An empirical criterion for predicting the glass-forming ability of amorphous alloys based on electrical transport properties

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ABSTRACT

Based on the Anderson's theory and Mott–CFO model for the electrical transport properties of disordered materials, an empirical criterion has been proposed for predicting the glass-forming ability (GFA) of amorphous alloys, which is termed as the relative electrical resistivity difference between the amorphous and fully crystallized states at room temperature (RT), i.e., $\Delta\rho = (\rho_{amor}^{RT} - \rho_{crys}^{RT})/\rho_{crys}^{RT}$, ρ_{amor}^{RT} and ρ_{crys}^{RT} denote the room-temperature electrical resistivities of an amorphous alloy and its corresponding crystal, respectively. A higher $\Delta\rho$ value of an alloy always correlates with a better GFA, which has been unambiguously confirmed by a large number of results in the Cu–Zr–Al–Ag, La–Ce–Al–Co, and Fe–Mo–Y–B alloy systems. Compared with the widely used criteria the reduced glass transition temperature T_{rg}, the supercooled liquid range ΔT_x, and the parameter γ, in which the glass transition temperature T_g is necessary and its determination is sometimes arbitrary with inaccuracy for some amorphous alloys, $\Delta\rho$ can be quite easily and more exactly obtained, and is more consistent with the GFA. The empirical criterion is very useful especially for optimizing the compositions and pinpointing the best glass former with less cost in a given system.

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1. Introduction

Since the discovery of the Au–Si binary metallic glass in 1960 [1], various empirical parameters have been proposed to assess the glass-forming ability (GFA) of metallic glasses and were expected to serve as guidelines for designing and developing new metallic glasses. Among these GFA indicators, the reduced glass transition temperature T_{rg} ($= T_g/T_l$) [2], the supercooled liquid range ΔT_x ($= T_x - T_g$) [3], and the parameter γ ($= T_x/T_g + T_l$) [4] (T_g, T_x, and T_l denote the glass transition temperature, the onset crystallization temperature, and the liquidus temperature, respectively) are the most widely used. However, accumulated data show that they fail to predict the GFA in some cases [5–7]. Moreover, in the often-cited criteria T_{rg}, ΔT_x, and γ, T_g is indispensable and its determination is sometimes difficult and arbitrary without veracity for some metallic glasses, which reduces the feasibility and accuracy of these criteria.

From the viewpoint of physical metallurgy, the critical cooling rate R_c is the most direct GFA indicator. However, it is hard to be measured precisely in the actual cooling process. Another slightly less direct parameter is the maximum diameter D_{max} of a rod-like metallic glass that can be cast into fully amorphous structure. Although D_{max} is easier to be obtained than R_c, tedious experiments are inevitable to determine D_{max} for different compositions in an alloy system. In a word, the

aforementioned criteria all have some limitations more or less, therefore it is quite essential to look for another relatively universal criterion being able to be quantified easily to estimate the GFA of metallic glasses.

Previous studies on understanding the GFA mainly focused on atomic structures and related properties. It was lack of effective efforts to understand the GFA from electronic aspects and electronic transport properties. Recently, scientists have realized that there may be some relationships between the electronic structures or electrical transport properties and GFA of metallic glasses [8,9]. The excellent GFA of the $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ metallic glass is correlated with the decrease of the density of state (DOS) at the Fermi energy E_F, $N(E_F)$ [8]. Dong et al. [10] investigated the influence of the free electrons per atom e/a on the GFA of metallic glasses. Therefore, it is believed that exploring the electronic structures and electrical transport properties of glassy alloys will be helpful for better understanding the GFA.

Based on the Anderson's theory and Mott–CFO model for the electrical transport properties of disordered materials, the present paper will attempt to put forward an empirical criterion for predicting the GFA of metallic glasses. This criterion has been vindicated by lots of experimental results for the alloy systems of Cu–Zr–Al–Ag, La–Ce–Al–Co, and Fe–Mo–Y–B.

