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RAPID PUBLICATION

Solid Solubility of Carbon in Copper during Mechanical Alloying

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Solubility of carbon in solid copper during mechanical alloying using an Attritor type of ball mill was investigated by means of X-ray diffraction, microscopy, electron probe microanalysis and chemical analysis. Carbon atoms less than about 28.5 atomic percent are soluble in the solid copper consisting of nano-crystals during mechanical alloying of copper-graphite mixed powders. The supersaturated solute carbon atoms take the interstitial positions in the fcc α-Cu solid solution and result in the lattice expansion of the α-Cu.

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I. Introduction

In 1946[1] the solubility of carbon in molten copper[2] was determined to be, in wt%C, about 0.0001% at 1373 K, 0.00015% at 1573 K, 0.0005% at 1773 K and 0.003% at 1973 K, and redetermination of the the solubility of C in molten Cu by Fischer and Schumid[3] confirmed the previous work with an estimate of about 0.0005 wt% (0.0026 at%) at 1473 K[4]. From the experimental data of McLellan in 1969[5], it is evident that the Cu–C phase diagram is of peritectic type and that the maximum solubility of C in fcc terminal solid solution (Cu) is about 0.04 at%C at about 1373 K. In 1998, Chu *et al.*[7] reported that Cu–C pseudoalloy films prepared by R.F. magnetron sputtering were a nonequilibrium supersaturated solid solution of C in Cu with nanocrystalline microstructures. On the other hand, mechanical alloying (MA) has received considerable attention, because it can produce various non-equilibrium phases; highly supersaturated solid solution[8]-[10], nano-quasicrystalline[11], amorphous phases[10][12] and so on.

In the present work the maximum solubility of supersaturated carbon in copper solid solution during mechanical alloying(MA) of a copper-graphite powder mixture was determined. The results obtained were presented at the 121th meeting of the Japan Institute of Metals (Sendai, September 1997).

II. Experimental Procedure

Atomized pure copper powder (99.86 wt%Cu, particle size: ~45 μm and graphite powder (98.55 wt%C, particle size: ~6 μm) were used as elemental powders. Cu-10, 20, 25, 30, 40 and 50 at%C mixed powders were mechanically alloyed for various times by an Attritor type of ball mill in a glove box filled with pure Ar gas containing oxygen less than 300 ppm. The mill container was charged with a 96 g mixture of the elemental powders and 2,200-g hardened steel balls (SUJ2, dia.: 4.76 mm, volume: 410 cm^3). The rotating speed of the mill adopted was 175 rpm. The mechanically alloyed powders were removed from the container in an Ar-filled glove box and were subjected to X-ray diffraction by monochromatic CuKα radiation at 40 kV, optical, scanning electron microscopy and electron probe microanalysis.

The lattice parameters, crystal structures and sizes of MA-powders were determined through X-ray diffraction. The crystal size D of MA powders consisting mainly of α-Cu solid solution were estimated from the breadth of the most intense Bragg peak, α-Cu(111), using Scherrer's relation $D=0.9\lambda/\beta\cos\theta$, where λ is the wavelength of the X-ray radiation, β the integral width (peak area divided by peak height) of the diffraction peak and θ the diffraction angle.

Carbon content in the MA-powders were chemically analyzed by the decomposition in the oxygen-infrared absorption measurement.

III. Results and Discussion

Figure 1 shows changes in XRD patterns during mechanical alloying of Cu-20 at%C mixed powders, as one example showing solid solubility of carbon into copper. In the XRD pattern for 0 ks (as-mixed powders), Cu(111), Cu(200) and graphite (0002) diffraction peaks are observed. The graphite peak, however, disappears after 36-ks milling and the Cu peaks shift to the low-angle side. These peak shifts correspond to the increase in the lattice parameter of copper.

