An Observation of Thermoelastic Martensite in β' Phase Ag-Zn Alloys

It has been pointed out by Pops and Massalski [1] that a martensitic product might be expected to form during cooling of β' phase Ag-Zn alloys, because martensitic transformations are known to occur in the analogous alloys in the Cu-Zn, Au-Zn and Ag-Cd systems. Pops and Massalski [1] did not, however, observe such a transformation, even at liquid-helium temperatures, in the alloys of nearly equiatomic composition which they studied. Brown and Stewart [2] were similarly unable to observe any evidence at room temperature of a martensitic transformation in an Ag-39.63 at. % Zn alloy which had been cooled in liquid nitrogen.

In the current investigation a martensitic product was produced in alloys with Zn contents ranging from 37.4 to 39.5 at. % which had been quenched to retain the β' phase to room temperature. The transformation was observed in a scanning electron microscope equipped with a liquid-helium cold stage based on an Oxford Cryogenics continuous flow cryostat. The temperature was monitored during cooling with an Fe-Au thermocouple soldered to the stage near the sample, and $M_{\rm s}$ was determined for each sample by noting the temperature at which martensite was first observed. The $M_{\rm S}$ temperatures so determined are shown in fig. 1. Although there is a relatively high degree of scatter in the $M_{\rm s}$ temperatures shown in fig. 1, they exhibit a definite composition dependence, with a slope of approximately -50° C/at. % Zn.



Figure 1 Martensite start (i.e. M_s) temperatures for β' phase Ag–Zn alloys as determined by cold stage scanning electron microscopy.

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The transformation to martensite was found to be reversible, but the temperature interval over which the martensite reverted to β' was quite composition-dependent. In the picture of Ag-39.1% Zn alloy in fig. 2, for example, the structure shown in fig. 2a reverted to that shown in fig. 2b over a temperature interval of only 10°C. In the 37.4 and 37.8% Zn alloys, however, it was necessary to heat the samples by approx-





Figure 2 SEM photomicrographs showing morphology and reversible nature of martensite in an Ag-39.1 at. % Zn alloy. (a) Structure consisting of a large percentage of martensite at 51°K. (b) Structure containing only a small amount of martensite after the temperature was increased to 61°K.

imately 30° C to produce a comparable change. The reason for the compositional dependence of this hysteresis is not known.

The slope of the M_s line in fig. 1 (-50°C/at. % Zn) is quite comparable to the slope of -80°C/ 1325 at. % Zn in the Cu-Zn system [3]. The similarity of these two slopes suggests that the tendency toward martensite formation in the two systems is not as disparate as had been previously thought [1]. The two alloy systems only appeared to behave differently because the earlier investigators [1, 2] either did not study alloys low enough in Zn content (i.e. Pops and Massalski [1]), or they did not use low enough temperatures (i.e. Brown and Stewart [2]). The present experiments demonstrate, however, that even if Brown and Stewart had produced martensite at low temperatures, they would not have observed it at room temperature because it would have reverted to β' phase during heating.

Crystallisation in Vacuum Evaporated Germanium Films

Germanium films (~800 Å thick) grown onto NaCl single crystal and formvar substrates at room temperature by vacuum evaporation techniques are found to have an amorphous structure. The amorphous to crystalline transformation induced by electron beam irradiation inside an electron microscope showed random orientation immediately after crystallisation. Further bombardment caused recrystallisation in the film and their electron diffraction study revealed the predominance of (112) orientation.

It is well known that thin films of certain metals and metal oxides grow in the metastable phase having amorphous structure under suitable conditions of the film deposition. The amorphous structure of the metastable phase is known to undergo transformation upon annealing these films [1]. Recently a few papers [2-5] have appeared in which the crystallisation in amorphous films has been reported to be induced by electron irradiation. Although the amorphous structure of vacuum-evaporated germanium films and their transformation to the crystalline state, by annealing as well as by ionic irradiation [6], has been reported previously, there does not appear to have been a report on the type of transformation and the various stages involved in these films by electron irradiation. In the present communication the study of the amorphous to crystalline transition in vacuum-deposited germanium films by electron microscopy and electron diffraction techniques

References

- 1. H. POPS and T. B. MASSALSKI, Acta Met. 15 (1967) 1770.
- 2. L. C. BROWN and M. J. STEWART, Trans. Met. Soc. AIME 242 (1968) 1353.
- 3. H. POPS and T. B. MASSALSKI, Trans. Met. Soc. AIME 230 (1964) 1662.

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is described with a particular reference to the process of transformation involved in it.

Germanium films of about 800 Å thickness were prepared on freshly air-cleaved NaCl and formvar substrates maintained at room temperature (~25°C) in a vacuum of the order of 10^{-5} torr. The electron microscopic and electron diffraction examination of the as-deposited films showed structureless features and a few broad haloes respectively, indicating amorphous structure (fig. 1). However, thin films with a very small crystallite size also yield such diffraction patterns and structureless features, and therefore, the possibility that these vapour deposited films are micropolycrystalline in structure, cannot be



Figure 1 Electron micrograph and electron diffraction pattern (inset) of amorphous germanium film grown on NaCl at room temperature.