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Structure of isomorphous liquid Ag–Au alloys

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ABSTRACT

Liquid structure features of isomorphous Ag–Au alloys were investigated using an X-ray diffractometer. The mean nearest neighbor distance r_1 of Ag–Au melts at the same temperature remains stable at different compositions. For the eutectic melts under discussion, r_1 takes on a linear relationship with element component, and the slope of r_1 versus composition depends on the atomic size ratio. In addition, r_1 of both Ag–Au and Cu–Ni isomorphous melts stays stable with decreasing temperature above liquidus. Compared to these isomorphous alloys, the temperature-dependent r_1 of eutectic melts obviously exhibits. The structural differences of melts between isomorphous and eutectic alloy systems, as well as the correlation between liquid structure and the corresponding solid state were investigated. Finally, Gaussian decomposition was performed to get a better understanding of the liquid structures of Ag–Au alloys.

1. Introduction

Isomorphous alloys such as Ag–Au, Cu–Ni, Ni–Ru, and Ti–Zr possess some excellent properties and have extensive applications [1–6]. Especially for Ag–Au systems, the electrum of which is a naturally occurring alloy, the conductivity, oxidation resistance, ductility, and color make them useful for a wide range of applications, including wire, plumbing pipe, jewelry, photographic film, and batteries. In addition, bimetallic Ag–Au nanoparticles in glass can lead to specific linear and nonlinear optical properties [1]. Therefore, research on Ag–Au alloys attracts a lot of attention.

Based on phase diagrams, the solidification processes of isomorphous and eutectic alloys are quite different. As melts are the parent state of alloys, the liquid structures among these two alloy systems are bound to be diverse. It is generally accepted that liquid structures have close relationships with the properties of their corresponding alloys [7,8]. Thus, the properties and applications of isomorphous and eutectic alloys must be different from each other as well. In order to optimize the performances of isomorphous alloys and make full uses of them, investigating their liquid structures and comparing the differences between isomorphous and eutectic alloy melts become a necessity.

It was reported that in Ag–Au binary clusters, a partial electronic charge transfer from Ag to Au seems to be the main reason for the alloy formation, and Au atoms prefer to localize in the outer part of the bimetallic particle [2]. Recently, Silvia A. Fuente et al. [3] revealed that the Ag–Au bond stabilization depends on the relative position of each atom. In the present study, according to the structural parameters obtained from the experimental data of the X-ray diffraction, we mainly focused on the micro-structural behaviors of typical isomorphous Ag–Au melts, and made a comparison with those of the isomorphous Cu–Ni melts as well as some eutectic melts (the $Au_{81}Si_{19}$ alloy was chosen as a supplementary experiment, and other data were obtained from references), from the perspectives of both composition and temperature dependence. The aim of this work is to make clear the differences between the isomorphous alloys' liquid structure and that of the eutectic alloys, with an attempt to inspire further discovery in the solidification processes of the two different alloy systems and thus enlarge applications in various fields.

2. Experimental procedures

The samples $Ag_{99}Au_1$, $Ag_{95}Au_5$, $Ag_{90}Au_{10}$, and $Au_{81}Si_{19}$ (at.%) alloys used in the present study were prepared by pure Ag, Au, and Si of 99.99% purity. An ultrasonic washer was used to ensure a clean surface of the samples.

X-ray diffraction measurements were carried out using a high temperature θ–θ type X-ray diffractometer. Mo K_α radiation (wavelength $\lambda = 0.7089$ Å) was reflected from the free surface of the specimen and reached the detector through a graphite monochromator in the diffraction beam. A scintillation detector with a pulse height analyzer was used to measure the scattered intensity. The sample was placed in an yttria crucible, with a size of 23 mm × 18 mm × 8 mm. High temperature X-ray diffraction was carried out under a high purity helium (99.999%) atmosphere of 1.3 atm, before which the chamber was cleaned in a vacuum of 2×10^{-6} Pa. The scanning voltage of X-ray tube was 40 kV, the current was 25 mA, the exposure time was 20 s and the measured scattering angle 2θ was from 5 to 90°. The scanning steps were 0.5° for the range of 5–15°, 0.2° for 15–20°, 0.5° for 20–45° and 1°

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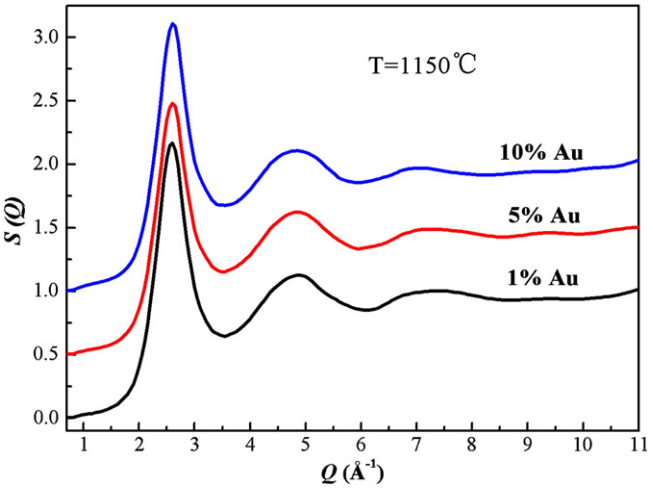

Fig. 1. Composition dependence of total structure factors of Ag–Au alloys.