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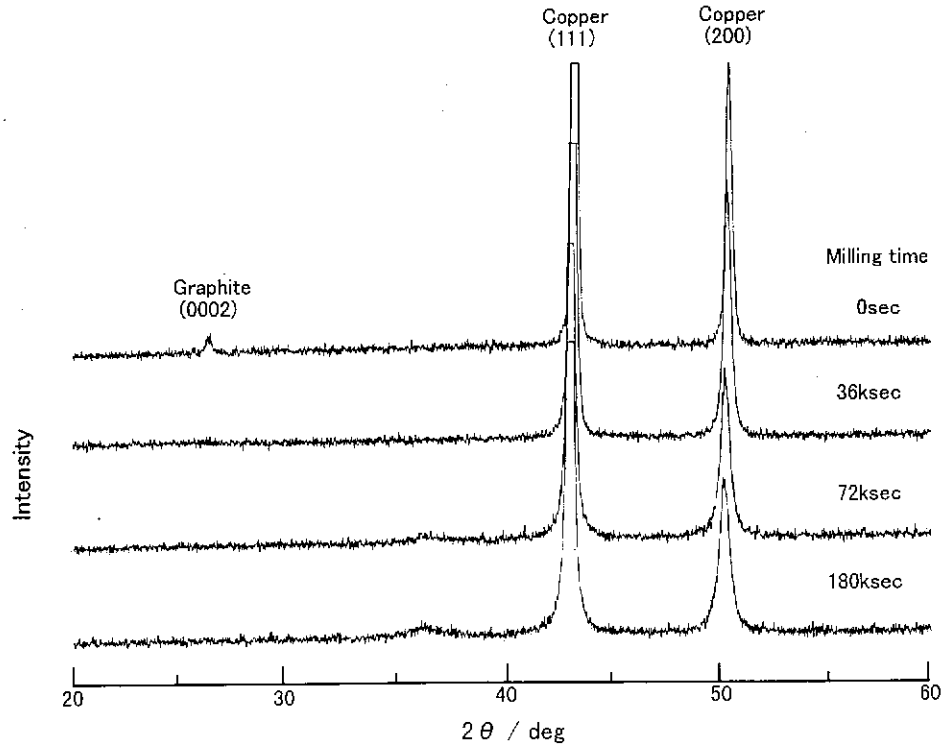

Fig. 1 Changes in X-ray diffraction Patterns during mechanical alloying of Cu-20 at%C mixed powders. As-mixed powders are expressed as 0 sec.

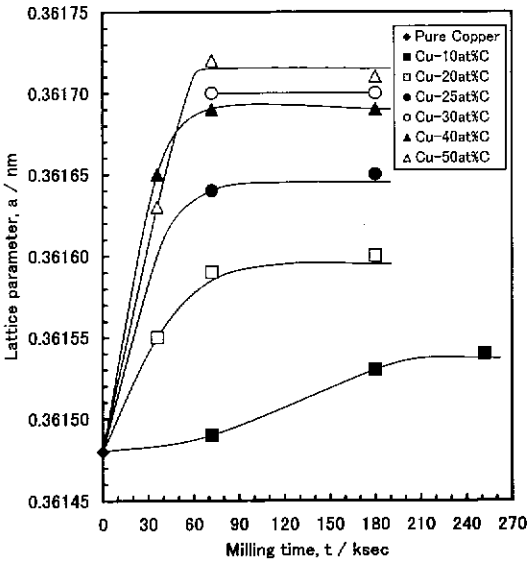

Fig. 2 Changes in the lattice parameter of the α-Cu phase with milling time during mechanical alloying of the various mixed powders with different graphite contents.

Figure 2 shows the changes in the lattice parameter of the α-Cu phase during mechanical alloying for the various mixed powders with different graphite contents. In all the cases, the lattice parameter increases with milling time and reaches a saturation value which depends on the graphite content. The higher the graphite content, the higher becomes the saturation value.

