Original Research

# Microstructural study and numerical simulation of phase decomposition of heat treated Co–Cu alloys

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## Abstract

The influence of heat treatment on the phase decomposition and the grain size of Co–10 at% Cu alloy were studied. Few samples were aged in a furnace for either 3 or 5 h and then quenched in iced water. The materials and phase compositions were investigated using energy dispersive spectrometry and X-ray diffraction techniques. X-ray diffraction analysis showed that the samples contained Co, Cu, CuO, $CoCu_2O_3$, $CoCuO_2$ phases in different proportions depending on the heat treatment regimes. The formation of dendrite Co phase rendered the spinodal decomposition while the oxidations prevent the initiation of the spinodal decomposition even for a deep long aging inside the miscibility gap. Since the Bragg reflections from different phases of Co–Cu alloy significantly overlap, the crystal structural parameters were refined with FULLPROF program. The shifts in the refined lattice constants ($a$, $b$ and $c$), the space group and the grain size were found to be phase- and heat treatment-dependant. Two-dimensional computer simulations were conducted to study the phase decomposition of Co–Cu binary alloy systems. The excess free energy as well as the strain energy, without a priori knowledge of the shape or the position of the new phase, was precisely evaluated. The results indicate that the morphology and the shape of the microstructure agree with SEM observation.
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Abbreviations: $T$, Absolute temperature; $r$, Crystal lattice position and its time derivative ($r'$ and $r''$); $p$, Position vector for the lattice points, and its derivatives ($p'$ and $p''$); $t$, Time; $c(r,t)$, Occupation probability of finding a solute atom at position $r$ in time $t$; $c(p,t)$, Occupation probability of finding a solute atom at position $p$ in time $t$; $c_0$, Average composition; $L(\mathbf{r}-\mathbf{r}')$, Matrix of kinetic coefficients related to probabilities of elementary diffusional jumps from lattice site $r$ to $r'$ of a Bravais lattice; $W\{\mathbf{p}'-\mathbf{p}'', c(\mathbf{p}'), c(\mathbf{p}''), T\}$, Function of a pair wise interaction energy between atoms, at interatomic distance ($\mathbf{p}'-\mathbf{p}''$); $W^{str}\{\mathbf{r}'-\mathbf{r}'', c(\mathbf{r}'), c(\mathbf{r}''), T\}$, Strain – induced interaction; $G_c$, Chemical free energy; $E_{str}$, Elastic strain energy; $G_T$, Total free energy; $\varepsilon$, Eigen strain, $\eta$ is the lattice mismatch; $K_B$, Boltzmann constant; $R$, Gas constant; $N_A$, Avogadro's number; $h$, Fourier wave number; $L$, Length of calculation field in real space; $N$, Maximum number of h; $Q_I(h)$, Fourier transform of $c(r)$; $Q_{j+1}(h)$, j[th] evolution of $Q_I(h)$; $V_j(h)$, Fourier transform of $W_j\{\mathbf{r}'-\mathbf{r}''\}$; $B(h)$, Fourier transform of $W_{str}\{\mathbf{r}'-\mathbf{r}''\}$; $M(h)$, Fourier transform of $L\{\mathbf{r}-\mathbf{r}'\}$; $\Delta t$, Time interval; $C_{ijkl}$, Elastic stiffness constant; F, Helmholtz free energy; $h_x$ and $h_y$, Directional components of the wave vector $\mathbf{h}$; $c_\alpha$, Atomic fraction of atoms of kind α

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Peer review under responsibility of Chinese Materials Research Society.

## 1. Introduction

Co–Cu alloys are important materials for various applications including magneto-resistivity and ferromagnetism [1,2], chemical sensing [3] and coating technology [4]. An aspect of Co–Cu systems that has been well studied for the past decades is their mechanisms of phase transition [5–10]. These mechanisms are spinodal decomposition [11,12], nucleation-growth [13], and growth by grain boundary diffusion [14]. Heat treatments (such as annealing and quenching) have been used to modify the properties of these alloys through homogeneous precipitation due to spinodal phase decomposition. In addition, their performances have been enhanced by changing the grain size and phase distribution [15,16].

Phase compositions in multiphase alloys can be quantified by X-ray diffraction (XRD) technique. However, due to significant overlapping of Bragg reflections for Co–Cu alloys, the possibility of texture effect becomes more dominant and accuracy of phase

quantification diminishes. An alternative method for structure refinement is the Rietveld method (RM) [17–22]. RM eliminates peaks overlapping by explicitly including all lines for each phase in the refinement. It also uses a reliable texture correction to minimize the undesirable effect of texture. More importantly, only knowledge of the phases and their respective crystal structures are needed [22]. RM is thus considered as a viable method for analyzing XRD spectra of our Co–Cu samples.

On the other hand, spinodal phase decomposition has been observed in some samples while the others not, even they all heat treated at the same conditions deeply inside the miscibility gap. For the best of our knowledge, no explanations for that phenomenon can be found in previous works. Moreover, phase quantification in Co–Cu system using RM is rare. Therefore, this paper reports a systematic experimental technique designed to reveal the effect of oxidation and the other phases on the initiation of spinodal or binodal decomposition. To obtain an accurate value of the grain size a correction for the instrumental broadening is considered in the present work.

