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Thermodynamic properties of liquid silver-gold–gallium alloys determined from EMF measurements with solid YSZ electrolyte

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ABSTRACT

The thermodynamic properties of liquid Ag-Au-Ga alloys were determined using solid oxide galvanic cells with zirconia electrolyte:

W, $Ag_xAu_yGa_{(1-x-y)}$, Ga_2O_3//ZrO_2 + (Y_2O_3)//FeO, Fe, W (I)

in the temperature range from 1023 to 1348 K. Measurements were conducted in the ternary Ag-Au-Ga system along three cross-sections specified by the ratio of mole fractions x_{Ag}/x_{Au} = 1:2, 1:1 and 2:1. Thermodynamic properties of the liquid phase were described with the Redlich-Kister-Muggianu formula. In this description procedure, the heat of mixing determined calorimetrically in the previous work was included. The results of the calculations were compared with the experimental data obtained in this work.

1. Introduction

Noble metals like silver, gold, platinum and palladium, which are often extracted in various amounts during production of copper, are usually sold as pure metals. Some of them can be used in chemical industry [1,2], catalysis [3–5], electronic circuits [6,7] and of course in jewelry [8–10]. Platinum is a superb catalyst mainly used in automobile exhaust systems. Today, it is being substituted with palladium, which is also applied in electromechanical contacts as relays, tooth coatings and in oil industry during distillation of petroleum fractions. Silver, traditionally used in photography and in silverware, due to its excellent conductivity, is applied in electronic industry. Silver alloys are the best substitutes of lead-containing solders. Finally, gold can also be used in contacts of electronic circuits, but first of all it is being used in jewelry.

However, due to their price and availability it seems more reasonable to use these metals in alloys. As an example, the Ag-Au-Cu system can be given, which is one of the best known alloy of noble metals with copper. The silver-gold-copper system is the most common gold jewelry [8]. Recently, the ternary systems based on gold and silver metals have found applications in the dental industry [11]. Moreover, it is known that different colours of gold are obtained by the introduction of various additions which decide about the colour which will be obtained [11–16]. So-called white gold is obtained due to palladium addition. Separate groups of special colours of gold like: purple, blue and brown are obtained by the application of indium, gallium and aluminium [17,18] additions, respectively. As it is seen, gallium appears as one of possible alloying elements in gold.

Gallium itself is a very interesting metal because its melting temperature is very close to the room temperature (302 K). It indicates that the introduction of gallium into a number of alloys can decrease their melting temperature significantly. Such effect can be utilized in the formation of proper interconnections between transition metals having high melting point [19]. However, the most exciting application of gallium in alloys is the formation of shape–memory materials. It was found that Ni-Mn-Ga alloys exhibit the giant magneto-mechanical effect [20,21] which allows magnetic-field controlled actuator materials to be developed. Surprisingly, the first shape memory effect was discovered in gold–cadmium alloys [22], and this effect in gold alloys can be used for gripping jewels in mounts during jewelry manufacturing. Thus, the search for new phases and the conditions of their formation in gold alloys seems to be a reasonable aim. From this point of view, the use of gallium in the Ag-X-Ga (where X = Au, Cu) systems seem to be interesting since these alloys can be used in jeweller's craft as a joint.

In the case of Ag-Cu-Ga system thermodynamic properties of the liquid phase and optimization of this ternary system were published recently [23,24]. The information about the other system i.e. Ag-Au-Ga, as well as its properties is missing in the monographs of Villars et al. [25] and Petzow and Effenberg [26]. In the literature one can find only two experimental works related to this ternary system. The first one, of Andronov et al. [27] provides information about wettability of the Ag-Au-Ga thin films. Consequently, the ternary Ag-Au-Ga system was studied as one of those who can be applied as a solder. The other one, published by Jendrzejczyk-Handzlik [28], reported the results of calorimetric measurements of the enthalpy of mixing along two cross-sections of this ternary system, with x_{Ag}/x_{Ga} = 1:1 and x_{Au}/x_{Ga} = 1:1, as well as at two temperatures 1223 and 1323 K. The results obtained in

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Table 1
Materials used in the experiments.

Manufacturer	Substance	Country of manufacture	Purity [mass.%]	Purification method	Analysis method
Alfa Aesar	Ag	Germany	99.99	None	Certified purity
Air Products	Ar	United State of America	99.999	None	Certified purity
National Mint	Au	Poland	99.99	None	Certified purity
Alfa Aesar,	Fe	Germany	99.99	None	Certified purity
Sigma Aldrich	Fe_2O_3	Germany	99.99	None	Certified purity
Alfa Aesar	Ga	Germany	99.99	None	Certified purity
Sigma Aldrich	$Ga2O_3$	Germany	99.99	None	Certified purity
Alfa Aesar,	W	Germany	99.99	None	Certified purity
Yamari	ZrO_2	Japan	doped by 8.5 of Y_2O_3	None	Certified purity
Powloka	Alumina crucibles	Poland	95.00	None	Certified purity

that experimental work showed that the enthalpy of mixing in this ternary system indicates negative deviation from Raoult's law and does not have a temperature dependence. Thermodynamic properties of the ternary Au-Ag-Ga system as well as the phase equilibria remain unknown. However, up to this time, thermodynamic properties and phase equilibrium data for three binary systems Ag-Au [29], Au-Ga [30] and Ag-Ga [31,32] were studied and can be found in literature.

