Spinodal decomposition and precipitation in Cu–Cr nanocomposite

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A R T I C L E   I N F O

Article history:
Received 17 September 2013
Received in revised form 3 November 2013
Accepted 4 November 2013
Available online 13 November 2013

Keywords:
Spinodal decomposition
Copper
Nanoaggregate
Kinetics
Mechanical alloying

A B S T R A C T

In this study, spinodal decomposition and precipitation mechanism of mechanically alloyed supersaturated Cu–3wt.%Cr and Cu–5wt.%Cr solid solutions was investigated under nonisothermal aging. Decomposition mechanism and kinetics were studied using differential scanning calorimetry (DSC) and X-ray diffraction (XRD) techniques. Also, the microstructure was characterized by transmission electron microscopy (TEM). Effect of Al2O3 reinforcement on the aging kinetics was also evaluated. It was found that Cu–3wt.%Cr and Cu–5wt.%Cr solid solutions undergo spinodal decomposition at initial stages of ageing. However, decomposition mechanism was changed to nucleation and growth by the aging progress. The aging kinetics for the Cu–Cr/Al2O3 composition appeared to be slightly faster than that for Cu–Cr, since the ageing activation energy is decreased in presence of Al2O3 nano-particles. This behavior is probably due to the higher dislocation density and other structural defects previously produced during ball milling. A detailed comparison of the DSC results with those obtained by TEM, showing good consistency, has been presented. The average size of Cr-rich precipitates was about 10 nm in the copper matrix.

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1. Introduction

Copper matrix composites reinforced with metallic precipitates, i.e. in situ composites, or ceramic particles have received a great deal of attention during last years. These composites possess advantageous properties, in particular high electrical and thermal conductivity and good mechanical properties. Thus, they are very attractive materials for variant industries [1]. Cu–Cr system is an in situ composite resulting from decomposition of supersaturated Cu–Cr solid solution. Different methods have been used to produce Cu–Cr solid solution. Among them, mechanical alloying has attracted a lot of attention in recent years. Extension of Cr solubility in Cu during mechanical alloying and effect of Al2O3 nano-particles reinforcement on the Cr solubility have already been investigated [2,3].

The phase separation phenomenon in various materials has been investigated earlier. For example, nano-scale phase separation in Cu-base glass system has been reviewed in detail by Kim et al. [4]. It has been known that a metastable solid miscibility gap exists in Cu–Cr binary phase diagram due to a large positive mixing heat between Cu and Cr in solid state [5]. Fig. 1 shows the miscibility gap (binodal lines) and spinodal lines imposed on the Cu–Cr binary phase diagram [6]. This characteristic is very close to Cu–Co and Cu–Fe systems [7–10].

By ageing heat treatment of Cu–Cr solid solution, Cr-rich precipitates in Cu matrix [11–13]. The refinement of Cr particles could clearly improve the electric properties [14,15]. Especially when the size of Cr is in nano-scale, many properties would be improved sharply [16]. Therefore, knowledge of both mechanism and kinetics of aging make it possible to characterize the microstructure resulting from different aging conditions. Also, by controlling the kinetics of the precipitation process, it is possible to take advantage of metastable phases in order to promote dispersion of fine-scale coherent particles, thereby enhancing physical or mechanical properties. In general, two precipitation mechanisms are considered: nucleation and growth in dilute Cu–Cr alloys in the miscibility gap and spinodal decomposition in concentrated alloys. Indeed, nucleation is characterized by metastability, while spinodal decomposition is considered to be the mechanism by which phase conversion occurs in an unstable system [17].

The experimental investigations in the liquid phase transformation for Cu–Cr system have been performed in detail by deep supercooling and rapid cooling technologies [18–21]. Additionally, many investigations have been devoted to study the solid state decomposition behavior of Cu–Cr solid solution in the aspects of microstructure, mechanical and electrical properties [11–13,22–28]. In our previous paper [29], Cr precipitation kinetics through nucleation and growth mechanism has been studied using thermal analysis in Cu–1wt.% Cr alloy. Specially, the effect of the Al2O3
nano-particle reinforcement on the kinetic of precipitation was also studied [29]. Based on Fig. 1, Cu–1wt.% Cr alloy composition lies within the miscibility gap. However, detailed investigation on decomposition mechanism of Cu–Cr solid solution with higher Cr composition has not been reported yet and there is considerable ambiguity regarding the nature of decomposition in alloys in the spinodal region. The aim of this work is to study the decomposition kinetics and its mechanism in Cu–3wt.% Cr and Cu–5wt.% Cr alloys which lies just inside the spinodal region using thermal analysis, XRD and TEM techniques. Also, the precipitation behavior of Cr particles in presence of Al2O3 nano-particle reinforcement was studied.

