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KINETICS ANALYSIS OF PRECIPITATION IN A QUASI-BINARY Cu–1 at.% CoTi ALLOY

E. Donoso[1]*, *G. Díaz*[1] *and J. M. Criado*[2]

[1]Universidad de Chile, Facultad de Ciencias Físicas y Matemáticas, Departamento de Ciencia de los Materiales, Casilla 2777 Santiago-Chile
[2]Instituto de Ciencias de Materiales de Sevilla, Américo Vespucio S/N Isla de la Cartuja, Sevilla, Spain

The precipitation process for a concentration of CoTi of super-saturated solutions of Cu–0.50 at.% Co–0.45 at.% Ti (Cu–1 at.% CoTi) was studied through differential scanning calorimetry (DSC) and microhardness measurements. The analysis of the calorimetric curves between the environmental temperature and 900 K shows the presence of only one exothermic reaction attributed to the formation of CoTi particles in the matrix of copper. The energy of activation estimated by using the modified Kissinger method came out much lower than the corresponding to the diffusion of the cobalt and titanium in copper. We may attribute this fact to the strong contribution of the vacancies introduced by quenching.

We used the formalism of Johnson–Mehl–Avrami (JMA) to assess the kinetic parameters. The energetic and kinetic evaluations and the molar heats of precipitation obtained from the isochor of van't Hoff allow us to infer that the reaction corresponds to the formation of CoTi precipitates. The isothermal kinetics of precipitation reaction could be represented satisfactory by an overall kinetic function based in a macroscopic parameter (Vickers hardness). The kinetic parameters obtained from microhardness model are in agreements with those obtained from DSC traces.

Keywords: *copper alloys, kinetics, microhardness, precipitation*

Introduction

The development of high strength ternary alloys has been the subject of a series of studies since the middle of the past decade. The majority of these studies explain such resistance by the formation of extremely fine binary and/or ternary precipitates resistant to shear by dislocations, lending the material a high yield stress. Good examples of this effect are the alloys of Cu–Co–Si [1–4], Cu–Co–Ti [5, 6], Cu–Al–Co [7], Cu–Ni–Al [8–10], etc.

In the case of the Cu–Co–Ti alloys, the precipitation process has been studied by diffraction of X-rays [11–13], transmission electronic microscopy (TEM) and energy dispersive of X-rays (EDX) [5, 6]. These studies indicate that, depending upon the concentrations of Co and Ti, spherical precipitates with cubic structure of CoTi and/or Co_2Ti may develop, with lattice parameters of 0.299 and 1.129 nm, respectively [12].

On the other hand, the experimental results of Mineau *et al.* [5] suggest that the limit of solubility of the phase CoTi in copper, within the temperature range of 773 to 1230 K, is much lower than the individual solubility of the Ti and the Co in the Cu matrix, with a strong tendency to form CoTi in the ternary alloy Cu–Co–Ti instead of particles of Co, Cu_3Ti or Cu_4Ti.

The principal objective of the present work is to evaluate both the thermodynamic and kinetic of the precipitation process of CoTi particles in a supersaturated solid solution of Cu–Co–Ti, using differential scanning calorimetry (DSC) and microhardness measurements. It has been clearly shown in literature [5] that the cubic CoTi phase is the only one developed under these concentrations of cobalt and titanium in the copper matrix. However, the study of the thermodynamic and kinetics of the precipitation process is still missing in spite of the great interest of these studies from the point of view of the potential application of the alloys as shown by a number of works on this topic recently published in this journal [14–21].

Experimental

The alloy used was prepared in an induction furnace under inert atmosphere (Ar), from electrolytic copper (99.95% purity) supplied by MADECO (Chile) and both a master alloy of Cu–10 mass% Co and titanium of high purity supplied by Goodfellow (England). The ingot was annealed at 1173 K during 24 h to achieve complete homogenization and furnace-cooled to room temperature. After chemical analysis, it was found that the alloy contained the following

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* Author for correspondence: edonoso@ing.uchile.cl

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

at.% of the constitutive elements: Cu, 99.07%; Co, 0.49% and Ti, 0.44% (Cu–0.49 at.% Co–0.44 at.% Ti hereafter). Subsequently, the material was cold-rolled to a thickness of 3 mm with intermediate anneals of 1 h at 1173 K. After the last anneal the material was water quenched.

