

Partial phase diagram of Au-Ag-Dy ternary system^①

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Abstract: On the basis of Au-Ag, Au-Dy and Ag-Dy binary phase diagrams, the 700 °C isothermal section of Au-Ag-Dy ternary system (Dy ≤ 35%, mole fraction) was established by X-ray diffraction analysis, differential thermal analysis and optical microscopy. It is found that there is a long single-phase region, Au(Ag) or Ag(Au), along the Au-Ag binary isomorphous system on the gold-silver rich side of the 700 °C isothermal section and between the binary compound Au₂Dy and Ag₂Dy there is the all proportional solid solution, (Au₂Dy) or (Ag₂Dy). It is confirmed that the partial 700 °C isothermal section consists of six single-phase regions: solid solution Au(Ag) or Ag(Au), (Au₂Dy) or (Ag₂Dy), Au₆Dy, Au₅₁Dy₁₄, Au₃Dy and Ag₅₁Dy₁₄; nine binary-phase regions: (Au₂Dy) + Au(Ag), Au₆Dy + Au(Ag), Au(Ag) + Ag₅₁Dy₁₄, Ag₅₁Dy₁₄ + (Au₂Dy), Au₃Dy + (Au₂Dy), Au₃Dy + Au₅₁Dy₁₄, Au₅₁Dy₁₄ + Au₆Dy, Au₅₁Dy₁₄ + Au(Ag) and Au(Ag) + Au₃Dy; four ternary regions: Ag₅₁Dy₁₄ + (Au₂Dy) + Au(Ag), (Au₂Dy) + Au(Ag) + Au₃Dy, Au(Ag) + Au₃Dy + Au₅₁Dy₁₄ and Au₅₁Dy₁₄ + Au(Ag) + Au₆Dy. No new ternary compound is formed in the gold-silver-rich field (Dy ≤ 35%) of the Au-Ag-Dy ternary system.

Key words: Au-Ag-Dy ternary system; phase diagram; isothermal section

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1 INTRODUCTION

Because of the good electrical conductivity and the corrosion-resistant properties, the Au-Ag alloys have found wide applications in electronics and computers etc. Recently some researchers tried to improve the strength of the Au-Ag alloys by adding the third element, of which the rare earth elements are good candidates.

The Au-Ag-Dy ternary system has relation to the three binary systems: Au-Ag, Au-Dy and Ag-Dy. The equilibrium diagram of the Au-Ag binary system is an isomorphous phase diagram including the liquid, L, and the fcc continuous solid solution, Au(Ag). The very narrow liquidus-solidus gap was predicted from thermodynamic considerations by Wagner^[1] and first confirmed experimentally by White^[2]. The lattice parameters of the fcc solid solution were measured by some investigators^[3-5]. Karmazin et al^[3] and Venudhar et al^[5] reported the lattice parameters change with composition. Okamoto and Massalski^[6] summed up the previous works and obtained a more exact Au-Ag binary phase diagram.

The Ag-Dy binary phase diagram has already been investigated by some researchers. The stoichiometry of the first Ag-rich phase in the Ag-Dy system was determined by McMasters et al^[7] to be Ag₅₁Dy₁₄. Gschneidner et al^[8] determined the eutectic temperature between Ag and Ag₅₁Dy₁₄ to be 805 °C. Delfino et al^[9] studied the Ag-Dy system

and reported three congruently melting compounds: Ag₅₁Dy₁₄, Ag₂Dy and AgDy. Guzei et al^[10] also studied the Ag-Dy system, but they reported the first Ag-rich compound to be Ag₃Dy. Ferro and Delfino^[11] published "Comments on the properties of Ag-rich alloys in the silver-rare earth systems". Gschneidner and Calderwood^[12] summed up the above works and obtained the assessed Ag-Dy system phase diagram including three intermetallic compounds: Ag₅₁Dy₁₄, Ag₂Dy and AgDy.

Rider et al^[13] studied gold-rich rare earth-gold solid solution. McMasters and Gschneidner^[14] first reported the experimental phase diagram for Au-Dy system. Gschneidner and Calderwood^[15] have combined these investigations and obtained a more complete Au-Dy binary phase diagram with six intermetallic compounds: AuDy₂, AuDy, Au₂Dy, Au₃Dy, Au₅₁Dy₁₄ and Au₆Dy.

Till now, no investigation on the Au-Ag-Dy ternary phase diagram has been reported. Based on the conclusions of Refs. [6, 12, 15], in this work the authors studied the 700 °C isothermal section of the Au-Ag-Dy ternary system containing 0 - 35% Dy (mole fraction).

