

## Extension of solid solubility of rare earth metals in copper by rapid solidification\*

Zhou Xinming, Ning Yuantao and Li Qubo

*Institute of Precious Metals, Kunming, Yunnan, 650221 (China)*

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### Abstract

Rapidly solidified Cu–RE (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Yb, Y) alloy foils of thickness 0.05–0.12 mm were prepared by an arc melt piston–anvil technique. The cooling rate was of the order of  $10^6$  K s<sup>-1</sup>. The metastable extended solid solubilities of the rare earth metals were evaluated by measurements of the lattice parameters of supersaturated solid solutions and verified by transmission electron microscopy. It was found that the extension of solid solubility of RE = La, Ce, Pr, Nd and Y in copper was negligible, while the extended solid solubilities of RE = Sm, Eu, Gd, Tb, Dy and Yb in copper were 0.95, 0.5, 1.2, 0.75, 1.0, 0.9 and 1.0 at.% respectively. The age-strengthening ability of some rapidly solidified Cu–RE alloy foils was also tested.

### 1. Introduction

In 1960 Duwez *et al.* [1] developed the rapid cooling technique and found that metastable extension of the solid solubility might occur if an alloy melt solidified rapidly enough. Since then the extension of solid solubility by rapid solidification has received considerable attention in science and technology [2]. Extensive research has indicated that metastable extension of the solid solubility offers a new way to develop solid solution strengthening or age strengthening of alloys. The extension behaviour of solid solubility in different alloy systems was found to vary. Knowledge of the metastable extension of solid solubility by rapid solidification is important in both practice and theory since it gives us a better understanding of the interactions of constituents. We have systematically studied the extension of solid solubility of alloying elements (including rare earth metals) in silver [3–5]. It is well known that small additions of rare earth metals often have beneficial effects on the properties of alloys. In this paper the metastable extension of solid solubility of rare earth metals in copper by rapid solidification is studied.

### 2. Experimental procedures

The alloys used in the present work were prepared from high purity copper (99.999%) and pure rare earth (RE) metals (99.0%–99.9%). The

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\*Dedicated to Professor W. Bronger and Professor Ch. J. Raub on the occasions of their 60th birthdays.

alloys were first melted by an arc or a high frequency induction current under an argon atmosphere. Then a small piece of alloy was re-melted and impacted into a thin foil of thickness 0.05–0.12 mm by a self-designed arc melt piston–anvil installation. The cooling rate during solidification was of the order of  $10^6 \text{ K s}^{-1}$ .

For selected Cu–RE foils, chemical analysis was performed by inductively coupled plasma atomic emission spectroscopy. Analytical results indicated that the actual composition was quite close to the nominal composition because the vaporization loss of RE had been taken into consideration. The listed compositions have been corrected according to the analytical results.

The metastable extension of the solid solubility limit was measured by the lattice parameter method and verified by transmission electron microscopy (TEM). The lattice parameters of copper-rich solid solutions were determined by the X-ray diffraction technique using Cu  $K\alpha_1$  radiation with a D/max-3B diffractometer. The positions of the diffraction peaks were corrected by an external reference standard. The lattice parameters were calculated from the corrected peak positions via least-squares refinement.

The measured lattice parameter of rapidly solidified pure copper was 0.361 50 nm. The lattice parameters of solid solutions change almost linearly with solute concentration in the range of solid solution. When the solute concentration goes beyond the solid solubility limit, a second phase will appear in the alloy and the composition of the solid solution in the alloy remains unchanged. From the measured lattice parameters *vs.* alloy composition and the accompanying TEM observations, the metastable extended solid solubilities of RE in copper under rapid solidification conditions can be determined.

### 3. Results and discussion

The dependence of the lattice parameters of rapidly solidified copper-rich solid solutions on the RE concentration in the alloys is shown in Fig. 1.

The atomic radius of copper is 0.1278 nm but the atomic radii of the rare earth metals are in the range 0.173–0.198 nm [6], *i.e.* much larger than that of copper. The lattice parameters of copper-rich solid solutions will increase with increasing RE concentration. When the RE concentration reaches or surpasses the solid solubility limit, the lattice parameter of the solid solution remains constant. The culminating point of lattice parameter of solid solution *vs.* RE concentration in the alloy is the metastable extended solid solubility by rapid solidification.

