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XRD AND EXAFS INVESTIGATION OF THE DECOMPOSITION OF Co-Cu SOLID SOLUTION PREPARED BY MELT SPINING*

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High solid-solubility $Co_{15}Cu_{85}$ alloys were prepared by melt spining and then submitted to isothermal and anisothermal annealing to obtain granular alloys. The synchrotron radiation X-ray diffraction patterns and extended X-ray absorption fine structure (EXAFS) spectra were measured to investigate the decomposition of supersaturated solid solution upon annealing. Experimental results indicated the precipitation of ultrafine Co-rich particles occurred at about 500 ℃ and the annealing had a great influence on the middle-range order of Co atoms. While the fitted EXAFS spectra showed that the interfaces of Co precipitates seem to be enriched with vacancy-type defects, leading to distorted interfaces.

PACC: 8140; 6155; 6110

I. INTRODUCTION

In recent years homogeneous granular alloys, e.g., Co-Cu, Fe-Cu, or Fe-SiO_2, with a much larger supersaturation far from equilibrium have been widely investigated[1,2] due to their remarkable mechanical, optical and magnetoelectrical transport properties, especially giant magnetoresistance effect (GMR) found in these materials. Granular materials are generally prepared by nonequilibrium techniques, e.g., ball-milling, sputtering and rapid quenching. Subsequent annealing produces homogeneous precipitates with grain size of several nanometers embedded in the immiscible matrix. Therefore the decomposition of solid solutions plays an important role in their macroscopic properties.

Among granular alloys Cu-Co is a simple peritectic alloy system with a large miscibility gap extending over nearly the whole concentration range of more than 95 at% at low temperatures. This originates from the large positive heat of mixing between Cu and Co. However, they have a pronounced solubility at high temperature. The Co-Cu alloys with small supersaturations of up to 2.7 at% have been widely investigated by different methods[3−5], e.g., transmission electron microscopy, field ion microscopy or X-ray diffraction (XRD), etc.

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In this work synchrotron radiation XRD and extended X-ray absorption fine structure (EXAFS) measurements are carried out to investigate the decomposition of the supersaturated solid solution of Co-Cu melt-spun alloys. Because of the local character, the two methods can complement to yield the information of local environment around Co and Cu atoms as well as the long-range order.

II. EXPERIMENTAL

The Co-Cu alloy solid solution with a nominal composition of $Co_{15}Cu_{85}$ was prepared by rapid quenching from the melt (Cu purity: 99.99 % and Co: purity 99.9 %). The peripheral velocity of the wheel was 40 m/s. The ribbons obtained were 25 μm thick and 5 mm wide. The as-cast alloys were then annealed at 400, 450, 500, 550 and 800 ℃ in an argon atmosphere for 1 h. Part of the as-cast samples was submitted to isothermal annealing, at 450 ℃, for 0.25, 0.5, 1.0, 2.0, 6.0 and 12 h.

The transmission EXAFS and XRD measurements were carried out in the 4B9A and 4W1B beamline in Beijng Synchrotron Radiation Facility(BSRF) operating at 30–50 mA and 2.2 GeV. The X-ray wavelength for the XRD experiment was adjusted to 0.15680 nm, around the absorption edge of Ni, in an attempt to minimize the resonant absorption of Co and Cu. Silicon powders were used as standard sample for calibration. The scanning scale, 2θ, ranges from 42° to 53°, and the absorption coefficient at Co K edge was determined using a Si(111) double-crystal monochromator and ion chamber as detectors. Harmonics were rejected by detuning of monochromator. We used program EXCURV88 for data analysis.

The X-ray absorption spectra were background-removed, μ_0-fitted, and then Fourier transformed to obtain the radial distribution function(RDF). Unusual multi-parameter fitting procedures were employed to determine the structural parameters: coordination numbers, the bond length, and Debye-Waller parameters.