2. Experimental procedure

Cu–Cr solid solution powders were used for the aging kinetic measurements. Alloys with nominal compositions of 3 and 5wt.% Cr were prepared through mechanical alloying for 80 h in a Fritsch P5 planetary ball mill with ceramic vial (350 ml) and balls (10 and 15 mm in diameter) under argon atmosphere. The ball to powder weight ratio and milling speed were 30:1 and 300 rpm, respectively. The milling of samples was carried out with 1 wt.% toluene as the process control agent. In the first step of milling, Cr and Al2O3 powder mixture was pre-milled separately for 10 h and then mechanically alloyed with Cu. Complete experimental details and details of extended solid solution formation were reported elsewhere [2,3].

The samples and chemical composition of prepared alloys are listed in Table 1.

DSC experiments were performed in a SDT Q600 instrument and argon gas flow of 100 ml/min was applied during the measurement. All experiments were carried out on samples in standard platinum pans, with an empty pan as the standard. The measurements were performed at four different heating rates, i.e. 5, 10, 15 and 20 K/min in the temperature range of 300–1273 K. Initial DSC results indicated that the decomposition of the Cu-Cr alloy, with the composition here studied, was not completed at heating rates higher than 20 K/min. Therefore, heating rates not higher than 20 K/min were used for recording the DSC diagrams. Once the samples were cooled down to room temperature, a second set of DSC curves was recorded at heating rates higher than 20 K/min. Therefore, heating rates not higher than 20 K/min were used for recording the DSC diagrams. Once the samples were cooled down to room temperature, a second set of DSC curves was recorded at the same heating rates previously used for recording the corresponding DSC curves of the first set to be used as base line. A precise measure of the heat flow can thus be obtained by measuring and integrating the difference between the first and second scans.

The phase identification of the products was carried out by XRD (Philips PW-3710) using Co Kα radiation (λ = 0.17407 nm). The lattice parameters were calculated from XRD data. High angle reflections (111), (200), (331), and (210) were used to estimate lattice parameters. The true lattice parameter was determined by least-squares regression of the values calculated from each reflection against cos2θ/2θ0, taking the lattice parameter as the intercept of the regression line [11]. The microstructure of the samples was examined by transmission electron microscopy TEM (Philips CM200, operated at 200 kV).

3. Results and discussion

DSC traces of the mechanically alloyed powders obtained at different heating rates are presented in Fig. 2. The DSC scans show overlapping exothermic peaks for all of the samples. Therefore, this system exhibits complex exothermic phase transformations in which the identification of the peaks requires several types of experiments and a detailed analysis of the data. This DSC feature, i.e. two or three broad and poorly separated exothermic peaks, is typical for the decomposition of highly supersaturated solid solutions [30–33]. However, DSC results of Cu–Cr alloy with a composition outside of the spinodal region, presented in our previous paper [29], consist of only one peak. Therefore, the large width of these traces indicates that the kinetics of decomposition in these alloys cannot be modeled by a single and simple nucleation and growth process, since this would give rise to a narrower DSC peak [34,35]. These evidences prove conclusively that the spinodal decomposition is probably responsible for the observed behavior in DSC experiments. In order to get a better understanding of the probable spinodal decomposition, more precise evaluations based on the enthalpy calculation, XRD and TEM results are needed.

The enthalpy changes associated with the exothermic peaks (ΔH,calculated) was calculated from the integration of the overall DSC curves. The average values of enthalpies for each sample are summarized in Table 2. On the other hand, theoretical exothermic thermal effects (ΔH, theoretical) accompanying with the decomposition of supersaturated Cu3 wt.% Cr and Cu-5 wt.% Cr alloys calculated using CALPHAD [32] method are summarized in Table 2. A quantitative agreement of the heat release during phase separation of the milled solid solution samples with the theoretical enthalpy is observed. This agreement is particularly remarkable in view of the fact that overall overlapped peak is related to the Cr precipitation.

The samples were further analyzed by XRD before and after DSC measurements. The XRD patterns of the mechanically alloyed and aged samples of S1, S2, S3 and S4 are shown in Fig. 3. Mechanically alloyed sample exhibits broadened peaks, typical of ball milled samples. Meanwhile, the peak width for the aged sample is smaller. Also, a small shift of Cu peak to higher angle after ageing observed in Fig. 3 reveals that Cu lattice parameter has decreased.

Cu lattice parameters before and after aging heat treatment are listed in Table 3. The decrease in the Cu lattice parameter to 0.36149 nm (approximately the same as that of pure Cu) may be attributed to the precipitation of the Cr. This could be attributed to the completion of the precipitation process. In fact, Cr solute atoms are driven out of the solid solution and Cu lattice parameter is decreased during the ageing. It should be noted that XRD results after DSC measurements at different heating rates did not show an obvious change, and similar results were obtained. Therefore, it was confirmed by XRD results that the exothermic transformation during thermal analysis is related to Cr precipitation. This also confirms that overall exothermic peaks were due to solid solution decomposition according with the conclusion from enthalpy calculations. However, the diffraction peak corresponding to Cr was not observed in the XRD patterns, due to its small quantity.