Very recently, Chu and his coworkers[7] have reported that the lattice parameter measured by XRD of Cu-C films prepared by R.F. magnetron sputtering increases with increasing carbon content in the range from 0~16 at%C. They have concluded that as-deposited Cu-C films exhibit a nanocrystalline structure consisting of C atoms in non-equilibrium supersaturated solid solutions of Cu.

Table 1 Carbon contents in the indicated Cu-C powders mechanically-alloyed for 180 ks, determined by chemical analysis.

(at%)

Sample	Milling time (ksec)	No. 1	No. 2	No. 3	Average
Cu-10 at%C	180	9.75	9.56		9.65
Cu-20 at%C		19.76	19.64		19.70
Cu-25 at%C		23.09	23.22	23.20	23.17
Cu-30 at%C		28.08	28.21		28.14
Cu-40 at%C		38.47	38.27		38.37
Cu-50 at%C		48.24	48.32	48.11	48.22

Table 1 shows the carbon contents determined by the chemical analysis in the various powders mechanically-alloyed for 180 ks. The average value of carbon obtained is a little smaller than the mixed value for all samples. Graphite powders adhering to the surface of MA-alloy powders were washed out before chemical analysis. The difference between the average and mixed value shows a tendency that washed out graphite powder increases with increasing mixed carbon content.

Figure 3 shows the relationship between the saturation values of the lattice parameter in Fig. 2 and the average carbon values determined by chemical analysis for the

MA-powders. The lattce parameter increase linearly with increasing carbon content to about 28.5 at%, beyond which it remains unchanged. The carbon content of about 28.5 at% corresponding to the break point in Fig. 3 gives the maximum value of supersaturated solid solubility of carbon in copper during mechanical alloying.

The crystal size of α-Cu(C) during MA decreases remarkably from about 5.5 μm for the atomized copper powder to about 16 nm for MA-powders, as shown in Fig. 4. The higher the content of the mixed graphite, the shorter the milling time for the nanocrystal size of about 16 nm.

Figure 5 shows the microstructures (OM) of various MA (180 ks)-powders which were embedded in the synthetic resin and polished. White particles or phase is determined to be a α-Cu(C) phase by EPMA and the gray one seems to be a graphaite phase. Almost all MA-powders prepared from Cu-10, 20, 25 and 30 at%C mixed powders show only the white α-Cu(C) phase as seen in Fig. 5(a), (b), (c) and (d). On the other hand, the MA-powders prepared from the Cu-40 and 50 at%C mixed powders consist of the gray graphite phase and the white α-Cu phase as shown in Figs. 5(e) and (f). These microstructures show that the graphite powder in excess of the

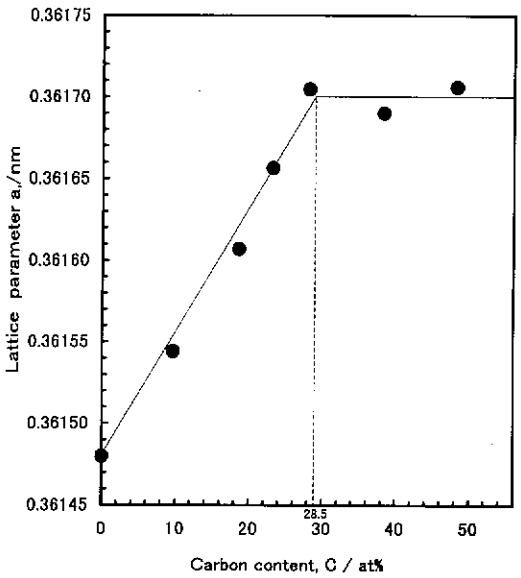

Fig. 3 The relationship between the saturation values of the lattice parameter during mechanical alloying and the average carbon content in MA powder determined by chemical analysis.

