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The ternary system Ag–Cu–Ho at 500 °C

Li Junqin, Zhuang Yinghong and Lin Weibo
Physics Department, Guangxi University, Nanning (China)

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Abstract

The solid state phase equilibria at 500 °C in the Ag–Cu–Ho (33.3 at.% Ho or less) ternary system were investigated mainly by X-ray powder diffraction, with the aid of differential thermal microanalysis, optical microscopy and electron probe microanalysis. The isothermal section (500 °C) of this system has been established. It consists of six single-phase regions, nine two-phase regions and four three-phase regions. No ternary compound was found in this system, only the binary compounds found in the Cu–Ho and Ag–Ho systems.

The maximum solid solubilities of Ag in Cu_5Ho, Ag in Cu, Cu in Ag_2Ho, and Cu in Ag are 42, 0.98, 28 and 2.93 at.% respectively. Cu_2Ho and Ag_3Ho are non-variable compounds.

1. Introduction

Ag–Cu alloys show good electrical and heat conduction and are corrosion resistant. They are very important alloys which are widely used in electrical equipment and as solder material. It is desirable for the development of new applied materials to investigate the RE–Ag–Cu alloys (RE, rare earth).

The Ag–Cu binary system was described in ref. 1. It is a simple eutectic system with two solid solutions, namely f.c.c. copper and f.c.c. silver. The eutectic temperature is 779 °C. The solubilities of Cu in Ag, and Ag in Cu reported by different researchers show some differences. The maximum solubility of Cu in Ag at 500 °C reported by Ageew and Sachs [2] is 2.84 at.% and that reported by Owen [3] is 3.02 at.%. The maximum solubility of Ag in Cu at 500 °C reported by Smith and Lindlief [4] is 0.5 at.% and that reported by Schmid and Siebel [5] is 0.89 at.%. The phase diagram of the Cu–Ho binary system is given in ref. 6. The authors indicated that the compounds in this system are Cu_5Ho, Cu_2Ho, CuHo and possibly Cu_9Ho_2. The compound Cu_5Ho is hexagonal at high temperature (above 970 °C) but cubic at lower temperature. The temperature of the lowest solidus in this binary system is 830 °C. From the Ag–Ho binary phase diagram described in ref. 7, we know there are three compounds, namely Ag_7Ho_2, Ag_2Ho and AgHo, in this system. The temperature of the lowest solidus in this system is 775 °C. Observations by Wunderlin [8] indicate that Ag_3Ho is an intermediate phase in this system. Reference 9 gives the diffraction data for Ag_3Ho. The ternary system Ag–Cu–Ho has not yet been investigated. In this work we have studied this system (33.3 at.% Ho or less) at 500 °C.

2. Experimental details

The starting materials for synthesis of the alloys were commercially available metals of high purity (copper, 99.99%; silver, 99.9%; holmium, 99.95%). Alloy buttons (85 in total, each 3 g) were prepared by induction melting of the appropriate metals in alumina crucibles in pure argon. The weight losses were less than 0.6% and the alloys clearly did not react with the alumina crucibles during melting. Therefore no chemical composition analysis was carried out.

The homogenization temperatures of the alloys were chosen on the basis of the binary phase diagrams of the Ag–Cu, Cu–Ho and Ag–Ho systems and the solidi of some representative ternary alloys determined by differential thermal microanalysis. All the alloys were homogenized at 700 °C for 30 days, cooled at a rate of 10 °C h^{-1} to 500 °C, kept at 500 °C for 5 days and then quenched in an ice–water mixture.

Samples for X-ray diffraction analysis were powdered and annealed at 500 °C for 5 days in small glass tubes in vacuum and subsequently quenched in liquid nitrogen. X-ray diffraction analysis was performed using a Rigaku (3015) X-ray diffractometer with Cu Kα radiation and nickel filters. By comparing and analysing the X-ray diffraction patterns of samples annealed for different periods of time, it was shown that the phases in the alloys reached complete equilibrium and that the equilibrium state of the sample at 500 °C was retained by the above heat treatment.