The experimental results indicated that the extension of solid solubility of RE≡La, Ce, Pr, Nd and Y in copper by rapid solidification at a cooling rate of  $10^6 \text{ K s}^{-1}$  was negligible, while under the same conditions the extended solid solubilities of RE≡Sm, Eu, Gd, Tb, Dy and Yb in copper were 0.95, 0.5, 1.2, 0.75, 1.0, 0.9 and 1.0 at.% respectively.

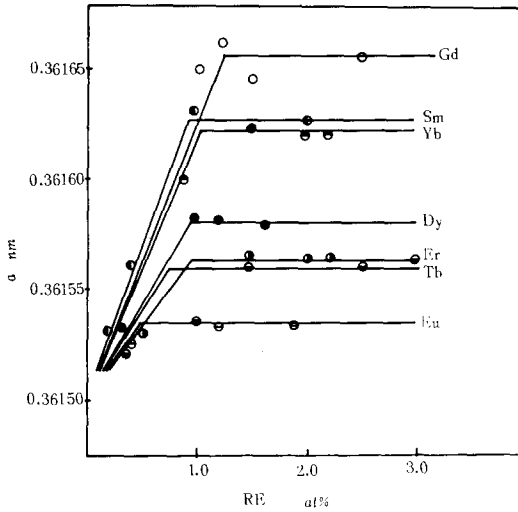


Fig. 1. Lattice parameters of copper-rich solid solution *vs.* RE concentration for rapidly solidified Cu-RE alloys.

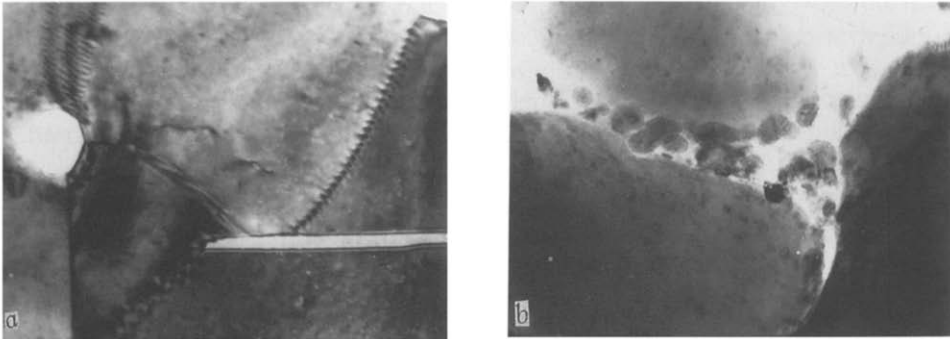


Fig. 2. Microstructure of rapidly solidified Cu-Gd alloys: (a) Cu-1at.%Gd alloy, solid solution (magnification,  $\times 150\,000$ ); (b) Cu-1.5at.%Gd alloy, solid solution and second-phase particles (magnification,  $\times 150\,000$ ).

The metastable extended solid solubilities determined by the lattice parameter method was in accordance with the results of TEM observation. Figure 2(a) shows the microstructure of rapidly solidified Cu-1at.%Gd alloy foil; it is simply a supersaturated solid solution. Figure 2(b) shows the microstructure of rapidly solidified Cu-1.5at.%Gd alloy foil; a large number of second-phase particles can be seen.

The atomic radius differences between rare earth metals and copper are in the range 35.8%–54.7%. According to the rule of Hume-Rothery and Raynor [7], the formation of a solid solution between them is not favourable. The equilibrium solid solubilities of rare earth metals in copper are very small [8]. It was found that the extended solid solubilities of RE in copper were also not large and were less than the corresponding values in silver

[3]. In rapidly solidified Ag-RE alloys the metastable extended solid solubility  $C_s$  of RE was dependent on the atomic radius of RE. As shown in Fig. 3, with decreasing atomic radius of RE or with increasing lanthanide contraction,  $C_s$  increased approximately linearly. This result indicated that the size factor was the main parameter controlling the extended solid solubility of RE in silver.

