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Thermodynamic assessment and experimental study of the Al-Ag-Ga phase diagram

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ABSTRACT

Ternary Al-Ag-Ga system was assessed both theoretically using thermodynamic calculations of phase equilibria based on CALPHAD method and experimentally using differential thermal analysis (DTA), scanning electron microscopy (SEM) combined with energy dispersive spectrometry (EDS) and X-ray powder diffraction (XRD) analysis. The calculated phase transition temperatures, isothermal sections at 300 and 500 °C and liquidus surface projection were experimentally validated by experimental study of selected long-term annealed alloy samples with overall compositions along four vertical sections Al-$Ag_{80}Ga_{20}$, Al-$Ag_{60}Ga_{40}$, Ag-$Al_{80}Ga_{20}$ and Ag-$Al_{60}Ga_{40}$.

1. Introduction

Al alloys are widely used in electronics, electrical appliances, aerospace industries and other transport applications [1] owing to their specific characteristics such as low density, high yield strength, high ductility, excellent electrical conductivity, thermal conductivity and corrosion resistance. Among others, alloys of the binary Al-Ag system have been extensively studied since they represent a rather important model system for study of precipitate nucleation and growth in Al alloys [2]. Besides that, they are typical electron compounds [3] and therefore create a solid basis for technically important higher order systems.

On the other hand, Ga is a very interesting as a possible third element in the system, since it is a metal with melting temperature very close to the room temperature (302 K) and boiling point temperature equal to 2673 K [4]. More to the point, different Ga containing alloys such as $AgXY_2$ (X = Al, Ga, In and Y = S, Se, Te) have been gaining a considerable attention due to their potential use in opto-electronic and nonlinear optical devices [5] such as solar cells [6], photovoltaic detectors, light-emitting diodes [7], modulators, optical light eliminator filters [8] and for optical frequency conversion in solid-state-based tunable laser systems [9]. Given that a binary Al-Ag system is also potentially significant for applications in opto-electronic devices [10], a ternary system that combines Al, Ag and Ga may also be very interesting from this point of view. Although a number of ternary systems such as Al-Ag-X (X = Cu, Au) [11–13] have been previously investigated, to our knowledge, up to now, no data related to phase equilibria and phase diagram of the ternary Ag-Al-Ga system has been reported in literature. Hence, the results on Ag-Al-Ga ternary system presented in this study may be significant in terms of possible practical applications of these alloys.

2. Experimental procedure

Samples of studied alloys each weighing about 3 g were synthesized using pure metals (Table 1) in an induction furnace under a high purity Argon atmosphere. Additional purification of the starting metals before preparation of the samples was not performed.

After melting, the samples prepared for microstructural study were sealed under vacuum (10^{-1} Pa) in quartz ampoules. First set of samples were annealed at 300 °C and second set of samples were

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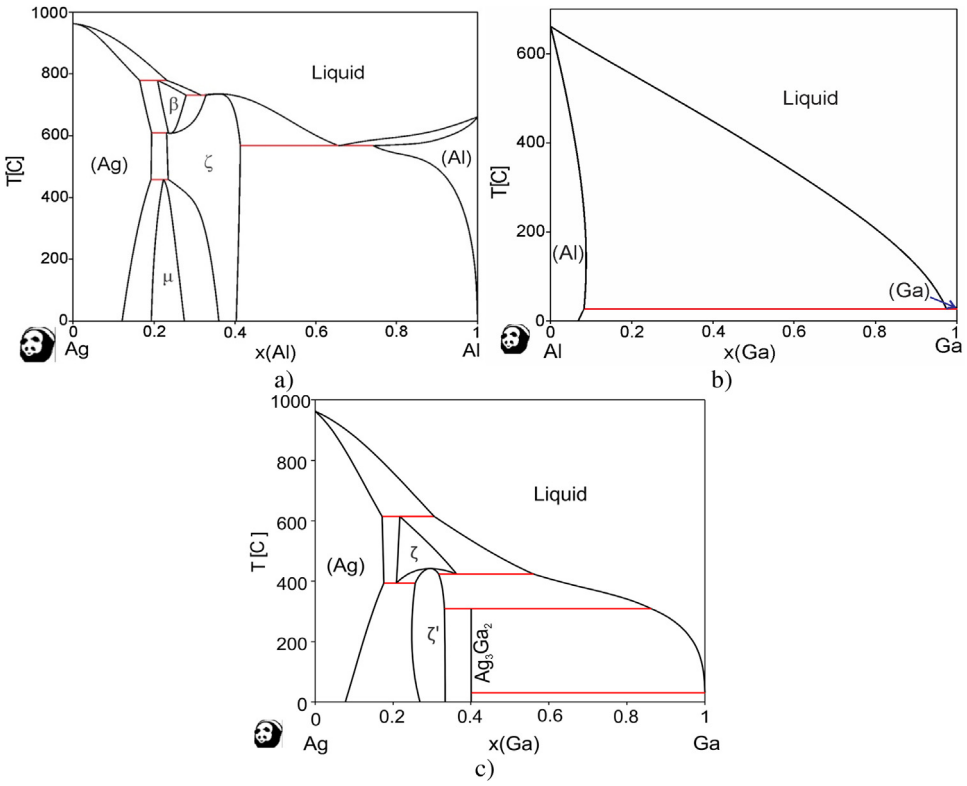

