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in the Ag-Al-X (X=Zn, Ga, Ge) Systems**

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**Phase relationships and stability of the μ - and ζ -phases
in the Ag-Al-X (X=Zn, Ga, Ge) systems**

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Abstract

Details of phase relationships in three ternary systems, Ag-Al-X (X=Zn, Ga, Ge) near the Ag-rich corner at 400°C are presented. Metallography, X-ray diffraction, scanning electron microscopy and X-ray spectroscopy have been used to establish the respective isothermal sections at 400°C. In each case, the μ -phase and the ζ -phase of the Ag-Al binary system extend into the ternary system and terminate at a three-phase region involving the Ag-rich primary solid solution (α_1 -phase) in the Ag-Al-Zn and Ag-Al-Ga systems, and the Ge-rich primary solid solution (α_2 -phase) in the Ag-Al-Ge ternary system. The stability ranges of the μ and ζ -phases follow approximately constant electron concentration lines. The solid solubilities of Zn, Ga and Ge in the μ -phase are relatively small, compared with those in the ζ -phase (up to 18 at.%). No ternary phase appears to exist in the Ag-rich portions studied in the three ternary systems.

Introduction

The binary system Ag-Al involves three intermediate phases, μ (complex cubic, β -Mn), ζ (hcp) and β (bcc)¹. The μ -phase forms by a peritectoid reaction at 450°C and the β -phase is stable only at high temperatures, above 603°C. The ζ -phase forms peritectically at 726°C. The ternary phase equilibria based on the Ag-Al system at low temperatures, where only the μ -phase and the ζ -phase are stable, have been studied previously in a few systems; Ag-Al-Mn², Ag-Al-Cd³, Ag-Al-In⁴ and Ag-Al-Sn⁵.

It is well known that the electron concentration is an important parameter in the Ag-rich systems with the polyvalent B-subgroup elements in the periodic table. It influences the ranges of stability and the types of the intermediate phases observed in these systems. The μ -phase is present only in a few systems. The competition for stability between the μ and ζ -phases in the binary system Ag-Al has been the subject of a detailed study some years ago⁶. Since the μ -phase is stable only at low temperatures in the binary system, it is of interest to study its stability in relation to the ζ -phase below the peritectoid temperature in the ternary systems containing some other B-subgroup elements of the periodic table. The elements Zn (lower valence than Al), Ge (higher valence than Al) and Ga (the same valence) provide suitable ternary additions. The μ -phase also has special characteristics such as an extreme brittleness. In order to study possible changes of the mechanical behavior of the μ -phase with ternary additions, the stability limits of the ternary extensions of this phase into the respective ternary systems must be considered first. In the present paper we report on the stability ranges of both the binary phases, μ and ζ , when alloyed with Zn, Ga and

Ge. Ag-rich portions of the respective ternary equilibrium phase diagrams have been investigated at 400°C, using metallographic and X-ray methods.

Experimental Details

Carefully weighed amounts of the starting pure metals were placed in narrow silica tubes, which were coated previously with a thin layer of carbon. The tubes were sealed after repeated evacuation and flushing with helium and then held in an oxy-acetylene flame and shaken vigorously for 5 min. after the contents had melted. The tubes were quenched in water. Nominal intended compositions of the alloys were accepted without chemical analysis if the weight losses during melting were less than 0.4 wt.%. The nominal compositions of the alloys are given in Table 1. An initial homogenization treatment of 24 hrs. at 750°C was given to each alloy, followed by iced water quenching. Homogenized samples were subsequently annealed at 400°C for six weeks followed by water quenching. Metallographic examination was done using optical microscopy and scanning electron microscopy. Compositional analysis of the phases present in the microstructure was done using energy dispersive X-ray spectroscopy (EDS). Filings obtained from bulk specimens were annealed at 400°C for 5 min. for stress-relief and used for X-ray diffraction to identify the phases present. High angle reflections corresponding to 2θ values above 140° were additionally recorded with a slow scanning speed and used to calculate the lattice parameters.

Results and Discussion

Partial isothermal sections for the systems Ag-Al-Zn and Ag-Al-Ga near the Ag-rich corner and a complete isothermal section for the system Ag-Al-Ge at 400°C have been established. All the phases observed have been identified to be extensions of the phases found in the binary systems, as listed in Table 2. No ternary intermediate

phases were found in the regions studied. Isothermal sections shown in Figs. 1 to 3 were constructed using tie line and tie triangle data after a phase-compositional analysis. Phase boundaries on the binary sides of each isothermal section were taken from the respective binary systems¹.