2 EXPERIMENTAL

All the alloys were prepared from gold

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(99.99%), silver (99.99%) and dysprosium (99.9%) using an induction furnace. For degassing, stoichiometric mixtures of gold and silver were refined in vacuum. Corresponding amounts of dysprosium were then added. The alloys were melted in boron nitride crucibles under a pure argon atmosphere. After remelting, the melts were cooled quickly, and homogeneous lumps of the alloys were obtained. It was determined by chemical analysis that the mass losses of the alloy elements in the specimens were less than 0.5% for both gold and silver, and 1% for dysprosium during melting. The results of the experiments were corrected accordingly. All of the specimens were sealed in silica tubes filled with argon. To determine the isothermal section at 700 °C, the specimens were homogenized at (700 ± 1) °C for 400 h, and then quenched.

The microstructure of the specimens was determined by X-ray diffraction analysis and was observed by metallograph. The X-ray diffraction experiments were performed with a Rigaku (RV-200 model) diffractometer, using Cu K α radiation ($\lambda = 0.15405$ nm). The diffraction data were adjusted with silicon powder as an internal standard. Thermal analysis experiments were made by a Perkin-Elmer DTA-1700-type differential thermal analyzer at the heating rate of 10 °C/min. The element distribution in a part of the alloy specimens was determined in an electro-probe microanalyser (EPM A-8705Q model).

3 RESULTS AND DISCUSSION

3.1 Intermetallic compounds of Au-Dy and Ag-Dy binary system

In this work, we measured and inspected the intermetallic compounds in both Au-Dy and Ag-Dy binary systems ($\text{Dy} \leq 35\%$). It is found that the crystal structures and the lattice parameter data of these compounds basically accord with the conclusions of Refs. [12, 15] and that the homogeneous

region of Au₂Dy at 700 °C is 32.5% - 34.2% Dy (mole fraction), but Au₃Dy, Au₅₁Dy₁₄ and Au₆Dy have a narrower width of homogeneous regions than 1% Dy. Table 1 lists the crystal structures and the lattice parameters of Au₆Dy, Au₅₁Dy₁₄, Au₃Dy, Au₂Dy, Ag₂Dy, and Ag₅₁Dy₁₄.

3.2 Solubility of Dy in Au-Ag alloys

Rider et al.^[13] reported that the maximum solubility of Dy in Au is 2.3% (mole fraction) at 808 °C, and decreases to about 0.5% Dy at 300 °C. Gschneidner et al.^[8] determined the solubility of Dy in Ag at 805 °C, the eutectic temperature between Ag and Ag₅₁Dy₁₄, to be 1.3%. In this work, the solubility of Dy in Au at 700 °C was determined to be 1.7%; in Ag to be 1.0%; in AuAg alloy of equal atom to be about 1.9%. These solubility data are based on the X-ray lattice parametric method — the variation of the lattice parameter vs composition for alloys quenched at 700 °C (see Figs. 1, 2 and 3). The solubility data of Dy in other Au-Ag alloys at 700 °C were inferred by the X-ray diffraction disappearing-phase method.

