitation was determined to be about $207 \pm 10$ kJ mol$^{-1}$, employing the Arrhenius plot of the time for a 10% of cellular precipitation. This value agrees fairly well with the activation energy for volume diffusion in this type of alloys and the activation energy determined for the discontinuous precipitation in Cu-Ti alloys. The theories of cellular or discontinuous...
precipitation, developed by Turnbull\(^{12}\) and Cahn\(^{13}\) for binary alloy systems, predict a time exponent \(n\) of about 3 and an activation energy similar to that for grain boundary diffusion, about 0.5 times the activation energy for volume diffusion.\(^{12}\) That is, the growth kinetics and activation energy for the cellular precipitation in Cu-Ti alloys are slower and higher, respectively, than those of the cellular precipitation theories. This behavior might be attributed to the simultaneous and competitive occurrence of the discontinuous precipitation of \(\beta\) phase and the continuous precipitation and coarsening of \(\beta\) phase during the aging of Cu-Ti alloys. This competitive precipitation process was not considered to occur in these theories. The agreement of the activation energy for this process with that for volume diffusion suggests that the volume diffusion is controlling the overall transformation.

The mean migration rate of the moving cell boundary was constant with time and determined to be about 120 and 300 nm s\(^{-1}\) for 773 and 873 K, respectively. This behavior is in agreement with the constant migration rate detected in the cellular precipitation of binary alloy system.\(^{12,13}\)

### 3.3 Aging curves

The aging curves of Cu-4 mass\% Ti alloy aged at 673, 773 and 873 K are shown in Fig. 8. The hardness for solution treated sample was about 250 VHN. The highest hardness of about 360 VHN was obtained for sample aged at 673 K for 300 ks. This increase in hardness seems to be associated with both the coarsening of \(\beta\) phase and discontinuous precipitation. The drastic drop in hardness for prolonged agings at 673 K seems to be related to the coarsening process of precipitates after a long aging, about 972 ks.

### 4. Conclusions

A study of the phase transformation kinetics in a Cu-4 mass\% Ti alloy was carried out and the conclusions are summarized as follows:

1. The variation of the modulation wavelength of the \(\beta\) phase showed a constant migration rate of the moving cell boundary, an exponent time \(n\) of about 1 and an activation energy of about 207 kJ mol\(^{-1}\).

2. The discontinuous precipitation of \(\beta\) phase showed a constant migration rate of the moving cell boundary, an exponent time \(n\) of about 1 and an activation energy of about 190 kJ mol\(^{-1}\).

### Acknowledgements

The authors wish to thank financial support from CGPI-PIFI-IPN and CONACYT.

### REFERENCES