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CORRELATION BETWEEN SUPERHEATED LIQUID FRAGILITY AND ONSET TEMPERATURE OF CRYSTALLIZATION FOR Al-BASED AMORPHOUS ALLOYS

KORELACJA MIĘDZY KRYTYCZNYMI PARAMETRAMI CIECZY I TEMPERATURĄ POCZĄTKU KRYSTALIZACJI DLA AMORFICZNYCH STOPÓW NA BAZIE Al

Amorphous alloys or metallic glasses have attracted significant interest in the materials science and engineering communities due to their unique physical, mechanical, and chemical properties. The viscous flow of amorphous alloys exhibiting high strain rate sensitivity and homogeneous deformation is considered to be an important characteristic in thermoplastic forming processes performed within the supercooled liquid region because it allows superplastic-like deformation behavior. Here, the correlation between the superheated liquid fragility, and the onset temperature of crystallization for Al-based alloys, is investigated. The activation energy for viscous flow of the liquid is also investigated. There is a negative correlation between the parameter of superheated liquid fragility and the onset temperature of crystallization in the same Al-based alloy system. The activation energy decreases as the onset temperature of crystallization increases. This indicates that the stability of a superheated liquid can affect the thermal stability of the amorphous alloy. It also means that a liquid with a large superheated liquid fragility, when rapidly solidified, forms an amorphous alloy with a low thermal stability.

Keywords: Superheated liquid fragility, Onset temperature of crystallization, Thermal stability

1. Introduction

Amorphous alloys or metallic glasses have attracted significant interest in the materials science and engineering communities due to their unique physical, mechanical, and chemical properties [1-3]. The viscous flow of amorphous alloys exhibiting high strain rate sensitivity and homogeneous deformation is considered to be an important characteristic in thermoplastic forming processes performed within the supercooled liquid region because it allows superplastic-like deformation behavior.

Supercooled liquid fragility (SCLF), proposed by Angell [4], is an important parameter in the study of amorphous alloys, and numerous investigations have focused on fragility. It has been proposed that there is an approximately linear correlation between the SCLF parameter (m) and the glass transition temperature Tg [5, 6]. In general, m can be estimated after the metallic glass has been produced.

Bian et al. [7] proposed a new concept: superheated liquid fragility (SHLF) designated (M), which is based on the variation rate of viscosity of superheated liquids, and reflects how difficult the variation of structure is, near the liquidus temperature (Tl). Compared with m, the parameter M can be estimated more easily because it can be measured before the amorphous alloys are prepared. However, there have been few investigations of M until now. Therefore, it is necessary to carry out extensive research on the SHLF parameter M.

It is well known that thermal stability is an important feature of amorphous alloys; hence this feature has been widely investigated since the development of amorphous alloys. Thermal stability is usually characterized by the glass transition temperature Tg or onset temperature of crystallization Tx, which can be measured by the differential scanning calorimeter (DSC) [8-10]. In previous investigations, the relationship between SCLF and thermal stability (Tg) has been built up [5, 6], and a correlation between SCLF and SHLF was also found [11]. Hence, there should be a correlation between the thermal stability of prepared amorphous alloys, and the SHLF parameter M, which can give further insight into the nature of the glass formation, and help us understand genetic behaviors during the quenching process.

In this paper, the reference data of M for seven Al-based alloy systems are compiled. The correlation of the superheated liquid fragility, the activation energy for viscous flow, and the onset crystallization temperature are analyzed and discussed.

2. Theory and analysis

Recently, the definition and experimental determination of the glass transition temperature have been reviewed in de-

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tail by Mazurin [12]. He explained that the glass transition temperature is a specific temperature in the glass transition range. A cooled metastable melt transformed gradually into a vitreous material within this range, and its structure remained unchanged during further cooling. For an alloy which has no obvious glass transition temperature, it can be replaced by the onset temperature of crystallization (Tx) [13, 14]. The correlation between the SHLF parameter M and the onset temperature of crystallization will be discussed below.