Microcalorimetric measurements was performed in a Dupont 2000 Thermal Analyzer, under an argon flow (10^{-4} m^3 min^{-1}) using a high purity well annealed copper disc as reference in order to increase the sensitivity of the measurements. The baseline was obtained using annealed copper both as reference and sample material under the same experimental conditions used for recording the corresponding DSC curves. The error estimated for the determination of the reaction enthalpy choosing this baseline was not higher than 6% [1, 22]. A set of DSC diagrams were recorded under these conditions at heating rates β of 0.08, 0.17, 0.33, 0.50 and 0.67 K s^{-1}, respectively, from room temperature up to 900 K. The samples were maintained at this temperature during 5 min, and then freely cooled down to room temperature. The set of cooling curves recorded were very similar to each other and had a shape very close to an exponential curve. Once room temperature was reached, a second set of DSC curves were recorded for the annealed samples at the same heating rates previously used for recording the corresponding DSC curve of the first set for being used as baseline. This baseline represents the heat capacity of the alloy as a function of the temperature under the existing thermal conditions. Its value was in agreement with the Kopp–Newmann rule. The resulting traces were later transformed into curves of differential heat capacity *vs*. temperature. The remaining heat capacity, ΔC_p, represent the heat associated to the reactions in solid state occurring during the DSC experiment. Thus, the picks observed in the curve ΔC_p *vs.* T may be characterized by an enthalpy of reaction to each particular event.

Microhardness measurements were performed in a high accuracy Duramin–1/–2 Struers machine employing a load of 1.96 N during 10 s in specimen discs. Such measurements were made using specimens quenched and subsequently annealed specimens for different times. The annealing temperatures used after quenching from 1173 K were 653, 723 and 793 K, respectively.

Results and discussion

DSC analysis

Typical DSC for quenched alloys recorded at different heating rates are shown in Fig. 1. The exothermic peaks recorded must be attributed to the precipitation of phase CoTi [5]. It is noteworthy to point out that the heat associated to the exothermic peaks is independent of the heating rates. Moreover, the fact that the peak temperature moves to higher temperatures by increasing the heating rate shows the kinetic control of the process [23].

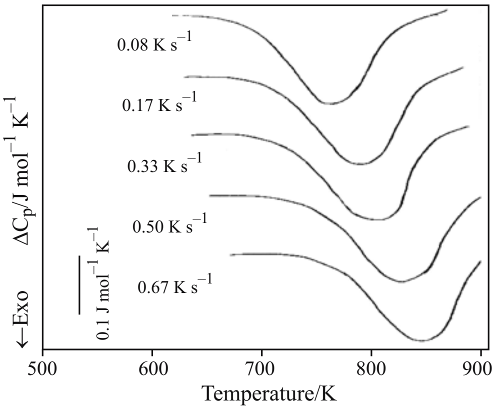

Fig. 1 Calorimetric curves at different heating rates obtained for Cu–1% CoTi samples previously quenched from 1173 K

Table 1 Reaction enthalpies from a set of DSC curves recorded at different heating rates starting from Cu–1% CoTi samples previously quenched from 1173 K

ϕ/K s^{-1}	0.08	0.17	0.33	0.50	0.67
ΔH/J mol^{-1}	133±7	128±6	127±6	132±7	129±7

*Data represent the average of 5 DSC runs

The enthalpies determined by integrating the area enclosed by DSC curve are shown in Table 1. The value reported at every heating rate has been determined as the average of 5 DSC experiments and the corresponding error has been estimated as the standard deviation of the mean value.