According to these solubility data, it is cor-

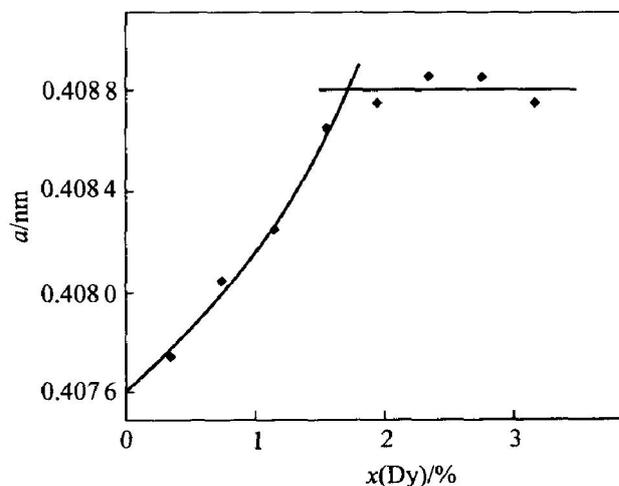


Fig. 1 Lattice parameters of (Au) vs composition of alloys Au_{100-x}Dy_x

Table 1 Crystal structure data in Au-Dy and Ag-Dy (0 - 35% Dy) binary system

Phase	Homogeneity range(Dy) / %	Space group	Proto-type	Lattice parameter/ nm			Ref.
				a	b	c	
Au ₆ Dy	14.3	P4 ₂ /ncm	Au ₆ Ho	1.030 ± 0.001		0.9670 ± 0.0010	[15]
Au ₅₁ Dy ₁₄	about 21.5	P6/m	Ag ₅₁ Gd ₁₄	1.256		0.9152 ± 0.0002	[15]
Au ₃ Dy	25	Pmmn	TiCu ₃	0.6091 ± 0.0003	0.4977 ± 0.0001	0.5088 ± 0.0002	[15]
Au ₂ Dy	33.3	14/mmm	MoSi ₂	0.3683 ± 0.0001		0.8962 ± 0.0001	[15]
	32.5 - 34.2	14/mmm	MoSi ₂	0.3676 - 0.3688		0.8956 - 0.8970	This work
Ag ₂ Dy	32.3 - 34.3	14/mmm	MoSi ₂	0.3694 ± 0.0004		0.9213 ± 0.0006	[12]
Ag ₅₁ Dy ₁₄	21.5 - 25.5	P6/m	Ag ₅₁ Gd ₁₄	1.2635 - 1.2670		0.9271 - 0.9289	[12]

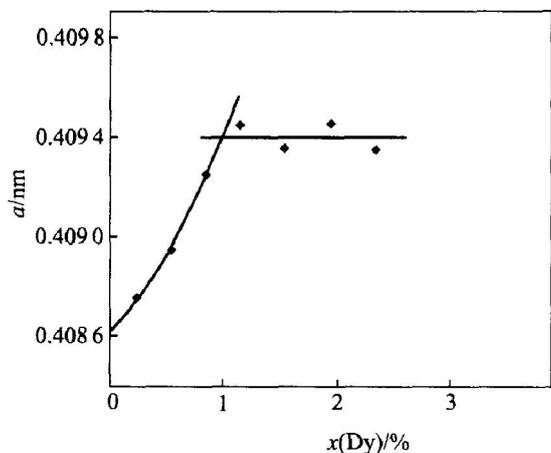


Fig. 2 Lattice parameters of (Ag) vs composition of alloys $Ag_{100-x}Dy_x$

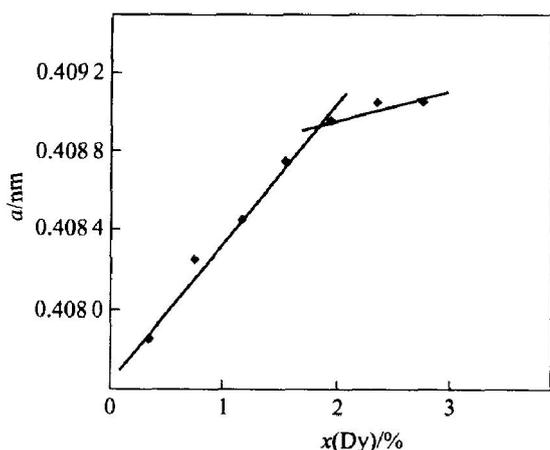
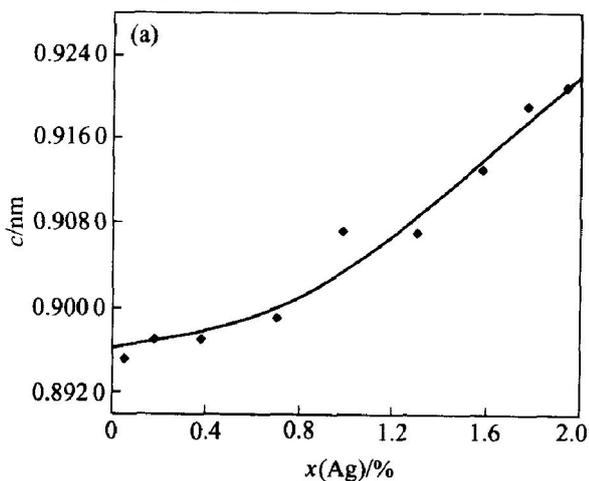


Fig. 3 Lattice parameters of Au(Ag) vs composition of alloys $Au_{50-x/2}Ag_{50-x/2}Dy_x$

firmly that there is a single-phase region, Au(Ag) or Ag(Au), with a fcc structure along the Au-Ag binary isomorphous system on the gold-silver-rich side in the 700 °C isothermal section of the Au-Ag-Dy ternary phase diagram. The region has long narrow shape with the width of 1.0% - 2.0%.