Qin et al. [5] investigated the correlations between the SCLF parameter m and Tg in polymers, small molecule organics, hydrogen bonding organics, inorganics, ionic, and metallic glasses. They found that m increased nearly linearly with the increase of Tg in bulk metallic glasses. Additionally, Qiao et al. [6] also found that the values of the fragility parameter m increased with Tg for bulk metallic glasses, so the correlation between m and Tg can be expressed by the following equation:

$$m \propto Tg. \tag{1}$$

A supercooled liquid is a kind of intermediate matter between superheated liquid and amorphous alloys. The study of Novikov et al. [15] indicates that SCLF is not only closely related with the amorphous state, but also associated with the superheated melt. In our previous study [11], it was found that the SCLF parameter was proportional to the product of the reduced glass transition temperature Tg/TL, and reciprocal of the parameter of superheated liquid fragility 1/M, in several glass-forming alloys. The correlation can be described as follows:

$$m \propto (Tg/TL) \times (1/M). \tag{2}$$

The SHLF has a correlation with the SCLF, while the SCLF has a positive correlation with the glass transition temperature. Hence, we can use the dynamic behavior of superheated liquids to study the thermal stability of amorphous alloys before the amorphous alloys are produced. If so, an alloy which has low glass-forming ability can also be investigated by the dynamic behavior of superheated liquid. Combining Eqs. (1) and (2), we can conclude that there should be a correlation between the superheated liquid fragility and glass transition temperature.

The reference data about activation energy for viscous flow E, the onset temperature of crystallization Tx, and the parameter of superheated liquid fragility M, of Al-based and Pr-based amorphous alloys, are shown in Table 1. As there is no obvious glass transition temperature in Al-based amorphous alloys, in the absence of reliable data for Tg, we used the onset temperature of crystallization Tx as a substitute for Tg, an action that has proven feasible in earlier work [12, 13].

3. Results and discussion

Viscosity of alloy melts varies as a function of the temperature during the cooling process and the activation energy for viscous flow E is related to the motion of fluid units [21]. For the superheated liquids without structural transformation, the activation energy is constant, which indicates the stability of the superheated melt [22]. The onset temperature of crystallization Tx reflects the thermal stability of an amorphous alloy. The reference data of E and Tx were analyzed in this study. Fig. 1 shows the correlations between Tx and E of seven kinds of Al-based alloy systems. It can be seen that there is a negative linear correlation between Tx and E in each alloy system. E of the liquid for an alloy is small, Tx of this alloy is large in the same Al-based alloys system. From this analysis, although we did not analyze quantitatively because there are large scatterings in data depending on alloys, we could see clear trends between E and Tx and between M and E (see Fig. 2).

TABLE 1

Activation energy for viscous flow (E), onset temperature of crystallization (Tx), and fragility of superheated liquid (M) of Al-based and Pr-based amorphous alloys

