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Thermodynamics of equilibrium and partitionless solidifications in glass forming binary eutectic alloys

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ABSTRACT

T_0 curves in the phase diagrams have been proven useful to understand thermodynamically glass formation in metallic alloys, emphasizing the importance of the metastable solid solutions crystallized partitionlessly. Here we focus on four typical binary eutectic alloys with distinct glass-forming abilities and interatomic interactions, $Ag_{60}Cu_{40}$, $Sb_{17.5}Pb_{82.5}$, $Au_{81.4}Si_{18.6}$, and $Ni_{24}Zr_{76}$. The thermodynamics involved in the liquid–solid solution transition at T_0 temperatures for the alloys of eutectic compositions are quantified, and the validity of the thermodynamic properties is evaluated. The comparison of the melting entropies for the equilibrium and partitionless solidifications reveals a basic relation. Based on the thermodynamics of the equilibrium phases and the solid solutions, an understanding of the glass formation of metallic alloys is proposed.

1. Introduction

Since the preparation of the first metallic glass [1], a series of landmark works [2–5] triggered immense interest in research of glassy alloys and the considerable progresses have been achieved [6,7]. However, the mechanism of the glass transition and the prediction of glass forming regions (GFRs) are still the main challenges and important issues [6,8–10]. From the kinetic point of view, liquid viscosity [11] and its two related quantities of the reduced glass transition temperature T_{rg} [12] and the T_g-scaled temperature dependence or fragility [13] are the main factors, and studies have found that systems with low fragility basically have higher glass-forming ability (GFA) [14–17]. Thermodynamically, the glass formation is found to be related to some fundamental quantities such as the Gibbs free energy difference between the liquid and the resulting crystalline phases [18,19], and enthalpy of mixing [20], formation and mixing enthalpy [21–23], configurational entropy [24] and mismatch entropy [25].

Meanwhile, the metastable crystalline phases involved in liquid–solid phase transitions are proven to be presumably crucial for glass formation, probably by suppressing the stable equilibrium phases to crystallize, among which the supersaturated solid solution solidified partitionlessly (SSS) is a typical metastable crystalline phase and have been emphasized [26]. The metastable phase is usually associated with the concept of T_0 curves, which was pioneered by Boettinger [27,28] and Massalski [29], and developed by extensive studies [30–34]. The T_0 curve defines a temperature at which the Gibbs free energy of the liquid phase for a multicomponent alloy coincides with that of the solid solution. Hence, with T_0 curves, a phase diagram can be addressed in an alternative manner by liquid and solid solution phases, and accordingly, T_0 curves means the minimum undercooling of a liquid before transformed into a SSS [27]. T_0 curves have been proven useful in evaluating the glass-forming tendency for a specific composition in multicomponent alloys, and it is commonly recognized that systems with shallow T_0 curves in phase diagrams usually have poor GFA, while the systems with steeply plunging T_0 curves are prone to be vitrified. The application of T_0 curves to predict the glass forming composition range (GFCR) is largely based on the fact that SSS forms with more ease during solidification among various metastable and equilibrium crystallines (ECs), since, kinetically, no long range atomic diffusion is needed for atomic rearrangement [35,36]. Recently, Zhou and Napolitano found that the GFCR of Al–La and Al–Sm binary systems were exactly located at the composition range bounded by T_0 curves [37,38]. Similar results have also been obtained in Al-rare earth alloys [39]. A series of success in predicting GFCR by T_0 curves suggest that the partitionlessly solidified solid solutions are of importance in determining the glass formation of alloys. It appears that more

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knowledge is expected to understand the metastable phases. Unfortunately, relevant studies remain inaccessible. In this work, the typical metastable phase is focused, and the thermodynamics quantified at T_0 temperatures for the liquid – solid solution transition are evaluated. The results together with the thermodynamics involved in the equilibrium solidification allow us to develop the understanding of glass formation.

2. Data analyses

In the present work, four binary eutectic alloys, $Ag_{60}Cu_{40}$, $Sb_{17.5}Pb_{82.5}$, $Au_{81.4}Si_{18.6}$ and $Ni_{24}Zr_{76}$, are chosen based on the remarkable difference in GFA and atomic interactions between unlike atoms. The two alloys of $Au_{81.4}Si_{18.6}$ and $Ni_{24}Zr_{76}$ can be vitrified by a conventional melt-spun with a cooling rate of ~10^6 K/s [1,40], whereas the amorphous $Ag_{60}Cu_{40}$ and $Sb_{17.5}Pb_{82.5}$ cannot be formed directly from the liquid quenching technique. Notwithstanding, amorphous states can be reached for these two alloys via the vapor deposition technique, giving a higher cooling rate of ~10^{10} K/s [41,42]. The phase diagrams of the four binary alloys are shown in Fig. 1 together with the compositional dependence of the activity coefficients, γ, of the components, which indicate the degree of deviation of the real solution from the ideal mixing ($\gamma = 1$), and are closely related with the interaction between unlike atoms in the alloys. The two cases of $\gamma < 1$ and $\gamma > 1$ mean the attractive and repulsive interactions between unlike atoms, respectively [43]. The values of γ of Ag–Cu, Sb–Pb, Au–Si and Ni–Zr alloys respectively are taken from the literature [44–47] measured at temperatures a bit above the highest T_l in each binary alloy. Consequently, the strong attractive interactions are expected in the Au–Si and Ni–Zr alloys, and the interatomic interaction in the Pb–Sb alloy is relatively weak, while for Ag–Cu, a repulsive interaction is visible due to the positive values of γ. The blue dashed lines in the phase diagrams present the T_0 curves of the alloys. Except for the Ag–Cu phase diagram where only one T_0 curve is present, the other three alloys all show two T_0 curves corresponding to the solid solutions with different crystalline lattice types. The thermodynamics of the solid solutions of the four alloys will be focused to make a connection to the glass formation of metallic alloys, and a relation is revealed.