3.3 Au₂Dy and Ag₂Dy phases



The binary intermetallic compounds Au₂Dy and Ag₂Dy are the congruently melted compounds. As shown in Table 1, both of these compounds have the same crystal structure of MoSi₂-type with the similar lattice parameter data. The homogeneous regions of the Au₂Dy in the Au-Dy binary system at 700 °C was determined to be 32.5% - 34.2% Dy and the Ag₂Dy in Ag-Dy binary system to be 32.3% - 34.3% Dy. Their single-phase ranges in the Au-Ag-Dy ternary system were studied by the X-ray parametric method. As shown in Fig. 4, the lattice parameters of Au₂Dy or Ag₂Dy phase in the (Au_{2-x}Ag_x)Dy alloys at 700 °C increase continuously with the silver content increasing. The result shows that any amount of Au atoms can be replaced by Ag to form an all proportional solid solution, (Au₂Dy) or (Ag₂Dy).

3.4 Au₆Dy, Au₅₁Dy₁₄, Au₃Dy and Ag₅₁Dy₁₄ phases

The single-phase regions of the compounds Au₆Dy, Au₅₁Dy₁₄, Au₃Dy and Ag₅₁Dy₁₄ in the Au-Ag-Dy ternary system were determined by the X-ray diffraction disappearing-phase method. It is found that the solid solubility of Ag in Au₆Dy at 700 °C is less than 1%, Ag in Au₅₁Dy₁₄ about 1%, Ag in Au₃Dy about 3%, Au in Ag₅₁Dy₁₄ about 5%.

3.5 Other phase regions

The other boundaries of the phase fields in 700 °C isothermal section of the Au-Ag-Dy ternary phase diagram (0 - 35% Dy) were determined by the X-ray diffraction disappearing-phase method, and checked by metallography. On the basis of the experiments, the compositions of all specimens are represented in Fig. 5. And no new ternary intermetallic phase was found.

According to the above investigations, the 700 °C isothermal section of the Au-Ag-Dy ternary phase diagram (Dy ≤ 35%) was confirmed and shown in Fig. 6.

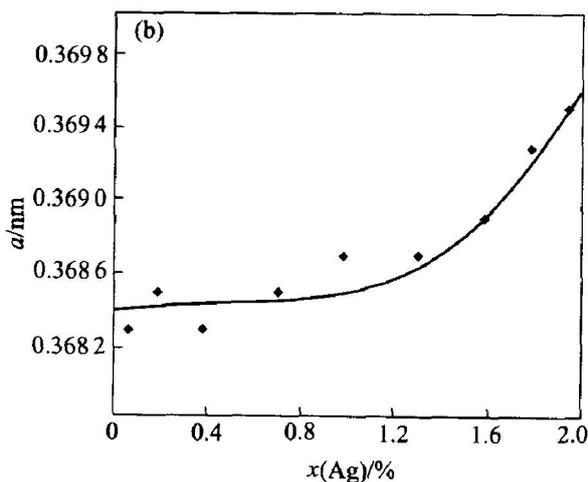


Fig. 4 Lattice parameters of (Au₂Dy) or (Ag₂Dy) vs composition of alloys (Ag_xAu_{2-x})Dy