Regarding to the Cr precipitation completion, the reasons of presence of two overlapping peaks in DSC traces can now be explained precisely. Fig. 4 shows the Cu-rich side of the partial Cu–Cr phase diagram in which the compositions of the samples are inserted. In the previous paper [29], it was shown that the phase decomposition in the Cu–1wt.%Cr alloy occurred through nucleation and growth mechanism. It is clear from Fig. 4 that, depending

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical composition</th>
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<tbody>
<tr>
<td>S1</td>
<td>Cu–3wt.% Cr</td>
</tr>
<tr>
<td>S2</td>
<td>Cu–3wt.% Cr–3wt.% Al2O3</td>
</tr>
<tr>
<td>S3</td>
<td>Cu–5wt.% Cr</td>
</tr>
<tr>
<td>S4</td>
<td>Cu–5wt.% Cr–3wt.% Al2O3</td>
</tr>
</tbody>
</table>
on alloy composition and temperature, Cr-rich precipitates can be formed in two ways: spinodal decomposition and/or nucleation and growth. This behavior was discussed in details by Kim et al. [4] for different systems. Since all S1, S2, S3, S4 samples have nominal compositions within the spinodal region, their decomposition at low temperatures should be of the spinodal type in the initial stage. When temperature is increased high enough over the spinodal line, precipitation will proceed through nucleation and growth. For example, decomposition mechanism in S1 and S2 samples at low temperatures up to 600 K is of spinodal type and at higher temperatures would be nucleation and growth. Similarly, the transition temperature for S3 and S4 samples is proposed to be 845 K. Appearance of two peaks in DSC curves during precipitation is probably related to transition of precipitation mechanism from spinodal to nucleation and growth.

In order to evaluate the transition temperature more clearly for experimental data, the fractional conversion, $\alpha$, can be easily obtained by partial integration of DSC curve [36]. Fig. 5 shows the $\alpha$-T plots at different heating rates for all samples. Based on the $\alpha$-T plots shape, experimental transition temperatures are shown by dashed arrows. As is seen, the aging process can be divided into two steps and the transformed fraction is small at the early stage of the aging. In summary, two conclusions could be drawn:

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta H_{\text{experimental}}$ (J/g)</th>
<th>$\Delta H_{\text{theoretical}}$ (J/g)</th>
<th>$E$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>45.50 ± 3.17</td>
<td>47.21</td>
<td>118 ± 4</td>
</tr>
<tr>
<td>S2</td>
<td>48.25 ± 3.50</td>
<td>47.21</td>
<td>85 ± 1</td>
</tr>
<tr>
<td>S3</td>
<td>79.50 ± 5.82</td>
<td>78.3</td>
<td>107 ± 1</td>
</tr>
<tr>
<td>S4</td>
<td>82.12 ± 5.80</td>
<td>78.3</td>
<td>58 ± 3</td>
</tr>
</tbody>
</table>

Fig. 2. DSC curves of S1, S2, S3 and S4 samples at different heating rates.
Theoretical approach to the precipitation mechanism change in the Cu–Cr system is valid, at least in the Cr rich side. However, experimental transition temperatures are lower than suggested equilibrium values by Fig. 4. This is more considerable for S3 and S4 samples. It can be explained by the following reasons. First, low precision of spinodal lines in Cu–Cr diagram. Second, the transformation in spinodal decomposition is essentially a diffusional process [37]. Low temperature range of spinodal decomposition could result in a decrease of transition temperatures due to a slower diffusion of atoms. But it is noteworthy to emphasize that the spinodal lines remain ambiguously defined because of the progressive transition from the spinodal decomposition to nucleation and growth process.

Table 3
Cu lattice parameters values (nm) before and after aging heat treatment for different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before aging</th>
<th>After aging</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.36237</td>
<td>0.36159</td>
</tr>
<tr>
<td>S2</td>
<td>0.36251</td>
<td>0.36157</td>
</tr>
<tr>
<td>S3</td>
<td>0.36293</td>
<td>0.36162</td>
</tr>
<tr>
<td>S4</td>
<td>0.36299</td>
<td>0.36160</td>
</tr>
</tbody>
</table>

Fig. 3. XRD patterns of S1, S2, S3 and S4 samples before and after aging.

Fig. 4. The Curich side of partial Cu–Cr phase diagram on the Cu-rich side [5] with samples compositions inserted in it.