2. Derivation of the empirical criterion

Metallic glasses are disordered materials without long-range order as compared to crystals. Anderson [11] divided the electronic states of

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a disordered system into the extended and localized states. The mean free path of the electrons in the extended state is larger than interatomic distance, while the electrons in the localized state are just limited within certain local regions. Based on the Anderson's theory, Mott–Cohen–Fritzsche–Ovshinsky (Mott–CFO) model [12,13] was developed. The energy eigenvalues are grouped in bands. Inside each band there exist critical energies E_c and E_c' (called mobility edges) which separate electron states into different natures. The states between E_c and E_c' are extended, while those in the tails of the density of states are localized. With the disordered degree increasing, the mobility edges move towards the center of the band, and more electrons are refined in the localized states. Meanwhile, the activation energy for the hopping of electrons from the localized states to the extended states increases. The extended-state electrons give the main contribution to the electrical conductivity σ ($\sigma = 1/\rho$, the reciprocal of the electrical resistivity ρ), whereas the contribution to the electrical conductivity coming from the localized-state electrons can be negligible unless activated to the extended states [14].

In a crystalline metal, the E_F falls within a band. The electron wave functions are extended-state Bloch functions, and in a partly filled band these plane-wave-like states give rise to the large electrical conductivity. But the conduction of amorphous alloys occurs via the relatively fewer extended-state electrons and is limited by disorder-induced scattering processes.

The electrical resistivity of amorphous alloys is often explained in terms of the Ziman theory. The Ziman theory, originally used to describe the electrical transport properties of liquid simple metals [15], is a nearly free electron theory in which the current is carried solely by an unhybridized sp band and the scattering is calculated by use of an appropriate pseudopotential. Evans et al. [16] extended this to apply to liquid transition metals by replacing the pseudopotential by a single-site, on-shell t matrix $t(q, E_F)$. This leads to the so-called extended Ziman formula. Meisel and Cote [17] pointed out that this extension could be applied to amorphous alloys as well.

Based on the simple assumption that the atoms in a liquid metal vibrate at about slowly-varying mean positions, Mott [18] has proposed an equation for the ratio of liquid/solid conductivity $\sigma_{e,l}/\sigma_{e,s}$ at a metal's melting point T_m, which is expressed as:

$$\sigma_{e,l}/\sigma_{e,s} = \exp\left(-80\Delta_s^l H_m/T_m\right) \tag{1}$$

where $\Delta_s^l H_m$ is the enthalpy of melting. Eq. (1) can be simplified to the following expression:

$$\rho_{e,l}/\rho_{e,s} = \exp\left(80\Delta_s^l S_m\right) \tag{2}$$

where $\Delta_s^l S_m$ is the entropy of melting. In spite of his simple treatment, the agreement obtained between theory and experiment for normal metals is surprisingly good. Based on the modern theory of electron transport, Ziman [15] has provided a reasonable interpretation for the ratio $\rho_{e,l}/\rho_{e,s}$ ($= \sigma_{e,s}/\sigma_{e,l}$), which is not covered in details here.

Entropy is an important variable which describes the randomness of a complex system. The larger the entropy of melting $\Delta_s^l S_m$, the more the disorder of the liquid. According to Eq. (2), a higher degree of disorder means a larger $\rho_{e,l}/\rho_{e,s}$. Hence, the value $\rho_{e,l}/\rho_{e,s}$ can be used as a measure of the disordered degree of a liquid metallic system. The larger the value $\rho_{e,l}/\rho_{e,s}$, the more disordered the melt, and it will be more difficult to transform into a crystal during the liquid cooling process because of the nucleation difficulty, and the disordered structure tends to be easily retained, often referred to as the "confusion principle" [19].