Fig. 1. Calculated phase diagram of the binary system: a) Al-Ag, b) Al-Ga and c) Ag-Ga.

Table 1
Sample table.

Chemical Name	Source	Initial Purity (mass.%)
Al	Alfa Aesar	99.99
Ag	Alfa Aesar	99.99
Ga	Alfa Aesar	99.999

annealed at 500 °C. The annealing time was two weeks in both cases. After annealing samples were quenched into ice water.

Microstructural analysis was carried out on the polished alloy samples prepared by the classic metallographic procedure without etching by using TESCAN VEGA3 scanning electron microscope (SEM) with energy dispersive X-ray spectroscope (EDS) (Oxford Instruments X-act). EDS elemental mapping was used firstly to check compositional homogeneity of the studied samples and possible segregation and then the overall compositions and the compositions of individual coexisting phases were determined using EDS point and area analysis.

Powder XRD analysis of the studied samples was carried out using D2 PHASER (Bruker) powder diffractometer with a dynamic scintillation detector and ceramic X-ray Cu tube (KFL-Cu–2 K) in a 2θ range 5°–75° and a step size of 0.02°. The recorded patterns were analyzed using the Topas 4.2 software and ICDD database PDF2 (2013).

Third part of prepared samples in as-synthesized state were subjected to DTA measurements. Phase transition temperatures were determined using SDT Q600 (TA instruments) thermal analyzer. Alumina crucibles were used and measurements were performed under flowing argon atmosphere. The reference material was empty alumina crucible. Samples weighing 20 mg were investigated at heating rate of 5 °C/min. Before performing DTA experiments, the sensitivity and temperature calibration of DTA were performed by measuring the melting temperatures of pure elements (In, Al and Ag) using the same working conditions. Every heating run was repeated three times. Based on the repeated DTA measurements the uncertainties of the determined phase transition temperatures were determined (Table S3. in Supplementary material).

3. Literature data

3.1. The Al-Ag binary system

There have been numerous studies on the phase equilibria of the Al-Ag binary system over the years [14–18]. The phase diagram was assessed by McAlister [19] and thermodynamically evaluated by Spencer and Kubaschewski [20] and Lim et al. [21].

The solubility of Al in solid Ag was reported by Foote and Jette [22]. Another study by Pollock [23] provided data on the solubility of Al in Ag for Al content <2.6 at% at 303 K determined by thermoelectric measurements. Additional study on the solubility of Ag in solid Al at a pressure of 1.04 GPa was carried out by Zakharova et al. [24].

The formation of Guinier-Preston (GP) zones has also been investigated to a great extent [25–32]. In these studies, it was found that the metastable miscibility gap (Al from 40 to 100% and below 450 °C) consists of two types of GP zones, GP1 zone above 170 °C and GP2 zone below 170 °C. A detailed study focused on thermodynamic analysis of GP zones in aged-supersaturated Al-Ag alloys has been published recently by Li et al. [33]. Structural, elastic, and electronic properties of bulk γ' phase in Al–Ag alloys were reported by Pang et al. [34].

Impurity diffusion coefficients of Ag in pure Al in the temperature range 600–900 K were measured both by Alexander and Slifkin [35] and Peterson and Rothman [36] whereas impurity diffusion coefficients of Al in pure Ag in the temperature interval 800–1300 K were investigated by Fogelson et al. [37]. Values of intrinsic diffusion coefficients were reported by Heumann et al. [38,39] and Abbott and Haworth [40]. Additional measurements