As can be seen from Figs. 1, 2 and 3, the μ and ζ -phases extend into the ternary systems and are in equilibrium with the Ag-rich primary solid solution (α_1 -phase) in the Ag-Al-Zn and Ag-Al-Ga systems, and with Ge-rich primary solid solution (α_2 -phase) in the Ag-Al-Ge system. Since the liquid phase is not involved in the Ag-Al-Ge system at 400°C, a complete isothermal section was established in this case. The unexplored portions of the ternary systems Ag-Al-Zn and Ag-Al-Ga are sketched only tentatively in Figs. 1 and 2 and are based on the respective binary phase diagrams. The stability ranges of the μ and ζ -phases generally follow constant electron concentration lines.

Fig. 4 shows back scattered and secondary electron images taken at different compositions in the three systems. The microstructures of three phase alloys ($\alpha_1 + \mu + \zeta$) in the systems Ag-Al-Zn and Ag-Al-Ga are shown in Figs. 4(a) and 4(c), respectively. Light gray regions and dark gray regions correspond to α_1 and ζ -phases, respectively. The contrast regions at the grain boundaries are mostly the μ -phase. The μ -phase formed through a typical peritectoid reaction at the interface between the α_1 and ζ . The presence of the μ -phase at the grain boundaries can be more clearly seen in the optical micrograph, which is also shown in Fig. 4(a). Secondary electron images could not produce sufficient contrast among different phases, as can be seen in Figs. 4(c) and 4(d), because the compositions of α , μ and ζ do not differ significantly from one

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another. So, the other microstructures in Figs. 4(b), 4(e) and 4(f) were observed using back scattered electrons.

The limits of solid solubility of the third element in μ and ζ -phases of the Ag-Al system are given in Table 3. It can be seen that the ζ -phase dissolves larger amounts of the third element than does the μ -phase. A complete range of solid solubility between two binary μ -phases in the Ag-Al-In system, as suggested by Campbell and Wagemann⁴, does not seem to be possible because a μ -phase (with the β -Mn structure) is not stable in the Ag-In binary system. However, in systems where the hcp ζ -phase is present in both binary systems, a continuous phase field has been reported in the ternary systems such as Ag-Al-Cd³, Ag-Al-In⁴ and Ag-Al-Sn⁵.

The measured lattice parameters in the μ -phase alloys of compositions close to the solid solubility limits are given in Table 4. Since, the silver content in these alloys is nearly the same as is in the binary μ -phase, the change in the lattice parameter with one at.% of the third element (Zn, Ga or Ge), da/dc can be calculated. The respective values for Zn, Ga and Ge are 0.00002, 0.00011 and 0.00018 nm/at.%. Ge addition is found to produce the largest lattice parameter increase, but the largest penetration into the ternary system occurs with Ga (up to 6.5 at.%). Hence the rate at which the μ -phase lattice becomes strained by ternary alloying additions does not seem to control the degree of phase penetration in the ternary system.

The general conclusion of the present work is that the μ -phase of the Ag-Al binary system is quickly destabilized when ternary alloying additions are introduced. Hence, even though the electron concentration ratio e/a remains the main parameter determining the appearance of this β -Mn structure in an alloy system, secondary

parameters appear to control its subsequent ranges of stability. We also note that the recently reported occurrence of the β -Mn structure in the ternary Au-Sn-Cu system^{7,8} is surprising because the observed very narrow phase field of this structure not only follows closely a constant e/a line of 1.60 (20at.% Sn), but the actual phase also occurs as a ternary phase in contrast to the present work. The e/a ratio within this phase in the Au-Sn-Cu system varies from 1.54 (18at.% Sn) to 1.62 (20.5at.% Sn) which is most surprising because all other μ -phases reported in alloy systems based on the noble metals occur only within the narrow band of e/a between 1.40 and 1.54. Clearly, further studies of this structure are of interest.

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Figures captions

Fig. 1. Isothermal section of Ag-Al-Zn ternary system at 400°C. Symbols show the alloys having different microstructures: ○ single-phase, ○ two-phase, ^ three-phase.

Fig. 2. Isothermal section of Ag-Al-Ga ternary system at 400°C. Symbols show the alloys having different microstructures: ○ single-phase, ○ two-phase, ^ three-phase.

Fig. 3. Isothermal section of Ag-Al-Ge ternary system at 400°C. Symbols show the alloys having different microstructures: ○ single-phase, ○ two-phase, ^ three-phase.

Fig. 4. Microstructures of Ag-Al-X (Zn, Ga or Ge) alloys, annealed at 400°C for 45 days.

