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**METASTABLE CLOSE-PACKED STRUCTURES
IN SILVER-RICH BINARY ALLOYS WITH
TIN, ANTIMONY AND SILICON**

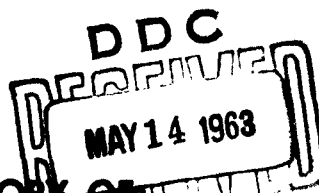
W. KLEMENT, JR.

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METASTABLE CLOSE-PACKED STRUCTURES IN SILVER-RICH BINARY
ALLOYS WITH TIN, ANTIMONY AND SILICON

by

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W. Klement, Jr.

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1. INTRODUCTION

A recent study⁽¹⁾ of Ag-Ge alloys rapidly quenched from the melt showed that the solid solubility in face-centered-cubic (fcc) silver could be metastably extended to 13.0 ± 1.0 at. pct. Ge. This composition corresponds to an electron concentration of 1.39 ± 3 , which is approximately the limit of primary solid solubility empirically established⁽²⁾ for many Cu-, Ag- and Au- base alloys with the Group B elements. At least two factors detracted from the cogency of the Ag-Ge results; (i) the fcc solubility limit was determined from lattice parameters which vary only slightly with germanium content and were barely outside the range of experimental uncertainty and (ii) some hexagonal close-packed (hcp) structures were detected in conjunction with the fcc phases in the quenched alloys. The present investigation was undertaken in order to attempt to metastably extend the primary solid solubility limit in Ag-base binary alloys with Sn, Sb and Si by rapidly quenching these alloys from the melt.

2. EXPERIMENTAL PROCEDURE

Alloys were prepared from elements of purity greater than 99.9% by means of techniques fully described elsewhere⁽¹⁾⁽³⁾. The quenching procedures and details of the Debye-Scherrer x-ray measurements were much the same as previously⁽¹⁾⁽³⁾⁽⁴⁾. Weight losses in the alloy preparation were negligible; the reproducibility of the lattice spacings suggests that the compositions are within ± 0.2 at. pct.

3. RESULTS

Lattice parameters obtained for the Ag-Sn and Ag-Sb alloys are presented in Fig. 1, together with the results of Owen and Roberts⁽⁵⁾. Diffraction lines from hcp phases were also detected on the films; the relative visual intensities of the fcc (200) and hcp (10.2) lines were visually estimated as:

	(200)	(10.2)
11.1 at. pct. Sn;Ag	m	vw
12.7	m	vw
12.9	m	vw
7.1 at. pct. Sb;Ag	m	vw
8.4	m	w
9.5	w	vw

For a quenched 13.6 at. pct. Sn;Ag alloy, the intensities were m for the (200) line and w for the (10.2), these being too much of the hcp phase to reliably obtain a lattice spacing for the fcc structure.

For these alloys, the lattice parameters vary linearly with composition up to ~8.0 at. pct. Sb and ~13.0 at. pct. Sn, respectively. These compositions will be referred to as the metastable solid solubility limits and may be compared with the maximum equilibrium solid solubilities⁽⁶⁾ of 7.2 at. pct. Sb. and 11.5 at. pct. Sn, respectively. The hcp phases, which were found together with the fcc phases, are believed to be of the same composition for those alloys of compositions less than the metastable solubility limits and this may be understood from a consideration of the solidification process.

It is necessary⁽³⁾⁽⁴⁾ to delineate the factors controlling both the nucleation and growth rates for the phases. For the present, rapidly