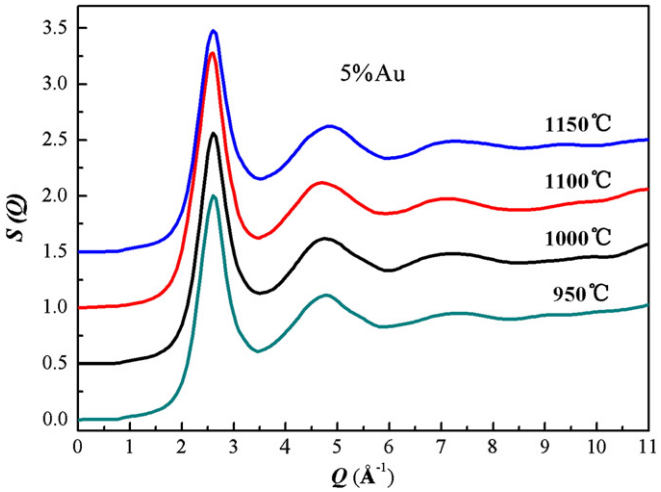

Fig. 3. Temperature dependence of total structure factors of $Ag_{95}Au_5$ alloy.

for 45–90°. The scattering temperatures were 950, 1000, 1100, and 1150 °C for $Ag_{95}Au_5$ alloy, 1150 °C for $Ag_{99}Au_1$ and $Ag_{90}Au_{10}$ alloys, 310, 360, 380, and 400 °C for $Au_{81}Si_{19}$ alloy. The samples were heated to 1400 °C and held for 30 min, and then cooled to the first scattering temperature and held for 30 min likewise before scattering start. Every time a new scattering temperature was started, the sample was held for the same time.

The scattering intensity which was measured in an arbitrary unit can be converted into the coherent scattering intensity per atom in an electron unit $I_{eu}^{coh}(Q)(Q=4\pi\sin\theta/\lambda$, and θ is the half scattering angle), using the generalized Krogh–Moe–Norman method [9–11]. Compton scattering was corrected using the values given by Cromer and Mann [12]

$$I_{eu}^{coh}(Q) = \langle f^2\rangle + \langle f\rangle^2 \int_0^\infty 4\pi r^2[\rho(r)-\rho_0]\frac{\sin(Qr)}{Qr}dr, \tag{1}$$

where, f is scattering factor, $\rho(r)$ is radial density function, ρ_0 is average density.

Then, the Ashcroft–Langredth structure factor $S(Q)$ can be obtained through the function [13,14] below

$$S(Q) = \frac{I_{eu}^{coh}}{\langle f^2(Q)\rangle} \tag{2}$$

with

$$\langle f^2(Q)\rangle = \sum_j c_j f_j^2(Q), \tag{3}$$

where, c_j is the mole fraction, and $f_j(Q)$ the total atomic scattering factor of jth component in the alloy. Multiple scanning, resulting in an accumulation of more than 3×10^4 counts per angle, reduces the total estimate of error for the structure factor $S(Q)$ to less than 2%.

The real space information can be reflected by the pair distribution function $g(r)$, which has a relationship with structure factor $S(Q)$ through the Fourier transformation

$$g(r) = \frac{\rho(r)}{\rho_0} = 1 + \frac{1}{2\pi^2 r\rho_0}\int_0^\infty Q[S(Q)-1]\sin(Qr)dQ, \tag{4}$$

where $\rho(r)$ and ρ_0 are the local and average number density, respectively. And the position of the first maximum of $g(r)$ represents the mean nearest neighbor distance r_1.

Another useful function is the radial distribution function $RDF(r)$:

$$RDF(r) = 4\pi r^2\rho_0 g(r). \tag{5}$$

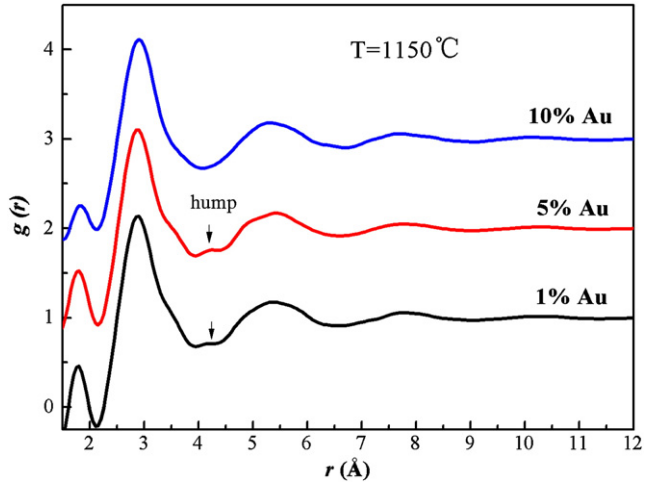

Fig. 2. Composition dependence of pair distribution functions of Ag–Au alloys.

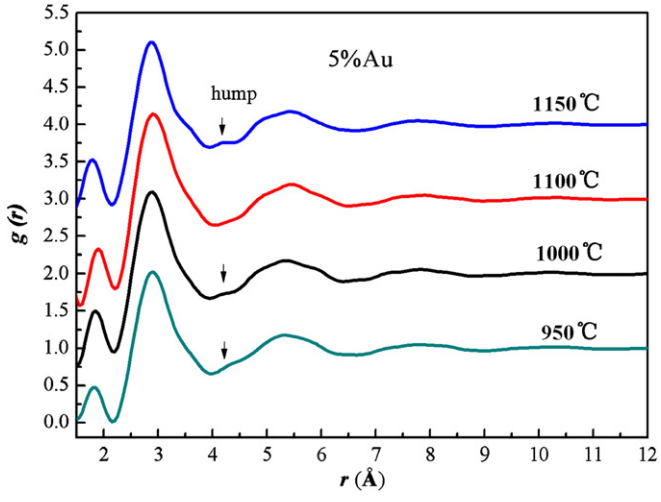

Fig. 4. Temperature dependence of pair distribution functions of $Ag_{95}Au_5$ alloy.