On the other hand, the heat of precipitation of CoTi, may be expressed as [22]:

$$\Delta H_c = \Delta H_p [c_{CoTi} - c_M(T_f)] \tag{1}$$

where ΔH_p is the molar heat of precipitation of CoTi in Cu, c_{CoTi} is the concentration of CoTi in the alloy and $c_M(T_f)$ is the composition of the matrix at the final temperature of the reaction. The values of c_M are obtained from the solubility curves proposed by Mineau *et al.* [5]. According to the thermodynamics of ternary systems [24], the compositions of dissolved Co (c_{Co}) and Ti (c_{Ti}) may be written as:

$$c_{Co} \cdot c_{Ti} \approx c_{CoTi}^2 \tag{2}$$

The value of ΔH_p was estimated by using van't Hoff isochore [22]:

$$\ln\left(\frac{c_1}{c_2}\right) = \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\frac{\Delta H_p}{R} \tag{3}$$

where c_1 and c_2 represents the concentrations of the precipitates at the temperatures T_1 and T_2, respectively. A value of ΔH_p=35.8 kJ mol^{-1} was obtained from

Mineau *et al.* [5] solubility curve. Taking this value and solving Eq. (1) for the final temperature of the reaction (851 K) when $\beta\to 0$, we get a precipitation heat ΔH_c of 138 J mol^{-1}. It can be observed that the average value of the experimental reaction heat obtained from DSC is approximately equal to the value calculated from Eq. (1), what confirms that this stage is due to CoTi precipitation according with the conclusions of other authors from XRD and TEM observations [5].

The kinetic analysis of the DSC curves shown in Fig. 1 has been carried out taking into account that the reaction rate is given by equation $d\alpha/dt=(1/S)(da_t/dt)$, where α is the reacted fraction at the time t, da_t/dt is the rate of heat flow, a_t is the area under the peak at time t, and S is the total area. The integration of the above equation leads to the expression $\alpha=a_t/A$ for the reacted fraction at the time t. The value for effective activation energies E are required as a necessary input for determining the kinetic function fitted by the experimental data. This value has been determined from the isoconversional Kissinger equation as modified by Mittenmeijer *et al.* [25], which allows determining the activation energy without any previous assumptions on the kinetic law obeyed by the reaction:

$$\ln\left(\frac{T_p^2}{\beta}\right)=\frac{E}{RT_p}+\ln\left(\frac{E}{RA}\right) \qquad (4)$$

where T_p is the peak temperature, A is a pre-exponential factor of Arrhenius and R is the gas constant. Therefore, E and A can be obtained from the plot $\ln(T_p^2/\beta)$ *vs.* $1/T_p$, as shown in Fig. 2. An activation energy E=130.6 kJ mol^{-1} and Arrhenius pre-exponential factor A=2.5·10^6 s^{-1} have been obtained from this plot. The activation energy for diffusion of Co into Cu ($E_{\text{Co}\to\text{Cu}}$=200.6 kJ mol^{-1}) and Ti in Cu ($E_{\text{Ti}\to\text{Cu}}$= 200.3 kJ mol^{-1}) estimated from the Brown and Ashby [26] correlations are much higher than the value calculated from the Kissinger method. This fact can be attributed to the strong contribution of quenching of vacancies, with an activating energy for migration of about one half of the above values.

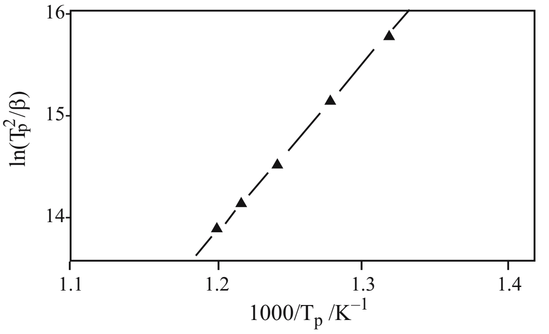

Fig. 2 Modified Kissinger plot for evaluating activating energy and pre-exponential factor

The kinetic analysis of the reaction was performed according to the Johnson–Mehl–Avrami (JMA) equation, which is usually used for heterogeneous reactions under nonisothermal conditions. According to this kinetic model the reaction rate can be expressed by the following equation:

$$\frac{d\alpha}{dt}=Ae^{-\frac{E}{RT}}n(1-\alpha)[-\ln(1-\alpha)]^{1-\frac{1}{n}} \qquad (5)$$

where α is the reacted fraction, n is a constant that depends of the reaction model, t is the reaction time and A is the Arrhenius pre-exponential factor.