(a) Alloy composition: 77 Ag, 19 Al, 4 at.% Zn; optical micrograph (OM) and back scattered electron image (BEI), observed phases ($\alpha_1 + \mu + \zeta$)

(b) Alloy composition: 74 Ag, 20 Al, 6 at.% Zn; BEI, observed phases ($\alpha_1 + \zeta$)

(c) Alloy composition: 77 Ag, 15 Al, 8 at.% Ga; secondary electron image (SEI), observed phases ($\alpha_1 + \mu + \zeta$)

(d) Alloy composition: 77 Ag, 11 Al, 12 at.% Ga; SEI, observed phases ($\alpha_1 + \zeta$)

(e) Alloy composition: 74 Ag, 20 Al, 6 at.% Ge; BEI, observed phases ($\mu + \zeta + \alpha_2$)

(f) Alloy composition: 20 Ag, 40 Al, 40 at.% Ge; BEI, observed phases ($\zeta + \alpha_2 + \alpha_3$)

Table 1: Nominal compositions of the alloys studied and the phases present

Alloy no.	Nominal composition (at.%)					Phases present
	Ag	Al	Zn	Ga	Ge	
A1	77	23	-	-	-	μ
Z1	80	18	02	-	-	$\alpha_1 + \mu$
Z2	80	16	04	-	-	α_1
Z3	80	14	06	-	-	α_1
Z4	80	12	08	-	-	α_1
Z5	77	22.5	0.5	-	-	μ
Z6	77	21	02	-	-	$\alpha_1 + \mu + \zeta$
Z7	77	19	04	-	-	$\alpha_1 + \mu + \zeta$
Z8	77	17	06	-	-	$\alpha_1 + \zeta$
Z9	77	15	08	-	-	α_1
Z10	74	24	02	-	-	$\mu + \zeta$
Z11	74	22	04	-	-	$\alpha_1 + \mu + \zeta$
Z12	74	20	06	-	-	$\alpha_1 + \zeta$
Z13	74	18	08	-	-	$\alpha_1 + \zeta$
Ga1	80	16	-	04	-	$\alpha_1 + \mu$
Ga2	80	12	-	08	-	$\alpha_1 + \mu + \zeta$
Ga3	80	08	-	12	-	$\alpha_1 + \zeta$
Ga4	80	04	-	16	-	$\alpha_1 + \zeta_1$
Ga5	77	19	-	04	-	μ
Ga6	77	15	-	08	-	$\alpha_1 + \mu + \zeta$
Ga7	77	11	-	12	-	$\alpha_1 + \zeta$

Ga8	77	07	-	16	-	$\alpha_1 + \zeta_1$
Ga9	74	21	-	05	-	$\mu + \zeta$
Ga10	74	16	-	10	-	$\alpha_1 + \zeta$
Ga11	74	11	-	15	-	$\alpha_1 + \zeta$
Ga12	65	20	-	15	-	ζ
Ge1	80	18	-	-	02	$\alpha_1 + \mu + \alpha_2$
Ge2	80	14	-	-	06	$\alpha_1 + \alpha_2$
Ge3	80	12	-	-	08	$\alpha_1 + \alpha_2$
Ge4	77	21	-	-	02	μ
Ge5	77	17	-	-	06	$\alpha_1 + \mu + \alpha_2$
Ge6	74	24	-	-	02	$\mu + \zeta$
Ge7	74	20	-	-	06	$\mu + \zeta + \alpha_2$
Ge8	74	18	-	-	08	$\mu + \alpha_2$
Ge9	60	10	-	-	30	$\alpha_1 + \alpha_2$
Ge10	17	62	-	-	21	$\zeta + \alpha_2 + \alpha_3$
Ge11	20	40	-	-	40	$\zeta + \alpha_2 + \alpha_3$

Table 2: Crystal structure identification of the phases

Phase	Structure
α_1	Ag-rich primary solid solution: FCC
μ	Complex cubic: β -Mn
ζ	HCP
ζ_1	Hexagonal
α_2	Ge-rich primary solid solution: Diamond
α_3	Al-rich primary solid solution: FCC

Table 3: Solid solubilities of third elements in μ and ζ phases of the Ag-Al system

Alloying element	Solubility limit (at.%)		Temperature (°C)	Reference
	in μ phase	in ζ phase		
Zn	0.8	9.0	400	present study
Ga	6.5	18.0	400	present study
Ge	2.5	10.0	400	present study
Cd	0.5	c.s.s.	438	(3)
In	-	c.s.s.	143	(4)
Sn	1.0	c.s.s.	25	(5)
Mn	5.0	4.0	400	(2)

c.s.s.: complete solid solubility

Table 4: Lattice parameters of a few μ phase ternary alloys.

Nominal composition (at.%)			e/a	Lattice parameter (nm)	da/dc
Ag	Al	third element			
77	23.0	-	1.460	0.69390	-
77	22.5	0.5 Zn	1.455	0.69391	0.00002
77	19.0	4.0 Ga	1.460	0.69435	0.00011
77	21.0	2.0 Ge	1.480	0.69425	0.00018

Ag-Zn Phase Diagram

Ag-Al Phase Diagram

Fig. 1

Ag-Ga Phase Diagram

Fig. 2

Fig. 3

Fig. 4(c)

Fig. 4(b)

Fig. 4(c)

Fig. 4(d)

Fig. 4(e)

Fig. 4(f)

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