Alloy system	Alloy	T_x (K)	M	E(kJ/mol)	Ref.
Al-RE	$Al_{90}Ce_{10}$	480	1.1440	12.19	[16]
	$Al_{92}Ce_{8}$	455	1.2122	12.36	[16]
	$Al_{90}Pr_{10}$	470	1.2073	12.72	[16]
	$Al_{90}Nd_{10}$	485	1.0561	11.24	[16]
Al-Yb	$Al_{89}Yb_{11}$	446	0.9849	8.88	[17]
	$Al_{90}Yb_{10}$	435	1.0432	9.30	[17]
	$Al_{91}Yb_{9}$	433	1.1271	10.01	[17]
Al-Ni-Nd	$Al_{84}Ni_{10}Nd_{6}$	544	1.3561	12.34	[18]
	$Al_{87}Ni_{8}Nd_{5}$	477	1.5636	14.31	[18]
	$Al_{87}Ni_{9}Nd_{4}$	460	1.7236	15.61	[18]
	$Al_{88}Ni_{10}Nd_{2}$	378	2.1502	19.48	[18]
	$Al_{84}Ni_{8}Nd_{8}$	571	1.6077	15.97	[18]
	$Al_{86}Ni_{4}Nd_{10}$	561	1.6624	16.52	[18]
Al-Ni-Yb	$Al_{90}Ni_{5}Yb_{5}$	584	1.0729	8.19	[17]
	$Al_{91}Ni_{4}Yb_{5}$	565	1.3970	10.69	[17]
	$Al_{87}Ni_{4}Yb_{9}$	501	1.7487	13.35	[17]
Al-Ni-Pr-(Cu/Si)	$Al_{84}Ni_{10}Pr_{6}$	554	1.0850	10.81	[19]
	$Al_{85}Ni_{10}Pr_{5}$	550	1.2025	11.97	[19]
	$Al_{85}Ni_{10}Pr_{3}Cu_{2}$	465	1.3572	12.45	[19]
	$Al_{87}Ni_{10}Pr_{3}$	452	1.4063	13.02	[19]
	$Al_{85}Ni_{10}Pr_{3}Si_{2}$	435	1.6044	14.99	[19]
Al-Co-Ce	$Al_{87}Co_{4}Ce_{9}$	573	1.1555	10.61	[7]
	$Al_{87}Co_{6}Ce_{7}$	562	1.2521	11.55	[7]
	$Al_{87}Co_{8}Ce_{5}$	558	1.3626	13.25	[7]
	$Al_{85}Co_{10}Ce_{5}$	562	1.5312	15.31	[7]
	$Al_{90}Co_{5}Ce_{5}$	481	1.5644	14.45	[7]
Al-Ni-Ce-(RE)	$Al_{84}Ni_{10}Ce_{3}La_{3}$	566	1.02	9.09	[20]
	$Al_{84}Ni_{10}Ce_{3}Pr_{3}$	555	1.046	10.11	[20]
	$Al_{84}Ni_{10}Ce_{3}Nd_{3}$	567	1.037	10.43	[20]
	$Al_{84}Ni_{10}Ce_{3}Gd_{3}$	561	1.05	10.73	[20]

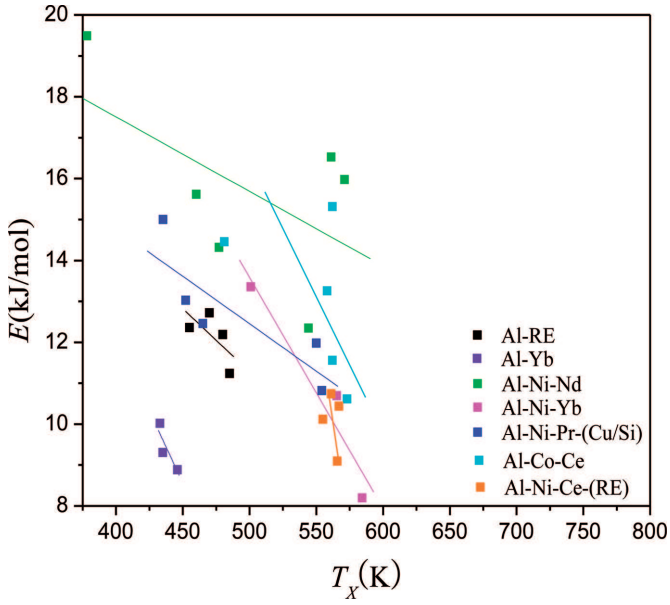

Fig. 1. Sh Correlations between Tx and E taken from seven kinds of Al-based alloy systems in the references [7, 16-20]

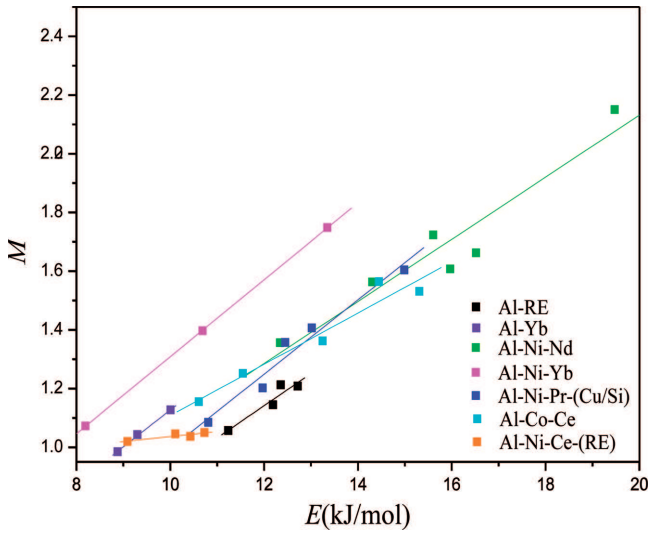

Fig. 2. Correlations between M and E of seven kinds of alloy systems in the references [7, 16-20]