The atomic radius differences between rare earth metals and copper are larger than those between rare earth metals and silver, reaching 35.8%–54.7%. The condition for the formation of solid solutions between rare earth metals and copper is more unfavourable than for silver. The experimental results indicated that there was no obvious relation between the extended solid solubility  $C_s$  and the atomic radius of RE or  $r_{RE} - r_{Cu}$ . Rider *et al.* [9], in explaining the formation of Au-RE solid solutions, pointed out that electron transfer from rare earth metals to gold or atomic size adjustment was thought to occur, and that it was favourable for the formation of solid solutions, but that if the pure metal size factor was larger than a critical value, then the adjustment to the size difference could not occur. Cu-RE alloys are of the same type. In this situation other factors such as the characteristics of the second phase or the nature of the phase diagram may become important effects influencing the extended solid solubilities.

The age-strengthening ability of rapidly solidified Cu-RE foils was measured by the change in hardness. Rapidly solidified foils of Cu-1at.%Yb Cu-1at.%Dy Cu-1at.%Gd and Cu-1at.%Er were aged at different temperatures for 1 h. The hardness *vs.* aging temperature is shown in Fig. 4. These alloy foils had some age-strengthening ability. The temperature yielding the highest

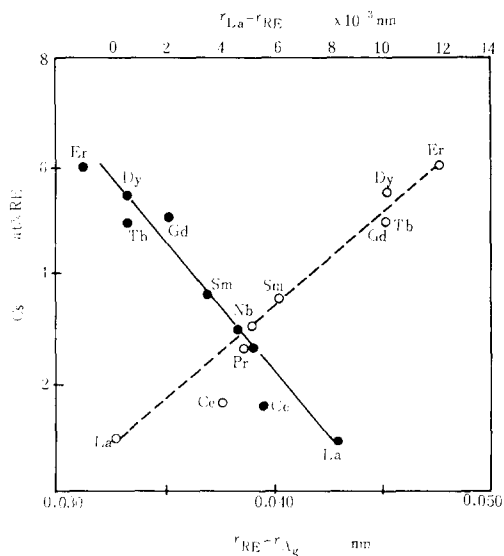


Fig. 3. Metastable extended solid solubility  $C_s$  of Ag-RE alloys *vs.* atomic radius differences  $r_{Ag} - r_{RE}$  and  $r_{La} - r_{RE}$ .

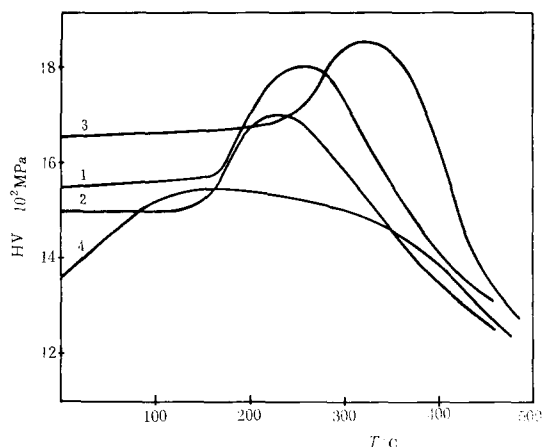


Fig. 4. Age-strengthening curves of rapidly solidified Cu-RE foils (aging time 1 h): 1, Cu-1at.%Yb; 2, Cu-1at.%Dy; 3, Cu-1at.%Gd; 4, Cu-1at.%Er.

strengthening effect was different for the different alloy foils, but after aging at 450 °C for 1 h, the hardness of all the foils decreased to nearly the same level.

#### 4. Conclusions

(1) A series of rapidly solidified Cu-RE alloy foils of thickness 0.05–0.12 mm were prepared by an arc melt piston-anvil technique. The cooling rate of rapid solidification was of the order of  $10^6$  K s<sup>-1</sup>.

(2) Under these conditions the extension of solid solubility of RE ≡ La, Ce, Pr, Nd and Y in copper was negligible, while the extended solid solubilities of RE ≡ Sm, Eu, Gd, Tb, Dy and Yb in copper were 0.95, 0.5, 1.2, 0.75, 1.0, 0.9 and 1.0 at.% respectively. There was no obvious relation between the extended solid solubility of RE in copper and the atomic radius difference  $r_{\text{RE}} - r_{\text{Cu}}$ .

(3) Rapidly solidified Cu-RE alloy foils showed some age-strengthening ability.

#### Acknowledgment

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