III. RESULTS AND DISCUSSION

A. The XRD results of Co-Cu alloy decomposition

The Cu-Co alloy decomposition is a typical precipitation of solid solution. It is known from phase diagram that Co has a very limited solubility in Cu at room temperature, its solubility drops sharply with decreasing temperature. Below 600 ℃ there is actually no solubility of Co in Cu. It is natural that its supersaturation and decomposition is closely associated with the characteristic of its solvus.[6]

The decomposition of Co-Cu solid solution can be seen clearly from Fig.1, which shows the XRD patterns of the Co-Cu alloys for the states of samples of as-cast and annealed at 400, 450, 500, 550 and 800 ℃, respectively. The diffraction peaks are from the fcc Cu(111), Cu(200) and the fcc Co(111). Due to the coherency of Co and Cu atomic lattice, the (111) peaks are partially superimposed, especially for the as-cast sample. The Co(200) peak is too weak to be observed. It is seen that during the rapid quenching, a small amount of Co is precipitated in the as-cast sample. Upon annealing the Co precipitates gradually develop and finally separate from the Cu (111) peak.

In order to get a clear insight into the decomposition of the Co-Cu alloy, the XRD peaks

of Cu(111) and the Co(111) were fitted by two Gaussian functions. If we assume the area of the Gaussian curve is directly proportional to the amount of the corresponding phase, a plot of the ratio of the amount of Co precipitates to that of the Cu phase can be obtained as a function of annealing temperatures, as shown in Fig.2. Below 500 ℃, few precipitates of fcc-Co can be detected. However, as temperature rises higher than 500 ℃, the precipitated amount of Co-rich phase increases significantly, indicating a thermal-excited process of Co-Cu decomposition.

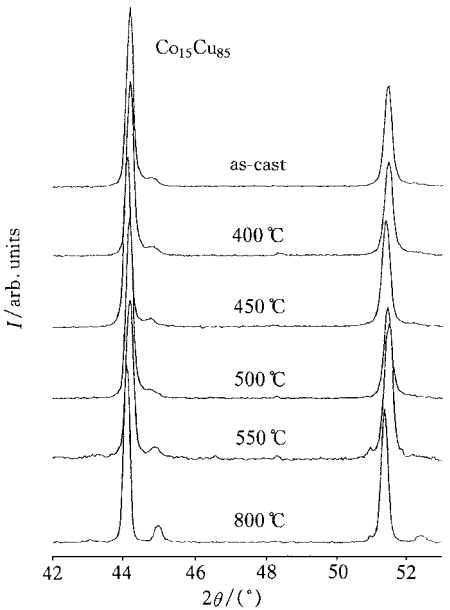

Fig.1. XRD patterns of the $Co_{15}Cu_{85}$ in the as-cast state and states annealed at different temperatures.

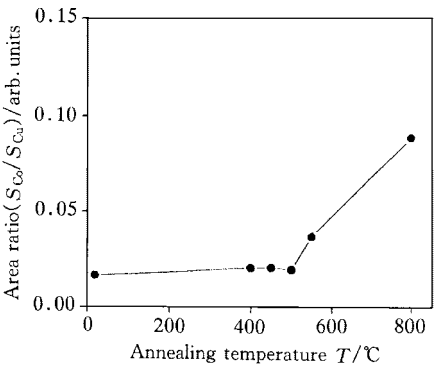

Fig.2. The ratio of intensity of Co(111) to that of Cu(111) as a function of annealing temperature.

The lattice parameter of the fcc-Co phase in the as-cast state is measured to be 0.3590 nm by using the XRD patterns, which is larger than that of pure fcc-Co(0.3545 nm). Thus, we conclude that the fcc-Co phase formed at rapid quenching is composed predominantly of Co with a small amount of Cu, i.e., Co-rich solid solution. Upon annealing, due to the atomic diffusion, the Co atom clusters will segregate among the Cu matrix. As a result, the lattice parameter of the Co-Cu alloy solution decreases and the diffraction peaks shift towards the high angle side as shown in Fig.3. At 800 ℃ the lattice constant drops to 0.3447 nm, close to that of the bulk-Co. On the other hand, at the initial state, the lattice constant of Cu-rich matrix

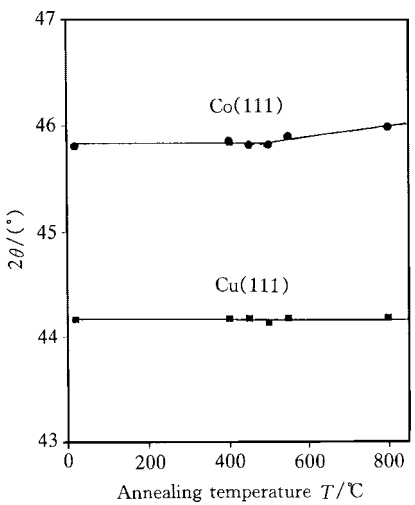

Fig.3. The peak positions corresponding to the Cu(111) and Co(111) as functions of annealing temperature.

is as large as 0.3610 nm.