The SHLF is characterized by the temperature dependence of the viscosity, scaled by the viscosity near the liquidus temperature, and reflects how difficult the variation of structure is, near the liquidus temperature. The parameter of SHLF indicates the stability of superheated melts around Tg. The compositions of amorphous alloys almost are eutectic, and the liquidus temperatures (Tl) are near the eutectic temperatures. Therefore, there is a positive linear correlation between M and E from the definition of M [22]. It can be seen that there is a positive linear correlation between M and E in the same Al-based alloy system, as shown in Fig. 2.

Figure 3 shows the correlations between M and Tx of seven kinds of alloy Al-based systems. It is easy to notice that M decreases with the increase of Tx in the same Al-based alloy system, as demonstrated in Fig. 3. Thus, it can be concluded that a negative correlation between M and Tx exists in the same Al-based alloy system, which is described by:

$$M \propto Tx. \tag{3}$$

Since the parameter of SHLF and the onset temperature of crystallization indicate the stability of superheated melt and the thermal stability of an amorphous alloy, respectively, the negative correlation between them builds up the relationship of the thermal stabilities between superheated liquids and amorphous solids.

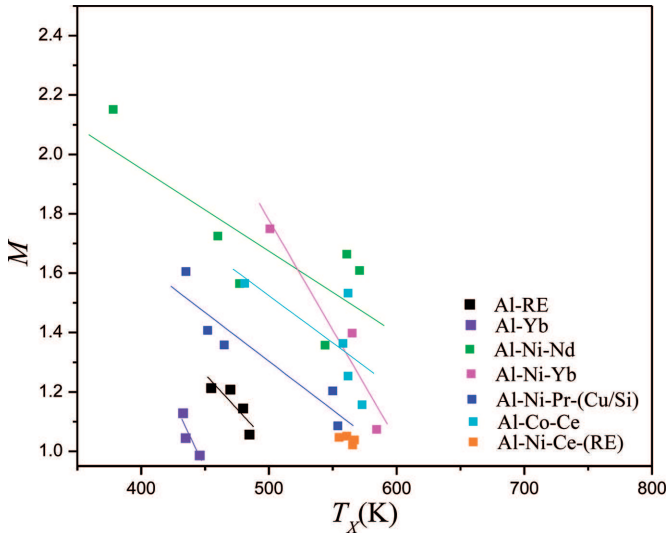

Fig. 3. Correlations between M and Tx of seven kinds of alloy systems in the references [7, 16-20]

Generally, amorphous alloys are prepared using the method of rapid solidification [23-27], and glass formation is a competition process between the liquid phase and the crystalline phases [28]. During the process, the melt can retain the metastable structures as in liquid, due to rapid solidification, and form the so-called disordered glassy state [29]. Thus, the process will be influenced by the stability of melt of the superheated melt. The melt with a small M means that the melt has good stability approaching Tl, and it is difficult for the structural transformation to happen in the melt. Moreover, Tx is an intrinsic temperature and the thermal stability of amorphous alloy can be characterized by it. An alloy with a low Tx has a low thermal stability of the amorphous solids. The negative correlation between M and Tx indicates that the stability of superheated melt will affect the thermal stability of the prepared amorphous alloy, and the melt with a small M is rapidly solidified to form an amorphous alloy which exhibits a high thermal stability.

4. Conclusions

The correlations among the activation energy for viscous flow of the liquids, the superheated liquid fragility, and the onset temperature of crystallization were investigated based on Al-based reference data. A negative correlation between the parameter of superheated liquid fragility and the onset temperature of crystallization was found in the same Al-based alloy system. A negative correlation was also found between the activation energy and the onset temperature of crystallization. This indicates that the stability of a superheated liquid can affect the thermal stability of the corresponding amorphous alloy and the liquid. Materials of the same alloys with a large

M or E are rapidly solidified to form amorphous alloys and have a low thermal stability.

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