Metallic glasses are essentially "frozen liquids", and to a large extent an amorphous solid inherits the structure from its original liquid metal, which is demonstrated by the sketch of the resistivity-versus-temperature characteristics of the amorphous and crystalline $Pd_{0.8}Si_{0.2}$ [20]. As Fig. 1 shows, the amorphous $Pd_{0.8}Si_{0.2}$ has much higher resistivity and much lower sensitivity to temperature than its crystal, which is

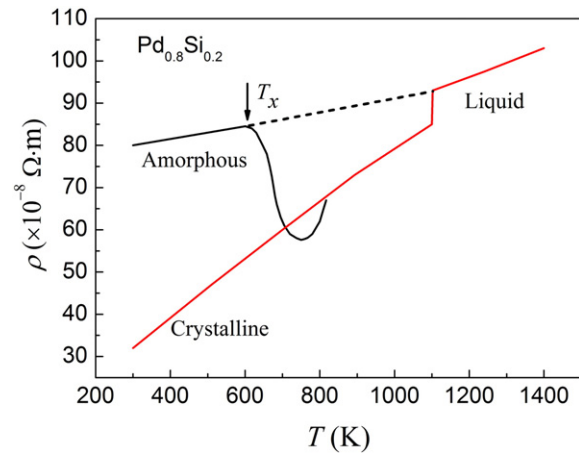**Fig. 1.** The sketch of the resistivity-versus-temperature characteristics of the amorphous metal $Pd_{0.8}Si_{0.2}$ and its crystalline form.

the intrinsic properties of an amorphous solid and can be understood in terms of the disorder inherent in the structure of an amorphous solid [20]. Further, there exists an interrelationship between the law of variation in electrical resistivity and the ordering degree [21].

From what has been discussed above, the value $\rho_{e,l}/\rho_{e,s}$ reflects the disordered degree of a liquid metallic system. However, it is hard to measure the liquid and solid resistivities at T_m, so the widespread use of $\rho_{e,l}/\rho_{e,s}$ for evaluating the disordered degree of a liquid metallic system is constrained in real practices. Due to much higher resistivity and much lower sensitivity to temperature of a metallic glass relative to its crystal, the ratio of the electrical resistivities of the amorphous and correspondingly fully crystallized states at room temperature (RT) $\rho_{amor}^{RT}/\rho_{crys}^{RT}$ is larger than $\rho_{e,l}/\rho_{e,s}$. An alloy with a larger $\rho_{e,l}/\rho_{e,s}$ will have an even larger $\rho_{amor}^{RT}/\rho_{crys}^{RT}$. So, in a sense, $\rho_{amor}^{RT}/\rho_{crys}^{RT}$ can more pronouncedly and sensitively disclose the disordered degree of a liquid metallic system than $\rho_{e,l}/\rho_{e,s}$, besides which, $\rho_{amor}^{RT}/\rho_{crys}^{RT}$ reflects the structure difference between an amorphous alloy and its corresponding crystal.

For a given alloy, the room-temperature electrical resistivities of the amorphous ρ_{amor}^{RT} and fully crystallized states ρ_{crys}^{RT} can be readily obtained. Here, $\Delta\rho$ is defined as the relative electrical resistivity difference at room temperature between two states, as shown in the following formula:

$$\Delta\rho = \left(\rho_{amor}^{RT} - \rho_{crys}^{RT}\right)/\rho_{crys}^{RT}. \tag{3}$$

According to the above discussion, $\Delta\rho$ can reliably and sensitively betoken the disordered degree of an original liquid and the structure difference between an amorphous alloy and its corresponding crystal, in spite of yielding no specific structural information. It can be logically deduced that the higher the value $\Delta\rho$ for an alloy, the larger the structure difference between an amorphous alloy and its corresponding crystal, the more the disorder of its liquid, the harder it is to crystallize the molten alloy in its solidification process because of the nucleation and growth difficulties, and the stronger the GFA. Thereby, $\Delta\rho$ is put forward for evaluating the GFA of metallic glasses. The higher the value $\Delta\rho$, the stronger the GFA will be.

It is worth mentioning that there are other factors influencing the electrical transport properties besides the number of the extended-state electrons and the disordered degree. For instance the amorphous alloy state (such as structural relaxation and metallic glasses containing few nano-crystalline particles) will affect the electrical resistivity of metallic glasses. The electrical resistivity of the crystallized alloys will also change with the crystallized alloy state (such as the grain size, crystal grain tropism, and defect). On the one hand, the amorphous and crystallized states are connected with the temperature–time history, on the