If the reaction is carried out at a constant temperature, the integration Eq. (5) leds to:

$$[-\ln(1-\alpha)]^{\frac{1}{n}}=kt \qquad (6)$$

where $k=Ae^{-E/RT}$ account for the constant rate at the temperature T.

However, if the reaction is conducted under a linear heating rate $\beta=dT/dt$, the integration of Eq. (6) using the Coats and Redfern approach [27] gives:

$$[-\ln(1-\alpha)]^{\frac{1}{n}}=\frac{ART^2}{E\beta}e^{-\frac{E}{RT}} \qquad (7)$$

which can be represented in logarithmic form in the following way:

$$\ln[-\ln(1-\alpha)]=n\ln A+n\ln\left[\frac{RT^2}{E\beta}\exp\left(-\frac{E}{RT}\right)\right] \qquad (8)$$

The term $\theta=RT^2/E\beta\exp(-E/RT)$, represents the reduced time introduced by Ozawa [28]. The use of θ for obtaining normalized master plots that can be indistinctly used for the kinetic analysis of isothermal and non-isothermal data was described in a previous reference [29]. The plot of $\ln\ln[1/(1-\alpha)]$ *vs.* $\ln\theta$ after introducing the value of E previously determined from the Kissinger method, leads to a straight line whose slope and intercept are equal to n and $n\ln A$, respectively, as shown in Fig. 3. The value of n and A found by this procedure have been n=1.16 and A=3.4·10^6 s^{-1}. The value of n is closely indicative of a process of nucleation and growth [30], although some precipitation could be taken place during quenching.

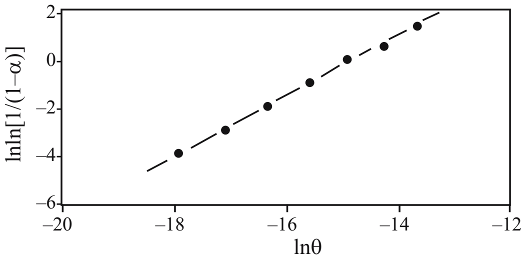

Fig. 3 Plot of lnln[1/(1–α)] calculated from DSC curves as a function of lnθ

Microhardness determinations

The isothermal change of the microhardness as a function of the time has been determined at a set of different temperatures in order to study the kinetics of precipitation of the phase CoTi under isothermal conditions. It has been considered that the microhardness change is proportional to the fraction of precipitate formed [31–36]. Thus, the reacted fraction at a given temperature can be expressed in the following form:

$$\alpha = \frac{H_{\rm V}(t)-H_{{\rm V}_0}}{H_{{\rm V}_{\max}}-H_{{\rm V}_0}} \qquad (9)$$

where $H_{{\rm V}_0}$ is the initial microhardness of the starting quenched material, $H_{{\rm V}_{\max}}$ is the value of $H_{\rm V}$ when the considered reaction is completed and $H_{\rm V}(t)$ is the value of the microhardness at the time t.

Each measure of $H_{\rm V}$ has been the average of six indentations and the $\Delta H_{\rm V}/H_{\rm V}$ relative error is about 2%. Hardness isotherms are shown in Fig. 4 at the indicated annealing temperatures for the alloy previously quenched from $T_{\rm q}$=1173 K. It can be observed that Vickers hardness values increase with time until a maximum value is reached, for the annealing temperature of 723 and 793 K. These values are indicative that an equilibrium precipitation degree is attained in each case. For the 653 K, at the ageing times, it is possible that the reaction is not completed. With the aim to perform a quantitative evaluation of precipitation kinetics, curves of Fig. 4 were transformed into conversional isotherms by means of Eq. (9). These curves are shown in Fig. 5 for two annealing temperatures (723 and 793 K).