By the comparison, the effectiveness of Al₂O₃ nano-particles on conversion rate of S2 and S4 samples can be found in both spinodal and nucleation and growth stages. In order
to compare the influence of Al$_2$O$_3$ nano-particles on aging kinetics behavior in more detail, activation energies, $E$, were calculated. Calculation of $E$ is based on a multiple-scan method in which several measurements performed at different heating rates. This value has been determined from the isoconversional Kissinger equation [32], and summarized in Table 2. It can be seen that $E$ was decreased in presence of Al$_2$O$_3$ nano-particles. For example in Cu–3wt.%Cr sample $E$ has been dropped from 118 kJ/mol to 85 kJ/mol in Cu–3wt.%Cr composition. These can probably be caused by the higher dislocation density and other structural defects generated during ball milling in presence of Al$_2$O$_3$ [3]. Both factors increase the effective diffusivity of Cr and also nucleation sites [29] which accelerate aging process. It should be noted that, there is probably some discrepancies in effectiveness of Al$_2$O$_3$ on spinodal and nucleation and growth stages. Spinodal process is accompanied by the spontaneous growth of the inherent concentration fluctuation at the beginning of aging, because there is no energy barrier for the decomposition and the precipitation of Cr-rich phase [38]. During the second stage of aging, structural defects and Al$_2$O$_3$–Cu interface serve as preferred nucleation sites.

Even though DSC results were strong evidences of alloy decomposition through both spinodal and then nucleation and growth mechanisms, it is desirable to get it confirmed by additional evidences. The aim of TEM studies was not only to characterize the microstructure but also to obtain additional evidence on the nature of transformation. Therefore, the microstructure of S3 sample after ageing in the range of first DSC peak was investigated by TEM. The S3 sample was aged up to 550 K with heating rate of 5 K/min and then quenched. TEM micrograph of this sample is shown in Fig. 6. It shows typical features of spinodal alloys such as periodic array of

![Fig. 6. TEM micrograph of aged S3 sample in the range of first DSC peak.](image)
phases and absence of preferential precipitation at microstructural inhomogeneities such as grain boundaries and dislocations. The corresponding ring-type selected area diffraction (SAD) pattern in the inset is related to copper. Also, additional spots can be seen in SAD pattern. In the case of spinodal decomposition composition fluctuations are typical with dominant wavelength, so additional spots on diffraction pattern could arise [4].

Fig. 7 shows TEM micrograph of the S3 sample aged up to 800 K at a heating rate of 5 K/min and then quenched. In fact, this microstructure is related to the sample after ageing in the range of second DSC peak. It can be seen that spinodally decomposed tweed-like morphology, characteristic of the spinodal products, has been decreased. It confirms some discrete second phase particles showed by arrows distribute within the matrix. As a matter of fact, Fig. 7 shows the microstructure at different ageing condition with nucleation and growth mechanism.

A typical TEM image of a S3 nanocomposite aged up to 900 K at a heating rate of 5 K/min is shown in Fig. 8. The morphology of decomposed phases consisted of discrete Cr-rich precipitates within the fine Cu grains. It can be found that at the end of the aging process the structure had changed to one consisting entirely of discrete particles. This final stage of morphological developments represents the loss of coarsened spinodal structures. Cu matrix grain size is less than 100 nm and also, the average Cr-rich precipitates size is about 10 nm.

4. Conclusions

Decomposition mechanism of supersaturated Cu–3 wt.%Cr and Cu–5 wt.%Cr produced by mechanical alloying was studied using DSC, XRD and TEM. DSC results showed that all samples exhibit a broad exothermic double peak upon heating which mainly originates from the decomposition of the supersaturated solid solution. A decomposition scheme which begins with spinodal decomposition and ends with nucleation and growth at higher temperature was proposed. Kinetics of decomposition is found to be faster in presence of $\text{Al}_2\text{O}_3$ nano-particles. It was found that the precipitation activation energy decreases in presence of $\text{Al}_2\text{O}_3$. Presence of $\text{Al}_2\text{O}_3$ accelerates ageing response, primarily due to the higher dislocation density and other structural defects generated during ball milling. Both factors increase the effective diffusivity of Cr and subsequently the rate of the ageing. Also, TEM images agree well with the DSC results. TEM results support the view that, at initial course of aging the microstructure was similar to that of spinodal decomposition. However, the homogeneously distributed Cr nano-particles in nanostructured copper matrix have been obtained at completely aged sample.

Acknowledgments

The support of this work by University of Tehran and Iran Nanotechnology Initiative Council is gratefully acknowledged. The ministry of science, research and technology of Iran is thanked for funding the first author’s sabbatical research in the Instituto de Ciencia de Materiales de Sevilla (CSIC – Universidad de Sevilla). We also thank to the Spanish government for financial support (Project ENE 2007-57924-C02-01).

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