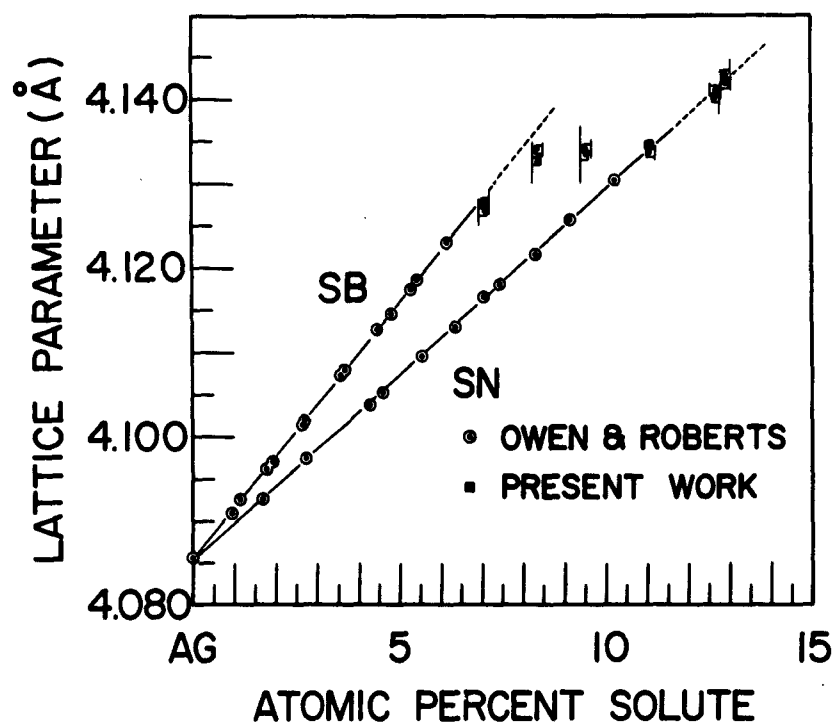


Fig. 1. Lattice Parameters of Silver-rich Solid Solutions with Sb and Sn.

quenched alloys, there is considerable undercooling of the melt and the growth rates of the solidifying phases are high. There should not be, however, much appreciable difference in growth rates between disordered fcc and hcp phases because of the similarity in packing. In nucleation, that phase with the lowest free energy will be favored. Since the difference in free energy between the fcc and hcp phases in the narrow two-phase equilibrium region is apparently small⁽⁷⁾ for the Ag-Sn and Ag-Sb alloys, it is plausible to expect both phases in the rapidly solidified alloys -- in accord with the experiments. The amount of the hcp phase present increases with increasing solute concentration since a slight advantage in nucleation accrues. Both fcc and hcp phases are of the same composition until the metastable solubility limit is approached -- it is then not possible to nucleate a fcc phase of greater solute concentration, probably because of an abrupt increase in free energy. A rapid increase in free energy at an electron concentration, $\lesssim 1.4$ has generally been considered to occur in a similar way for these Cu-, Ag- and Au- base alloys, although the mechanisms remain obscure⁽²⁾.

Equally obscure is an explanation for the limited metastable solid solubility of antimony in silver, compared to germanium⁽¹⁾ and tin. Proceeding from the above arguments, it may be that an abrupt increase in free energy occurs at a lower electron concentration for the Ag-Sb alloys. Concomitant with the decreasing difference in free energy between the fcc and hcp phases near the solubility limit, there should be a sizeable decrease in stacking fault energy. This is found for Ag-Sn alloys⁽⁸⁾ but not, apparently, for the Ag-Sb alloys⁽⁸⁾. Because of the similar behavior

of the Ag-Sn and Ag-Ge alloys in these rapid quenching experiments, it is suggested that the stacking fault energy for the fcc solid solutions decreases rapidly with increasing solute concentration for the latter alloys also.

At equilibrium, the Ag-Si and Ag-Ge systems are homologous⁽⁶⁾; the primary solid solubility of silicon in silver is, however, apparently quite limited. Despite much effort with quenched samples of several compositions, it has not been possible to obtain lattice spacings which are sufficiently critical to establish either the variation of lattice spacing with solute content or the limit of metastable solid solubility for the Ag-Si alloys. Previous work⁽⁹⁾ on these alloys indicates little solid solubility or variation in lattice parameter. The Si (111) diffraction line was not detected in alloy containing less than 16 at. pct. Si, due presumably to the difference in scattering power. For alloys in the range 10-25 at. pct. Si, faint low angle lines were detected and could be indexed as the (10.0), (00.2) and (10.1) reflections of an hcp structure with $a = 2.87 \pm 3$, $c = 4.52 \pm 3$ Å, $c/a = 1.57 \pm 2$. In contrast to Ag-Ge⁽¹⁾, there was no range of composition in which the hcp phase predominated at room temperature. The 16 at. pct. Si alloy was quenched to, and examined at, liquid nitrogen temperatures but no predominant hcp phase was found.

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