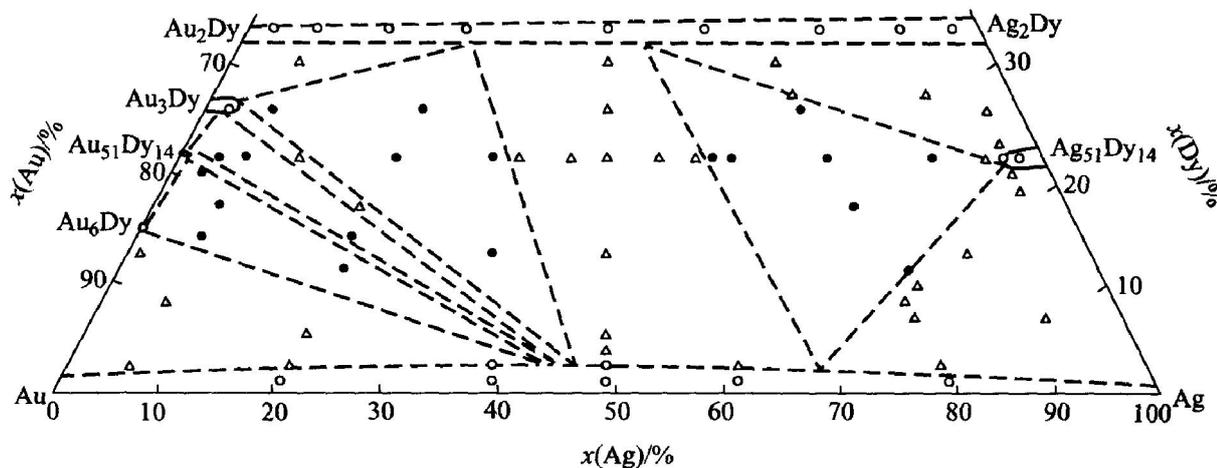


Fig. 5 Phase fields in 700 °C isothermal section of Au-Ag-Dy ternary system determined by X-ray diffraction disappearing-phase method
○—Single phase; △—Two phase; ●—Three phase

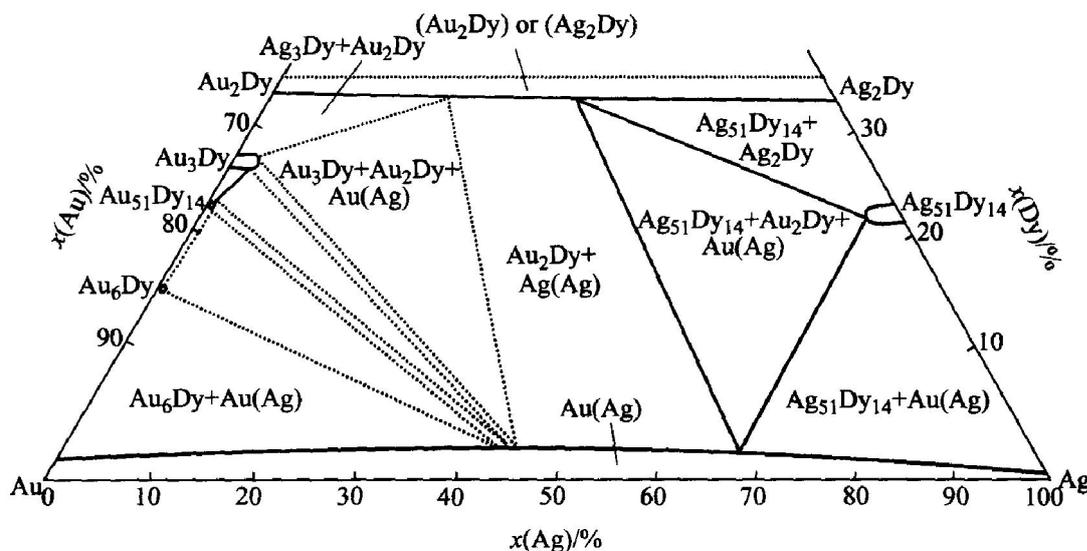


Fig. 6 700 °C isothermal section of Au-Ag-Dy ($Dy \leq 35\%$) ternary system

4 CONCLUSIONS

1) There is a long single-phase region, Au (Ag) or Ag(Au), along the Au-Ag binary isomorphous system on the gold-silver-rich side of the 700 °C isothermal section. And between the binary compound Au₂Dy and Ag₂Dy there is the all proportional solid solution, (Au₂Dy) or (Ag₂Dy). No new ternary compound is formed in the gold-silver-rich field ($Dy \leq 35\%$) of the Au-Ag-Dy ternary system.

2) The partial 700 °C isothermal section consists of six single-phase regions: solid solution Au (Ag) or Ag(Au), (Au₂Dy) or (Ag₂Dy), Au₆Dy, Au₅₁Dy₁₄, Au₃Dy and Ag₅₁Dy₁₄; nine binary-phase regions: (Au₂Dy) + Au(Ag), Au₆Dy + Au(Ag), Au(Ag) + Ag₅₁Dy₁₄, Ag₅₁Dy₁₄ + (Au₂Dy), Au₃Dy + (Au₂Dy), Au₃Dy + Au₅₁Dy₁₄, Au₅₁Dy₁₄ + Au₆Dy, Au₅₁Dy₁₄ + Au(Ag) and Au(Ag) +

Au₃Dy; four ternary regions: Ag₅₁Dy₁₄ + (Au₂Dy) + Au(Ag), (Au₂Dy) + Au(Ag) + Au₃Dy, Au(Ag) + Au₃Dy + Au₅₁Dy₁₄ and Au₅₁Dy₁₄ + Au(Ag) + Au₆Dy.

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