It has been established that phase decomposition in multiphase alloy is controlled by the change in free energy of the system. For such a system, the combined effect of the bulk free energy, interfacial energy, as well as the elastic strain energy must be considered for a valuable treatment of the phase decomposition. Khachaturyan [23] pointed out that the strain energy of a two-phase mixture of an arbitrary morphology gives rise to a strain accommodation which results in a certain optimal microstructure. That accommodation is important in the later stage of the phase decomposition. Introducing additional free energy due to the formation of oxide interfaces prevent the formation of the mottled structure. Based on Refs. [23,24], we conducted two-dimensional (2D) computer simulations to study the phase decomposition of Co–10 at% Cu binary alloy system. We precisely evaluated the excess free energy as well as the strain energy without a priori knowledge of the shape or the position of the new phase. Thermodynamics data related to the equilibrium phase diagram of these systems were used. The calculated microstructures were compared to the experimental results.

## 2. Experimental

### 2.1. Sample preparation

Rod samples of Co–10 at% Cu alloys were synthesized from a mixture of pure Cu and Co pellets by means of the arc melting technique [14]. The samples were re-melted five times to enhance dispersion of Cu and Co particles. Small strips of about 1–2 mm thick were obtained for experimental study. Four samples were thermally treated in a quartz-glass tube under the same temperature and purified argon atmosphere but different aging times. The conditions were chosen to study the influence of thermal treatment on the quality and quantity of phases and grain/crystal in the samples. All samples were solid solution treated (SST) at a temperature of 1500 K and a heating rate of about 50 K/min. While sample S1 was thermally treated for 3 h, the others were treated for 5 h. All

the samples (S1, S2, S3 and S4) were thermally aged according to the following conditions: S1 was aged in air at 1000 K for 10 min and then quenched in iced water. S2 and S3 were aged at 500 K for 5 h and 10 min in air, respectively, and then quenched in iced water. S4 was encapsulated in an evacuated quartz tube, aged at 1000 K for 10 min and then quenched in iced water.

The microstructures of the polished samples were observed by using JOEL-JSM-5400LV scanning electron microscopy equipped with energy dispersive spectrometry. The phases, crystal size and texture were investigated by X-ray diffraction techniques using a Phillips X-ray diffractometer with Cu $K_\alpha$ radiation. The spectra were acquired within the range of $2\theta = 40–110°$ at a scanning step and a speed of $0.02°$ and $0.06 °/s$, respectively. FULLPROF program was used to quantify the crystal phases. The optimized parameters for the refinements were background coefficients, displacement correction, peak shapes, and cell parameters. The residual values of the refinement, R-weighted pattern ($R_{wp}$), R-expected ($R_{exp}$), and goodness-of-fit ($\chi^2$) were evaluated. The geometric structural parameters of the treated samples were determined from the refined lattice parameters while the crystal size was estimated from the modified Scherrer formula.

### 2.2. The kinetic model and time evolution

According to the previous study [19], the kinetic equation describing the time evolution of the occupation probability of finding an atom at crystal lattice position, $\mathbf{r}$, and at time, $t$, takes the form of the following equation:

$$\frac{\partial c(\mathbf{r}, t)}{\partial t} = \sum_{\mathbf{r}'} \frac{L(\mathbf{r} - \mathbf{r}') c_0 (1 - c_0)}{RT} \left\{ \frac{\delta G_T}{\delta c(\mathbf{r}', t)} \right\} \qquad (1)$$

with

$$\begin{aligned} \frac{\delta G_T}{\delta c(\mathbf{r}')} &= \sum_j \frac{j+2}{2} c^{j+1}(\mathbf{p}') \sum_{\mathbf{p}''} W_j(\mathbf{p}' - \mathbf{p}'', T) \\ &+ \sum_{\mathbf{p}''} W_A(\mathbf{p}' - \mathbf{p}'', T) c(\mathbf{p}'') \\ &+ RT \sum_{\mathbf{p}'} [\ln c(\mathbf{p}') + \ln \{1 - c(\mathbf{p}')\}] \\ &+ \sum_j \frac{j+2}{2} c^{j+1}(\mathbf{r}') \sum_{\mathbf{r}''} W_j^{str}(\mathbf{r}' - \mathbf{r}'', T) \\ &+ \sum_{\mathbf{r}''} W_A^{str}(\mathbf{r}' - \mathbf{r}'', T) c(\mathbf{r}'') \end{aligned}$$

Eq. (1) contains the contribution of the chemical free energy and that of the strain energy while the summation is carried out over all $N$ lattice sites. Taking the Fourier transform of Eq. (1) the following equations result in:

$$\left\langle \frac{\partial c(\mathbf{r}, t)}{\partial t} \right\rangle_h = \frac{1}{N^3} \sum_{\mathbf{r}} \left\{ \frac{\partial c(\mathbf{r}, t)}{\partial t} \right\} \exp(-ih\beta\mathbf{r}) = \frac{\partial Q_1(h, t)}{\partial t} \qquad (2)$$

$$\begin{aligned} &\left\langle \frac{c_0(1 - c_0)}{RT} \sum_{\mathbf{r}'} L(\mathbf{r} - \mathbf{r}') \left\{ \frac{\delta G_T}{\delta c(\mathbf{r}', t)} \right\} \right\rangle_h \\ &= \frac{c_0(1 - c_0)}{RT} \left( \frac{1}{N^3} \right) \sum_{\mathbf{r}} \left[ \sum_{\mathbf{r}'} L(\mathbf{r} - \mathbf{r}') \left\{ \frac{\delta G_T}{\delta c(\mathbf{r}', t)} \right\} \right] \exp(-ih\beta\mathbf{r}) \end{aligned}$$