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Investigation of atom distribution in Mg-9wt.%Al melt using small-angle X-ray scattering and molecular dynamics simulation

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ABSTRACT

Two kinds of atom distribution in Mg-9wt.%Al melt, undissolved particles and atom aggregation, were investigated by synchrotron small-angle X-ray scattering (SAXS) and molecular dynamics simulation, respectively. The SAXS results indicated that no undissolved particles exist in Mg-9wt.%Al melt after short-time equilibration. The simulation results indicated that atom Mg and Al have a tendency to form bonds in Mg-9wt.%Al melt and the sizes of aggregated Al-centred clusters are within the characteristic scale of medium-range order; the degree of atom aggregation in Mg-9wt.%Al melt increases slightly with increasing temperature.

1. Introduction

Mg-Al alloys are popular commercial lightweight alloys and are widely used in the industry to achieve the goal of energy conservation and emission reduction. Melting and casting are crucial processes to achieve high-quality Mg-Al components. It has been found that the inhomogeneous atom distribution in the melt plays significant role in the evolution of the physical properties of the melt, and the nucleation behaviors during casting [1–5]. Thus, it has practical significance to study the atom distribution in Mg-Al melt. Undissolved particles and atom aggregation are two main types of atom distribution in the melt.

Generally, for the binary alloy without containing third element, after sufficient equilibration the melt would achieve a thermodynamically stable state, which corresponds to a single liquid phase as shown in the phase diagram. However, some researchers reported that in the binary eutectic and monotectic alloys, nano-sized undissolved particles enriched in one atom could survive in the melt after equilibration and a system of multi-phases is built, which is at a thermodynamically metastable state [2,3,6–9]. Though this theory of metastable melt hasn't been widely discussed, the theory has been successfully used to explain the non-coincident behavior of the physical behavior during heating and cooling, such as ultrasound velocity in Ga-Pb melt [2], viscosity and density of Al-Si melt [3] and magnetic susceptibility of Fe-B melt [9]. The theory has also been used to explain the elimination of the layered microstructure in Al-20 at.%In alloy by melt superheating [3] and the modification effect on the solidified Si phase by superheating Al-16wt.%Si melt [10]. The more direct evidence comes from the study on high purity binary Al-Si melt by using small-angle neutron scattering (SANS), where the signals from the particles with several nanometers were found [7,8]. However, it still remains a question that if the undissolved particles exist in binary Mg-Al melt after equilibration. As an ideal way to detect nano-sized particles in the melt [7,8,11,12], small-angle scattering is used in this study.

After achieving the thermodynamically stable state, however, the atom distribution is still not homogeneous from the atomic scale. In the binary alloys, the difference of binding tendency between atoms could result in different degrees of atom aggregation in the melt [13,14]. Molecular dynamics simulation is a powerful method to study the atomic structure. To the author's knowledge, there are not any reports on the molecular dynamics simulation on the atomic structure or atom aggregation in Mg-side Mg-Al melt [15,16].

Thus, in the present study, aiming to understand the atom distribution in binary Mg-Al melt, the existence of undissolved particles in Mg-9wt.%Al melt was first checked by synchrotron SAXS, and the atom aggregation in the melt was then investigated by classical molecular dynamics simulation.

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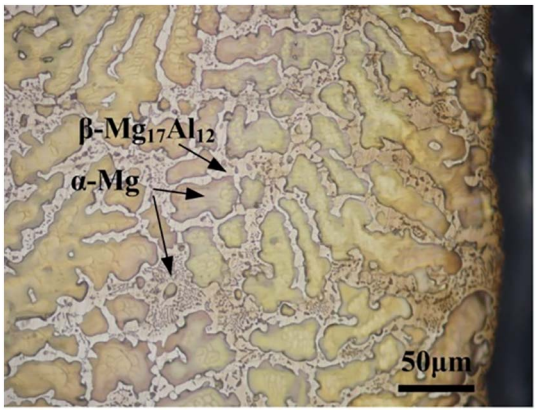

Fig. 1. Microstructure of the sample.

2. Simulation and experimental details

2.1. Experimental details

The Mg-9wt.%Al alloy were prepared by mixing pure Mg (99.99 wt %) and pure Al (99.99 wt%) in the inactive MgO crucible under the protection of the mixture gas Ar + 0.5 vol.%SF_6 at 1053 K. The melt was then cooled in the crucible. Stirring, refining and pouring processes were skipped to avoid introducing oxides and impurity elements into the melt. The liquidus of Mg-9wt.%Al is 873 K obtained from continuous cooling curve. The sample was sliced into piece with the dimension of 5 × 4 × 0.5 mm, and was polished before experiment. Fig. 1 shows the microstructure of the sample, which is composed of α-Mg and β-$Mg_{17}Al_{12}$ phases, indicating that element Mg and Al were well mixed during melting process.