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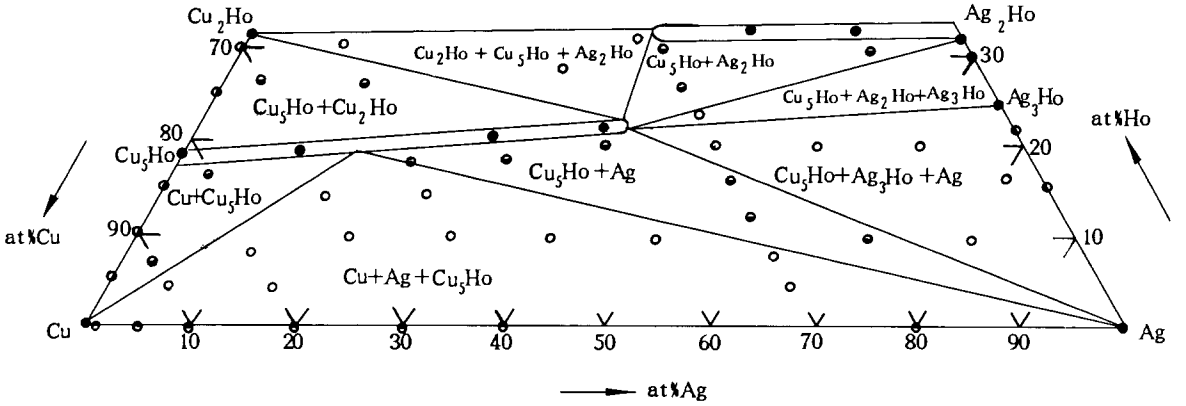

Fig. 1. Isothermal section (500 °C) of the phase diagram of the Ag–Cu–Ho ternary system (33.3 at.% Ho or less).

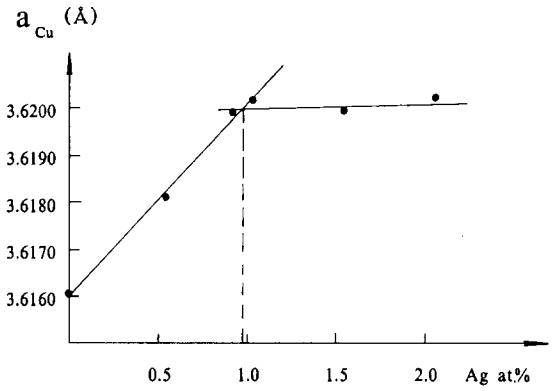

Fig. 2. Variation in Cu lattice parameter with Ag content.

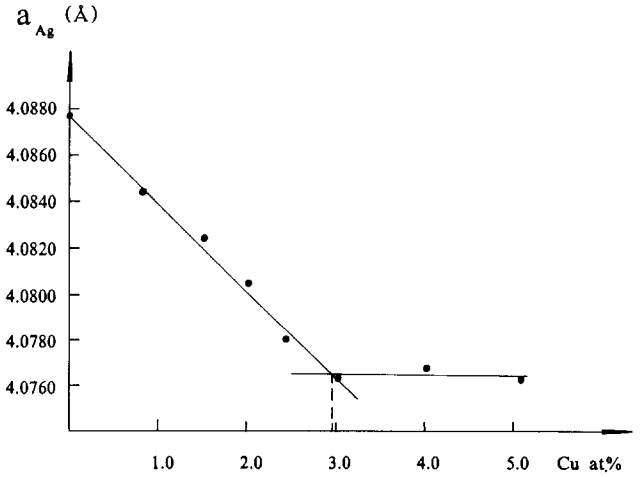

Fig. 3. Variation in Ag lattice parameter with Cu content.

The isothermal section was mainly determined by X-ray diffraction analysis. The phases in some alloys were determined by optical microscopy and electron probe microanalysis (EPMA) to check the results of X-ray diffraction analysis. The etchant used for the specimens consisted of $FeCl_3$ (8 g), HCl (20 ml) and C_2H_5OH (100 ml).