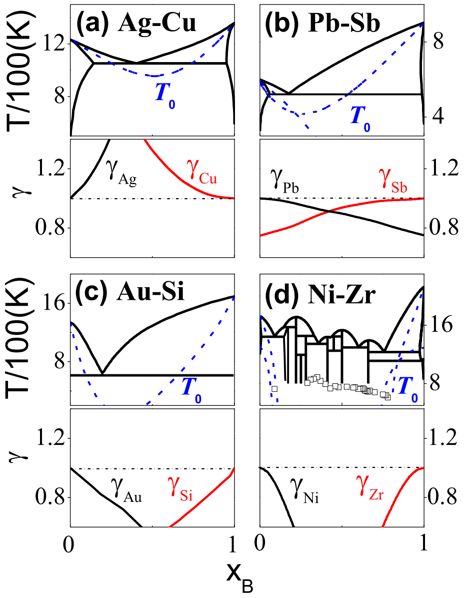

Fig. 1. Phase diagrams of four typical binary eutectic alloys with distinct atomic interactions expressed by the activity coefficients γ. The γ values are from Refs. [44–47]. x_B is the mole fraction of the second components in the binary alloys. The T_0 curves of the eutectic alloys calculated with the Gibbs free energies reported in Refs. [30,45,50,47] are shown by the blue dashed lines. The open square in (d) denotes the glass transition temperature recorded in Ref. [40]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The substitutional solution model allows the Gibbs free energies of liquid and solid phases to be expressed using the CALPHAD method,

$$G_l = x_A G^0_{lA} + x_B G^0_{lB} + RT(x_A \ln x_A + x_B \ln x_B) + G^{ex}_l \quad (1)$$

$$G_s = x_A G^0_{sA} + x_B G^0_{sB} + RT(x_A \ln x_A + x_B \ln x_B) + G^{ex}_s, \quad (2)$$

where G^0_l and G^0_s are the Gibbs free energies of the pure constituents in liquid and solid phases which can be taken from the SGTE database [48]. $-R[x \ln x + (1-x)\ln(1-x)] = S^{id}_{mix}$ is the ideal entropy of mixing for the binary systems, and R is the ideal gas constant. G^{ex}_l and G^{ex}_s denote the excess Gibbs energies of mixing in liquid and solid phases, which are usually expressed by the Redlich–Kister formalism [49],

$$G^{ex} = x_A x_B \sum_0^n {}^iL_{AB}(x_A - x_B)^i \quad (3)$$

where ${}^iL_{AB}$ are the interaction parameters between unlike components. The expressions of ${}^iL_{AB}$ for Ag–Cu, Sb–Pb, Au–Si and Ni–Zr alloys are available in literature [30,45,50,47]. The reliability of the data can be inferred from the excellent consistency of the calculated results with the experiment measurements.

It should be pointed out that the $Sb_{17.5}Pb_{82.5}$ and $Ni_{24}Zr_{76}$ alloys both could have two types of solid solutions, the fcc and the rhombohedral solid phases for $Sb_{17.5}Pb_{82.5}$, fcc and bcc for $Ni_{24}Zr_{76}$. T_0 of the fcc solid solution in the two alloys are higher, which means this phase should be preferentially encountered during the partitionless solidification against glass formation. Hence, the fcc solid solutions are mainly discussed for $Sb_{17.5}Pb_{82.5}$ and $Ni_{24}Zr_{76}$. For the Ni–Zr systems, the glass transition has been reported at compositions near the eutectics such as $Ni_{91}Zr_9$, $Ni_{64}Zr_{36}$, and $Ni_{36}Zr_{64}$ [51,52]. However, the data of melting thermodynamics are available only for $Ni_{24}Zr_{76}$ from the literature, which is necessitated to make a comparison with other three binary glass formers. Moreover, the T_0 lines within the composition of Ni from 33.3% to 77.8% have not been reported, which makes the calculation of the thermodynamics for the solid solution phases to be inaccessible.

It is known that the entropy of fusion of a crystalline phase can be derived from the first-order temperature derivative of the Gibbs energy difference between a liquid and its EC phase at the melting temperature, independent of the expression of the Gibbs energy difference [53–55]. Similarly, the practice is expected to be effective for the determination of the entropy of fusion of a SSS, $\Delta S_{m\text{-}ss}$, using the temperature derivative of the Gibbs energy difference between the liquid and solid solutions $\Delta G = G_l - G_s$ at T_0. With the reported data, ΔG between the liquid and solid solution is immediately available for the four eutectic alloys. $\Delta S_{m\text{-}ss}$ of the SSS with eutectic compositions are calculated. With the values of $\Delta S_{m\text{-}ss}$ and T_0, the heat of fusion of the SSS $\Delta H_{m\text{-}ss}$, can also be determined by the equation of $\Delta H_{m\text{-}ss} = \Delta S_{m\text{-}ss} T_0$. The T_0 values of the four eutectic alloys can be obtained in Fig. 1. Fig. 2(a) and (b) show $\Delta S_{m\text{-}ss}$ and $\Delta H_{m\text{-}ss}$ together with the earlier reported melting entropies and heats of ECs denoted by $\Delta S_{m\text{-}ec}$ and $\Delta H_{m\text{-}ec}$ [45,55–57]. The thermodynamic parameters involved in the partitionless and equilibrium solidifications are listed in Table 1.