The SAXS experiments were performed on the BL16B1 beamline of Shanghai Synchrotron Radiation Facility (SSRF). The energy of the X-rays was set to 15 keV, corresponding to the wavelength λ of 0.0827 nm. The diameter of the beam is smaller than 0.5 mm. The 2D X-ray patterns were recorded by Mar CCD165 with the single pixel of 7.9×10^{-5} m. The distance between the sample and the detector was 5.07 m, giving the minimal scattering vector q of 0.05 nm^{-1}. The sample temperature was controlled using a heater of TS1500 (Linkam, UK) (Fig. 2(a)) and a homemade sample holder. The sample holder is made of stainless steel (Fig. 2(b)) and monocrystal alumina X-ray window. Fig. 2(c) shows the schematic diagram of the equipment. The sample chamber is carefully sealed, and the mixture gas Ar + 0.5 vol.% SF_6 was used to prevent the sample from oxidation and evaporation during the experiments. Before measuring, the sample was first isothermally holding for 600 s at the selected temperature, and then the scattering X-rays for the melt were recorded for 180 s. The measuring temperatures were 903 and 1053 K. The temperature of 903 K is close to the liquidus of Mg-9wt.%Al, while 1053 K is the refining and holding temperature for Mg-9wt.%Al melt during practice application. The background signal for subtracting was also recorded. The intensity curve was obtained from 2D X-ray patterns by using Fit2D software.

2.2. Simulation details

In the molecular dynamics simulation, the software LAMMPS was used. The total number of atoms in the simulation system was set to 14,400, and 1164 Al atoms was randomly distributed in the box, corresponding to Mg-9wt.%Al alloy. Periodic boundary conditions were used in the three directions. The time-step was 1×10^{-15} s. The system was first equilibrated at 1200 K and cooled to 1100, 1050, 1000, 950 and 900 K at a cooling rate of 5×10^{12} K/s in the isothermal isobaric (NPT) ensemble. At each temperature, the system was then equilibrated in the NPT ensemble for 5×10^{-11} s and recorded for further analysis.

The interatomic potential using modified embedded-atom method developed by Kim et al. [17] was adopted in the simulation. The transferability to the liquid properties of the potential was checked firstly. During the development of the potential, most physical properties of pure Mg, pure Al and Mg-Al alloys in the solid state were repeated, which indicates that the potential is with high accuracy. Especially, the melting point of pure Mg and Al calculated by this potential are 926 and 937 K, which are quite close to the experimental value of 922 and 933 K. The mixing enthalpy of Mg-Al alloys at 1100 K also falls in the scope of experimental results. Finally, the most important parameters of the melt, the structure factor and pair correlation function (PCF) were checked in the present study. The calculated structure factors for Al melt (Fig. 3(a)) and Mg melt (Fig. 3(b)), and the PCF and structure factor for Al-33 at.%Mg melt quite well reproduce the experimental values. Thus, this potential is reliable to be used to study the atom aggregation in Mg-9wt.%Al melt.

3. Results and discussion

3.1. Existence of undissolved particles

The existence of undissolved particles in the melt was determined from the SAXS intensity profile for the melt. The SAXS intensity profile I-q is related to the fluctuation of electron density in the sample. The intensity I is described as [18]:

$$I = \frac{1}{\rho_0}\overline{(\Delta(\rho(r)b(r)))^2}\int_0^\infty \gamma(r)\frac{\sin qr}{qr}r^2 dr \quad (1)$$

where ρ_0 is the mean atomic number density, $\rho(r)$ and $b(r)$ are the atomic number density and scattering length at position r, $\gamma(r)$ describes the correlation function of scattering length density ($\rho(r)\cdot b(r)$) at position r and q is the scattering vector. The range of intensity I is determined by the squared fluctuation of scattering length density and the curve shape of intensity I is determined by $\gamma(r)$. If the distribution of scattering length density is homogenous in the materials, a characteristic SAXS signal would not be observed. Thus, the contrast between the scattering length density of atom Mg and Al should be first checked. For simplicity, one atom is treated as the scattering unit. The atomic number density ρ is equal to $1/V_{atom}$, where V_{atom} is taken as the atom

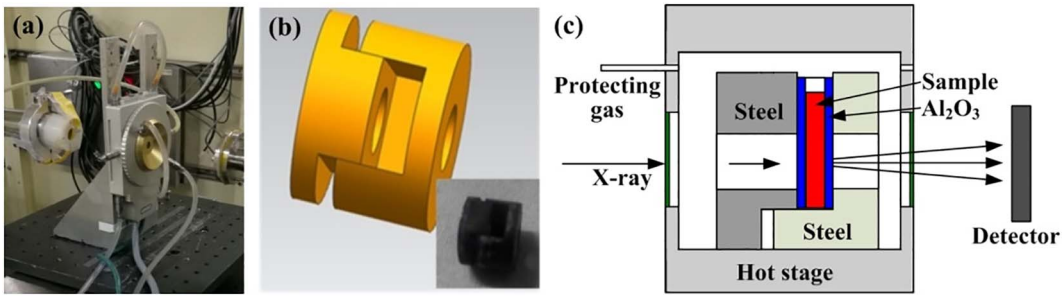

Fig. 2. (a) Heater; (b) stainless steel fixer; (c) schematic diagram of the equipment.