Two of them (i.e. Au-Ga and Ag-Ga) were recently investigated and re-optimized by using CALPHAD method [30,32]. The third one, i.e. Ag-Au system, was investigated by several authors but it was not optimized by our group. Calorimetric measurements were conducted first time by Kawakami [33] who studied the enthalpy of mixing of the Ag-Au system at 1473 K. He found that the heat of mixing is close to zero and concluded that this binary solution is ideal. Next, Oriani and Murphy [34] measured the enthalpy of mixing in liquid Ag-Au system at 1396 K by using reaction calorimeter. The measurements were done in the composition range from 0.3 to 0.5 x_{Au}. Itagaki and Yazawa [35] measured the enthalpy of mixing in the liquid silver-gold system at 1473 K in the composition range from 0.1 to 0.88 x_{Au} by applying adiabatic calorimeter. All these high temperature data are rather different, and a new determination of the enthalpy of mixing in the liquid Ag-Au system seems to be necessary. Topor and Kleppa [36] measured the enthalpy of mixing in this liquid binary system by using reaction calorimetry at 1379 K in the composition range from 0.1 to 0.89999 $x_{Au.}$ In the same year (1984), Rakotomavo et al. [37] determined the enthalpy of mixing of these liquid alloys at 1373 K by using high-temperature calorimeter in the composition range from 0.240 to 0.969 x_{Au}. The newest data of the enthalpy of mixing in this binary liquid system are given by Fitzner et al. [38], who carried out measurements at 1375 K. Measurements were conducted by using novel in-situ mixing technique in the composition range from 0.3999 to 0.8999 x_{Au}. The enthalpies of mixing obtained by a number of authors [36–38] are in good agreement. However, the results published by Oriani and Murphy [34] are more negative than those published in [36–38]. Similarly, the experimental data reported by Itagaki and Yazawa [35] differ considerably from other measurements.

In turn, the activity of silver in the liquid Ag-Au binary system was determined by Wagner and Engelhardt [39] at 1358 K in the composition range from 0.15 to 0.75 x_{Au}, who used EMF method with molten salts electrolyte. Next, Oriani [40], who investigated the activity of silver at 1344 K in the composition range from 0.3 to 0.9 x_{Au}, used the cell with the liquid LiCl-AgCl electrolyte. Activity of silver in the liquid Ag-Au system reported by the authors [39,40] shows slight negative deviation from the Raoult's law, and they are in very good agreement despite the fact that they were completed almost 25 years apart.

Thus, there is a strong evidence that respective binary systems are well known, and in principle, properties of the binaries can be used to predict ternary system from the respective "end–members" i.e. respective binary systems using CALPHAD method. However, there are at least two obstacles to follow this procedure:

- Au-Ga and Ag-Ga binary systems exhibit intermetallic phases and since the ternary phase diagram is not known, one cannot exclude the existence of the solid ternary phases. Moreover, the range of solid solubility of gallium in Ag-Au solid solution is not determined. In such a case prediction from the respective binaries will fail.
- the temperature dependence of thermodynamic functions of binaries cannot be simply extrapolated into a ternary system. These functions should be measured to get precise description of the thermodynamic properties of the liquid phase.

Consequently, new experimental data are needed to enlarge our knowledge about the phase diagram and melting behaviour of the Ag-Au-Ga system. The present work refers to EMF measurements, which are suitable to determine precisely the activity of gallium in the solution. Experiments were carried out on the liquid phase along three cross sections for the ratio of x_{Ag}/x_{Au} = 1:2, 1:1 and 2:1. The thermodynamic functions of the liquid phase were described by the Redlich-Kister-Muggianu polynomial [41].

2. Experimental

2.1. Materials

The provenance and mass fraction purity of the materials used in this study are listed in Table 1. Silver-gold-gallium metallic alloys of a chosen composition (about 2 g) were prepared from pure metals before EMF experiments. Weighed metal samples were placed inside quartz tubes, and then they were sealed under vacuum. Next, alloys were prepared by melting during heating sealed ampoules in the operating furnace up to 1373 K. During EMF measurements an ultra-high purity atmosphere was argon.

2.2. Electrochemical measurements

In order to determine the activity of gallium in liquid Ag-Au-Ga alloys, the EMF cells of the type

$$W,\ Ag_xAu_yGa_{(1\text{-}x\text{-}y)},\ Ga_2O_3/ZrO_2 + (Y_2O_3)/FeO,\ Fe,\ W \quad (I)$$

were used.

A schematic representation of the cell assembly is shown in Fig. 1.

A small amount of pressed Ga_2O_3 powder was placed at the bottom of a YSZ tube. The tube of the solid zirconia electrolyte contained about 2 g of metallic alloy of a chosen composition. The tungsten wire, kept inside the alumina shield, acted as an electric contact with the liquid metal electrode. The tungsten wire was also used as an electric lead to the working electrode. A solid electrolyte tube was inserted into an alumina crucible filled with the mixture of Fe + FeO powder (which was produced by heating the mixture of Fe and Fe_3O_4 powders under argon up to T = 1273 K) and sealed inside it with alumina cement. The whole cell was placed inside a silica tube, which was suspended on an upper brass head which closed the tube of a resistant furnace. Due to