B. The EXAFS results of Co-Cu alloy decomposition

Fourier transformed EXAFS data can provide element-specific, short range-order information which complements the XRD studies. It is expected that the variation of local environment of Co in the decomposition of Co-Cu alloy can be investigated due to the sensitivity of EXAFS to the decomposition of solid solution. The isothermally annealed $Co_{15}Cu_{85}$ was chosen and the X-ray absorption spectra with respect to K absorption edges of Co were measured.

The X-ray absorption spectra for the annealed samples were background-removed, μ_0-fitted and then Fourier transformed. The radial structure function (RSF) obtained around a Co atom for Co-Cu samples in the as-cast state or in annealed states, as well as the fcc-Co standard sample, are presented in Fig.4. The RSF of fcc-Co standard sample was characterized by a main peak around 0.23 nm, corresponding to the nearest coordination shell 1 and several weaker peaks around 0.34, 0.41, 0.48 nm, corresponding to those coordination shells with Co-Co nearest coordination numbers of 12, 6, 24, 12 and 24, respectively. The coordination peaks cannot be separated out for a distance in R space less than 0.05 nm with $\Delta k = k_{\max} - k_{\min}$ less than 12.

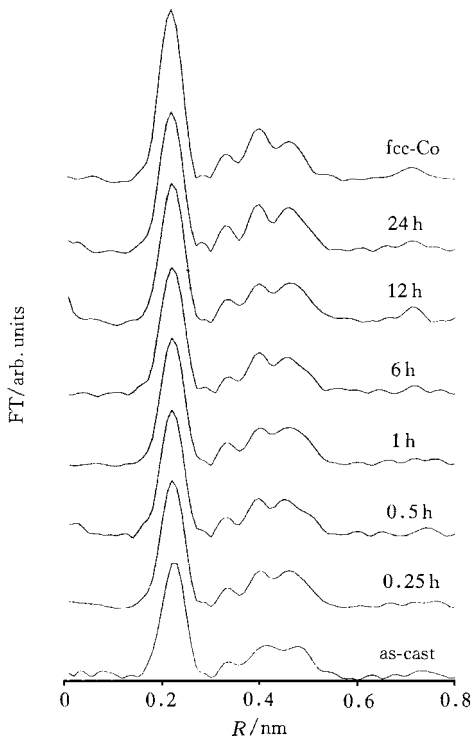

Fig.4. Fourier transformed Co EXAFS data for $Co_{15}Cu_{85}$ in the as-cast sample, and those annealed at 400, 450, 500, 550 and 800 °C, respectively. Similar data for Co(fcc) standard sample are also presented for comparison.

From Fig.4 it is seen that the as-spun sample exhibits the characteristics of a fcc structure, however, with a smaller intensity in the coordination peaks, especially for the next nearest shell. It suggests a kind of structural disorder existing in the as-spun sample. In view of the variation of coordination peaks with the annealing temperature, it is seen that the intensity corresponding to the first nearest neighbor changes little with the annealing time. On the contrary, the peak intensities associated with the second, third and fourth neighboring shells increase significantly. The decomposition of Co-Cu solid solution is well known to be a process of changing from structural disorder to order. The present result indicates that a significant variation occurs largely associated with the medium range of coordination shell. The first nearest environment of Co atom has not changed a lot by isothermal annealing. In order to further demonstrate this, the first coordination peak of

RSF is fitted by Co-Co coordination only, and also by Co-Co and Co-Cu coordinations, simultaneously. The values of amplitude and phase shift for Co-Co are taken from that of the Co standard sample, and those of Co-Cu are calculated theoretically. The result indicates that the latter case, i.e., fitting the RSF 1 st peak by both Co-Co and Co-Cu coordinations agrees well with the experimental curve. Table 1 lists the results of Co-Cu samples in the as-spun state and that annealed for 0.5 and 24 h. The nearest distance of Co-Co coordination is determined to be 0.251 nm, very close to that of the fcc-Co sample(0.2509 nm). However, the bond length of Co-Cu is over 0.261 nm, larger than the sum of Co and Cu atomic radius(0.2556 nm). An explanation for this may be as follows: in the fcc Co-Cu solid solution, the Cu atoms may exist in a distorted lattice, far from the equilibrium position.