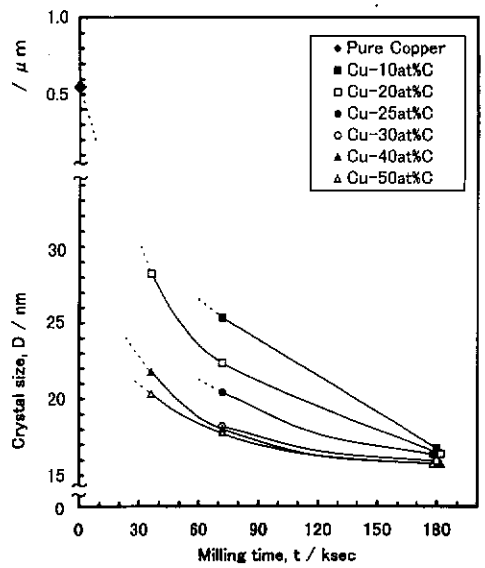

Fig. 4 Changes in the crystal size of α-Cu(C) phase with milling time for the indicated Cu–C mechanically alloyed powders.

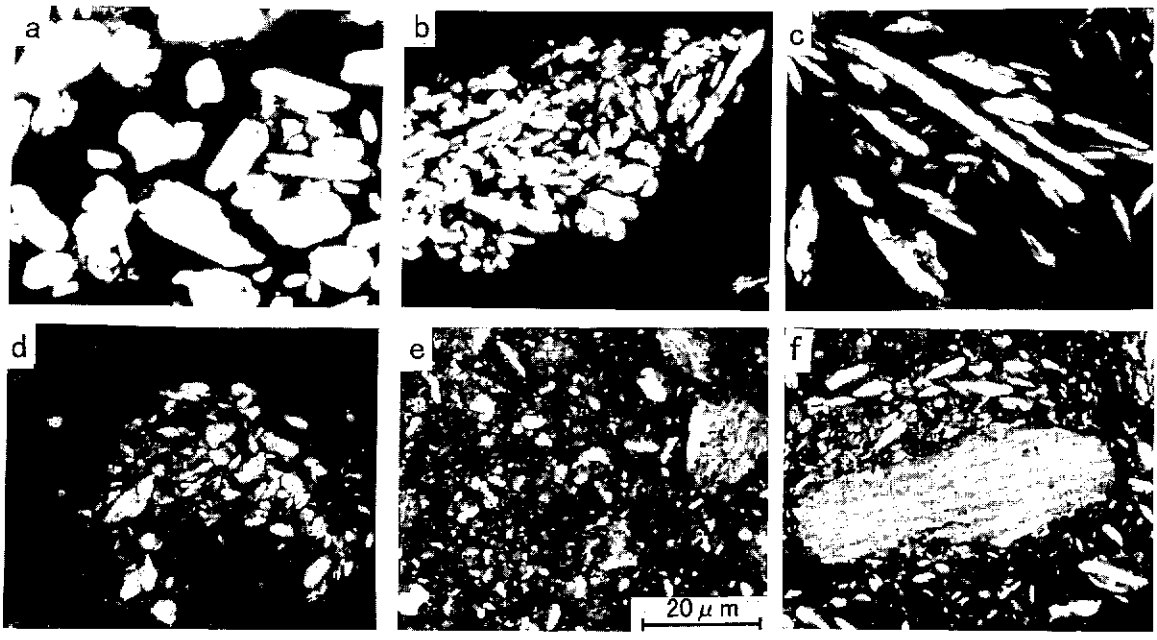

Fig. 5 Optical microstructures of Cu-10 at%C (a), -20 at%C (b), -25 at%C (c), -30 at%C (d), -40 at%C (e), and -50 at%C (f), powders mechanically-alloyed for 180 ks.

maximum solubility of supersaturated C in α-Cu during MA forms composite particles with the α-Cu phase.

The thermal stability and properties of the new material prepared by MA method are interesting subjects.

In conclusion, carbon atoms less than about 28.5 at% are soluble in the solid copper in the non-equilibrium state during MA of copper-graphite mixed powders. The supersaturated solute C atoms in fcc α-Cu take the interstitial positions and result in the lattic expansion of the Cu solid solution.

Acknowledgments

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