According to Eq. (6), the plot lnln[1/(1–α)] *vs.* ln*t*, leads to a straight line of slope *n* and intercept equal to a (*n*ln*k*). The plots of the values of α determined from Eq. (9) as a function of the time at different isothermal temperatures are shown in Fig. 6. Values of *n* ranging from 1.24 to 1.26 and *k* ranging from $1.26\cdot10^{-3}$ to $3.0\cdot10^{-3}$ for annealing temperatures of 723 and 793 K, respectively, are obtained. Values of A=$3.4\cdot10^{6}$ and $1.2\cdot10^{6}$ s^{-1} were obtained at 723 and 793 K, respectively, after taking into account the activation energy *E* determined from the Kissinger method. It can be observed that these *n* and *A* values are in very good agreement with those obtained from DSC traces. It has been reported that all deviations from *n*=1 are due to the annealing out of point defects in high temperature quenched alloys [37, 38].

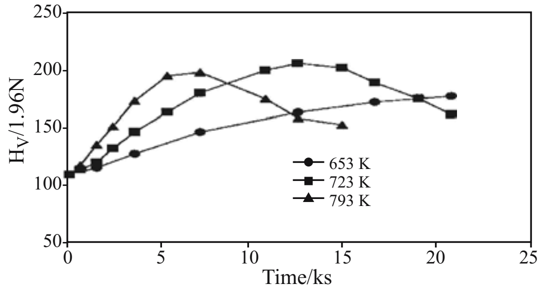

Fig. 4 Vickers microhardness *vs.* time determined at different temperatures for samples previously quenched from 1173 K

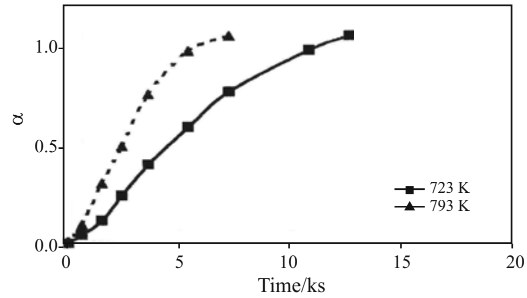

Fig. 5 Reacted fraction determined from microhardness measurements, according with Eq. (9), as a function of the time

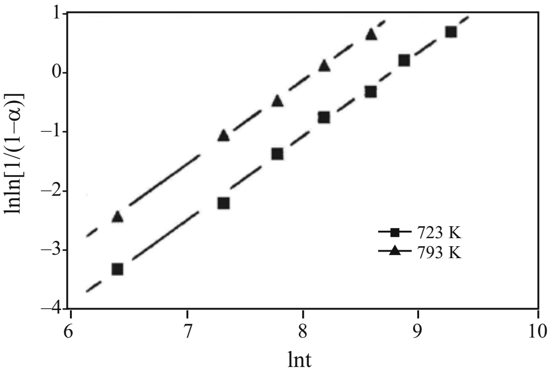

Fig. 6 Plot of the values of lnln[1/(1–α)] calculated from the data included in Fig. 5 *vs.* the corresponding values of ln*t*

Conclusions

The foregoing results conduce to the following conclusions:

- The calorimetric curves permit to infer that the precipitation evolves in only one stage, and corresponds to the particles of CoTi.
- The activating energies found turned out to be lower than those corresponding to the diffusion of cobalt in copper and titanium in copper, due to the contribution of the vacancies introduced during the tempering.
- The value obtained for the constant *n* suggests that the formation of the phase CoTi occurs through a process of nucleation and growth starting from a solid solution.
- The isothermal kinetics of precipitation reaction of the studied alloy could be represented satisfactory by an overall kinetic function based in a macroscopic parameter ($H_{\rm V}$).

- The kinetic parameters obtained from microhardness model are in agreements with those obtained from DSC traces.

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