Table 1. The fitted coordination number n, bond length r, and Debye-Waller factors σ for Co-Cu samples in the as-spun state and those annealed for 0.5 and 24 h. The subscripts 1, 2 refer to Co-Co, Co-Cu coordinations, respectively. The error bars are approximately 0.002 nm for r, 0.5 for n, 0.0001 nm^{-1} for σ.

Time t/h	r_1/nm	r_2/nm	n_1	n_2	σ_1^2/nm^{-1}	σ_2^2/nm^{-1}
as-cast	0.251	0.261	6.7	3.3	0.0007	0.0005
0.5	0.251	0.262	9.12	0.80	0.0006	0.0001
24	0.252	0.265	9.56	0.40	0.0006	0.0001

The coordination number of Co-Cu, n_2, and the overall coordination, $n_1 + n_2$, (n_1 refers to the coordination number of Co-Co) are presented as functions of the annealing temperature, as shown in Fig.5. The coordination numbers n_1, n_2 for the as-cast sample are 6.7 and 3.3, respectively, indicating a Co-rich solution phase with Cu as solute. Upon annealing for 0.25 h, n_2, drops greatly, suggesting that the Cu in the Co-rich phase is rejected into the Cu matrix. It should be noted that even a 24 h annealing cannot completely preclude the Co-Cu coordination, this may be ascribed to the mixing interfaces between the Co particles and Cu matrix, or to the residual Co in the Cu matrix. The EXAFS cannot distinguish these. The present results are in agreement with those obtained by vibrational sample magnetometer.[7] And the magnetization curves showed that after a long time of annealing, the saturation magnetization of Co precipitates was still less than that of bulk Co, due to the solid solubility of Co in Cu matrix, or the solid solubility of Cu in Co precipitates.

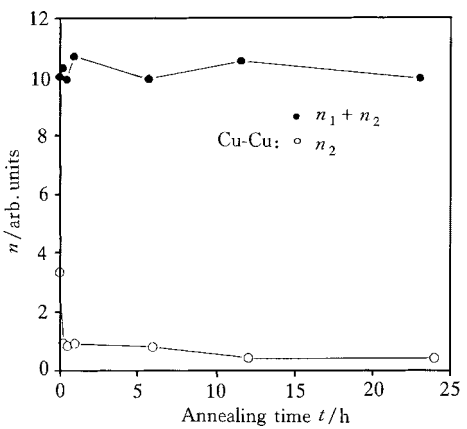

Fig.5. Coordination number of Co-Cu, n_2, and the overall coordination, $n_1 + n_2$, (n_1 refers to the coordination of Co-Co) are presented as functions of the annealing temperature.

Bulk Co metal is of hexagonal phase at room temperature.[8] Cobalt with a fcc structure can only be stabilized at temperatures higher than 425°C, which is in contrast to our present results. From the viewpoint of thermodynamics, one possibility for this is the epitaxial

surface forces exerted by the enveloping Cu matrix. Due to the high coherency of Co and Cu, fcc-Co can be stabilized and preserved to reduce the surface energy.

The coordination number $n_1 + n_2$ ranges between 11 and 12. It seems incredible. The results obtained by field ion microscopy demonstrate that after a long period of annealing (12 h), the average size of Co particles is of about 6 nm.[9] Therefore, the interfacial Co or Cu atoms are expected to be dominant. During rapid quenching a plenty of vacancy-like defects may be preserved in the Co-Cu alloy in solid solution state. Upon annealing these vacancy-like defects may diffuse into the interfacial region and are preserved against the further annealing. As a result, the coordination numbers of Co-Co, and Co-Cu decrease. The decrease of coordination number shows some kind of lattice distortion (lattice expansion) and deviation from the equilibrium position. As a result the atomic distance of Co-Cu increases. It is known that the interfacial structure of Co-Cu granular alloys play an important role in giant magnetoresistance properties.

IV. CONCLUSION

The synchrotron radiation XRD and EXAFS spectra were measured to investigate the decomposition of supersaturated solid solution of $Co_{15}Cu_{85}$ upon isothermal annealing. The results indicate the thermal-excited precipitation of ultrafine Co-rich particles from the residual Cu matrix, accompanied by the co-diffusion of Co and Cu. The fitted EXAFS spectra indicate that the interfaces of Co precipitates seem to be enriched with vacancy-type defects, leading to a distorted interface.

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