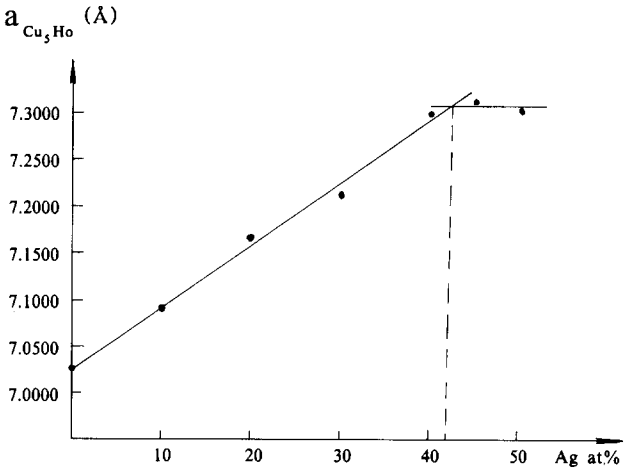

Fig. 4. Variation in Cu_5Ho lattice parameter with Ag content.

3. Results

3.1. Isothermal section (500 °C)

By comparing and analysing the X-ray diffraction patterns of 85 samples and identifying the phases in each sample, the isothermal section (500 °C) of the phase diagram of the ternary Ag–Cu–Ho system (33.3 at.% Ho or less) was determined. It is seen from Fig. 1 that this section consists of six single-phase regions (Ag, Cu, Cu_5Ho, Cu_2Ho, Ag_3Ho and Ag_2Ho), nine two-phase regions (Ag + Cu, Cu + Cu_5Ho, Cu_5Ho + Cu_2Ho, Cu_2Ho + Ag_2Ho, Ag_2Ho + Ag_3Ho, Ag_3Ho + Ag, Ag_3Ho + Cu_5Ho, Ag + Cu_5Ho and Cu_5Ho + Ag_2Ho) and four three-phase regions (Cu_2Ho + Cu_5Ho + Ag_2Ho, Cu_5Ho + Ag_2Ho + Ag_3Ho, Cu_5Ho + Ag_3Ho + Ag and Cu + Ag + Cu_5Ho).

3.2. Solid solubility

The single phases Cu, Ag and Cu_5Ho are cubic with $a = 3.614$, 4.0856 and 7.016 Å respectively at 25 °C. In this work we determined the variations with composition in the lattice parameters of the Cu, Ag and Cu_5Ho phases by using high angle diffraction lines with silicon

as internal standard (Figs. 2–4 respectively). The solid solubility of Ag in Cu, Cu in Ag, and Ag in Cu_5Ho at 500 °C obtained by the lattice parameter method are 0.98, 2.93 and 42 at.% respectively. The solid solubility of Cu in Ag_2Ho determined by X-ray diffraction using the phase disappearance method is 28 at.%. The phases Ag_3Ho and Cu_2Ho represent non-variable compositions.

3.3. Optical microscopy observation and EPMA

The results obtained by optical microscopy observation and electron probe microanalysis of sample 34 (70Cu20Ag10Ho, in at.%) in the $Ag+Cu+Cu_5Ho$ three-phase region and sample 38 (70Cu4Ag26Ho, in at.%) in the Cu_5Ho+Cu_2Ho two-phase region agree well with those obtained by X-ray diffraction analysis.

3.4. Discussion

From an analysis of the X-ray diffraction patterns of samples close to the compositions Cu_9Ho_2 and Ag_7Ho_2 we were not able to confirm the existence of these compounds. The phases in the sample of Cu_9Ho_2 are Cu_5Ho and Cu_2Ho and those in the sample of Ag_7Ho_2 are Ag and Ag_3Ho. Zhuang and Zhang [10] indicated that Cu_9Ho_2 did not exist at 500 °C. The X-ray diffraction data for Ag_3Ho were in good agreement with its powder diffraction data reported in ref. 9. Experiment showed the compound Cu_5Ho to be cubic with $a=7.029$ Å at 500 °C, which is in agreement with ref. 6. The X-ray diffraction data for Cu_2Ho and Ag_2Ho were fundamentally in agreement with the data reported in ref. 6 and the powder diffraction data for Ag_2Ho [11] respectively.

The solid solution ranges of Cu_5Ho and Ag_2Ho are nearly parallel to the Cu–Ag line. This means that the RE concentration remains fixed in these two phases or varies only slightly. Ag and Cu can be mutually replaced to a certain degree in these two phases.

Acknowledgments

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