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The Solubility of Holmium in Copper, Silver and Gold*

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Abstract

The solid solubility of holmium in copper, silver and gold was determined using metallographic techniques. The composition of the first intermetallic compound in these systems was found to be Cu_4Ho , Ag_7Ho_2 , and Au_3Ho . These compounds form eutectics with the solvent metals which melt at 868, 787, and 778°C, respectively.

INTRODUCTION

In a study by Gold, et al.,¹ on the effect of small amounts of soluble impurities on the electrical resistance and thermoelectrical properties of copper, traces of iron were shown to have drastic effects on the thermoelectric power due to the magnetic scattering of the conduction electrons. Since little is known about the state of the iron ion when dissolved in copper, Professor Gold had hoped to repeat these experiments using certain rare earths as the magnetic scattering

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centers; because of the tightly bound 4f electrons it is not expected that their spectroscopic state would be affected by alloying. In such an experiment the sole role of the trace rare-earth impurity would be to magnetically scatter the copper conduction electrons without producing appreciable distortions in the otherwise pure copper matrix. Since holmium was chosen for such a study because of its high magnetic moment, it was necessary to establish precisely its solid solubility in copper. The study was extended to include the solvents silver and gold, so that an evaluation of the data using classical solubility parameters could be made.

No previously reported work on the systems of holmium with copper, silver, or gold was found in the literature. Information on the solubility of other rare earths in these three metals is also very meager. The solubility limit of yttrium in copper was reported as less than one wt pct, the solubility of praseodymium in gold as 0.35 wt pct, while no references were found on solubility studies of rare earths in silver.

EXPERIMENTAL

Materials. The materials used in this investigation were distilled holmium prepared in this Laboratory, OFHC* copper, electrorefined silver (99.9 pct) and gold with the analyses given in Table I.

Sample Preparation. Samples weighing 1 to 2 g were prepared by arc-melting the components together on a water cooled copper plate under a purified argon atmosphere. The samples, turned and remelted

*OFHC = Oxygen-free high conductivity.

Table I
Analysis of the Metals Employed, ppm

Impurities	Metals			
	Holmium (ppm)	Copper	Silver	Gold
C	50	--*	--	--
N	27	--	--	--
F ₂	60	--	--	--
Fe	100	Trace	Faint Trace	N. D.†
Si	200	N. D.	Faint Trace	N. D.
Ta	1000	N. D.	N. D.	N. D.
Ca	500	Faint Trace	Faint Trace	N. D.
Cu	100		Weak	Trace
Ag	N. D.	Trace		Trace
Au	N. D.	N. D.	N. D.	
Mg	N. D.	Faint Trace	Faint Trace	Faint Trace

* -- = not determined.

† N. D. = not detected spectrographically.

at least five times to ensure homogeneity, showed negligible weight changes after melting. Samples containing less than 0.7 wt pct Ho were prepared by diluting 1 to 2 wt pct Ho alloys with the pure solvent, while samples with concentrations greater than 0.7 wt pct Ho were prepared directly from the metals. The samples were wrapped in tantalum foil,

sealed in Vycor tubing under helium, annealed at each of the various temperatures for at least 24 hr and then quenched by shattering the Vycor tube in cold water.

Metallographic Methods. Standard mechanical polishing methods were used in preparing the silver and gold alloys for examination; while the copper alloys were electropolished using a 40 pct solution of orthophosphoric acid as the electrolyte. Current densities of approximately 50 ma/cm^2 for 5 to 10 min were found to give satisfactory results; the samples with the greater holmium concentrations were the easiest to polish to a smooth surface without pitting.

The etchants used were those which are listed in Kehl⁴ and are as follows: copper alloys - 15 sec in equal parts of concentrated NH_4OH , hydrogen peroxide (3 pct) and water; silver alloys - 15 sec in equal parts of KCN (5 pct) and $(\text{NH}_4)_2\text{S}_2\text{O}_3$ (5 pct); and gold alloys - 30 sec in equal parts of KCN (10 pct) and $(\text{NH}_4)_2\text{S}_2\text{O}_3$ (10 pct). The alloys were then examined microscopically at magnifications of 200 and 1000.

RESULTS

Solubility. The solubility limit of holmium in copper was found to be extremely small, lying between 0.05 and 0.06 wt pct and did not evidence any temperature dependence as shown in Fig. 1. Photomicrographs showing a one phase and a two phase alloy are given in Figs. 2 and 3. The solubility of holmium in silver and gold was found to be higher than in copper and to exhibit a temperature dependence as shown in Table II and in Figs. 4 and 5. The solubility of holmium in silver

and gold was determined to 0.1 pct and the values given in Table I are the highest holmium concentrations which still appeared as single phase alloys.

Table II
Solubility Limit at Various Temperatures
in wt pct

Alloy	Temperature(°C)				
	600	700	750	800	900
Holmium in silver	0.4	1.0	1.4	2.1	0.8
Holmium in gold	1.5	2.5	3.0	3.0	1.2

Eutectic Temperatures. The temperatures shown in Figs. 1, 4, and 5 for the eutectic horizontals were determined by differential thermal analysis of alloys containing 10 wt pct holmium in the various solvents. The liquidus temperatures observed in the copper, silver, and gold alloys were 1025, 800, and 858°C, respectively.

Intermetallic Compounds. The composition of the first intermetallic compound on the noble-metal-rich side was determined by metallographic examination of as-arc-cast and homogenized alloys and the results are shown in Table III. Also listed in Table III are the first compounds reported for gadolinium,⁵ dysprosium,⁵ and lanthanum⁶ with copper, silver, and gold. Since gadolinium and dysprosium are more similar to holmium

than lanthanum, it is believed that the stoichiometry of the first compound in these systems should be the same as those observed in this study with holmium, but very possibly different from the case of lanthanum.

Deoxidation of Copper with Holmium. During the first part of this investigation the deoxidizing effect of holmium on copper was noted. Initial experiments indicated the solubility limit of holmium in copper to be around 0.2 wt pct; however, it was discovered that the copper being used had an appreciable oxygen content. The holmium was apparently "gettering" the oxygen from the copper by forming holmium oxide which floated to the surface during melting as evidenced by a skin on the surface of the alloy. The oxygen content of the copper was lowered from approximately 220 ppm to 40 ppm by adding enough holmium to exceed the

Table III

Noble-Metal-Rich Compounds with Holmium, Gadolinium
Dysprosium,⁵ and Lanthanum⁶

Noble Metal	Holmium	Gadolinium	Dysprosium	Lanthanum
Copper	Cu_4Ho	$\text{Cu}_5 \text{ or } 6 \text{ Gd}$	$\text{Cu}_5 \text{ or } 6 \text{ Dy}$	$\text{Cu}_6 \text{ La}$
Silver	Ag_7Ho_2	Ag_3Gd	Ag_3Dy	Ag_3La
Gold	Au_3Ho	Au_3Gd	Au_3Dy	Au_3La

solubility limit. Assuming formation of Ho_2O_3 this would cause enough holmium to be removed to lower its concentration in the "0.2" wt pct alloy to about 0.05 wt pct which agrees with the results found when using the OFHC copper. Subsequently the OFHC copper was used to ensure no loss of holmium due to this deoxidizing effect of the holmium.

The oxygen was not a problem in the silver and gold samples, since there was a smaller amount present originally. Also, since the holmium solubility was much greater in the silver and gold, the small amount removed by the oxygen in these solvent metals would not have changed the observed solubility of holmium significantly.

DISCUSSION

Since the solubility of holmium in copper was found to be very low, the study of the effect of holmium on the electrical resistance and thermo-electrical properties of copper that prompted this study was not carried out. It was believed the effect due to the strain on the copper lattice by the presence of holmium would be greater than the effect due to the magnetic scattering of the conduction electrons. However, the extension of the study to include the solvents silver and gold leads to some interesting comparative results.

The methods of predicting solid solubility which have been devised such as the classical Hume-Rothery rules and the graphical method by Gschneidner⁷ have used the solubility limit of 5 pct as the arbitrary figure above which a metal is called soluble and below which it is called insoluble. The fundamental properties of the solute and solvents which are used in these methods to predict solubility are listed in Table IV.

Table IV
Some Physical Properties of Ho, Cu, Ag, and Au⁸

Element	Radius (CN = 12)	Electronegativity	Valence
Cu	1.278	1.8	1
Ag	1.445	1.8	1
Au	1.442	2.3	1
Ho	1.766	1.2	3

Since the solubility of holmium in all three of these solvents is less than 5 pct, its insolubility was correctly predicted by both of these methods. Unfortunately these methods are not capable of predicting the slight difference in solubility noted in this study.

The size disparity between solvent and holmium is the greatest for the case of copper and therefore, the solubility should be the lowest, as observed. However, the solubility of holmium is greater in gold than in silver in spite of the increase in disparity in electronegativity. Since the first compound on the noble-metal-rich side of these systems decreases in holmium content in the order copper, silver, and gold, while the solubility is in the reverse order, the usual inverse relationship between the tendency to form compounds and the formation of terminal solid solutions does not appear to exist in these alloys.

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FIGURE CAPTIONS

Fig. 1. Expanded view of the copper-rich side of the Cu-Ho phase system.

Fig. 2. Copper - 0.05 wt pct holmium. Quenched from 500°C. Single phase. 200X

Fig. 3. Copper - 0.07 wt pct holmium. Quenched from 900°C. Two phase. 200X

Fig. 4. Expanded view of the silver-rich side of the Ag-Ho phase system.

Fig. 5. Expanded view of the gold-rich side of the Au-Ho phase system.

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Fig. 4. Expanded view of the silver-rich side of the Ag-Ho phase system.

Fig. 5. Expanded view of the gold-rich side of the Au-Ho phase system.

END