Journal of Alloys and Compounds xxx (2012) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Vitrification and devitrification processes in metallic glasses

D.V. Louzguine-Luzgin *

WPI Advanced Institute for Materials Research, Tohoku University, Aoba-Ku, Sendai 980-8577, Japan

ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Glass-transition
Vitrification
Devitrification
Crystallization
Metallic glasses

ABSTRACT

The phenomenon of vitrification on cooling, also called the glass-transition still remains not fully understood. Recent studies by different techniques were performed in order to shed light on this and on the converse phenomenon of devitrification. Devitrification may either lead to the formation of a supercooled liquid, a crystal(s) or a quasicrystal(s). The present paper is a review of recent findings on the processes of vitrification and devitrification in metallic glasses.

1. General introduction to metallic glasses (glassy alloys)

Glassy alloys (or metallic glasses) were first formed in an Au–Si alloy [1] by using a rapid solidification technique. Pd–Cu–Si and Pd–Ni–P system alloys were produced in a bulk form after flux treatment which helps to suppress heterogeneous nucleation and were considered as the laboratory curiosity at that time owing to their enormous cost compared to conventional engineering alloys [2,3]. Later, a large number of bulk glassy alloys defined as 3-dimensional massive glassy (amorphous) articles with a size of not less than 1 mm (by another definition $\geqslant$ 10 mm) in any dimension have been produced [4–6].

2. Formation of glassy phase

There are still several gaps in obtaining a clear picture of the glass-transition, especially in metallic liquids [7,8]. Recent studies were undertaken to shed more light on this issue.

The specific volume (V) of a liquid phase decreases faster (while its density (ρ) increases faster) with temperature than that of a competing crystal. According to several studies, the linearity of $d\rho/dT$ slope maintains not only in equilibrium but in the supercooled liquid region as well [9,10]. Fig. 1(a) shows a typical density versus temperature (T) diagram for pure Ni plotted according to Ref. [11]. By analogy with the well-known Kauzmann's entropy crisis [12,13] one can suggest that a liquid metal should not have a volume lower (or a higher density), at a given temperature, than its crystalline counterpart provided that it contracts upon solidification and there are no changes in the chemical bond character. Face-centered cubic (FCC) and hexagonal close packed (HCP) lattices are the densest packing structures for crystalline pure metals, and thus, a liquid or a glassy monoatomic phase should not become denser than them.

Fig. 1(a) suggests an ideal glass-transition temperature (T_g) of Ni to be higher than about 1000–1200 K depending on the thermal expansion coefficient of liquid Ni which is not very precisely defined. The insert shows the atomic structure of Ni cell obtained by the molecular dynamics (MD) simulation at 1000 K. Two radial distribution functions (RDF(R)) are shown in the insert of Fig. 1(b). The coordination numbers in the first coordination shell at 1800 and 1000 K are 11.23 and 11.86, respectively. The former value is typical for a liquid metal [14] while the later one likely represents a glass. An empirical criterion for the glass-transition based on the reduced radial distribution function or pair distribution function (PDF(R)) can be described by: $\Re = \mathrm{PDF(R)}_{min}/\mathrm{PDF(R)}_{max}$ where max and min indicate the first maximum and minimum of PDF(R), respectively, [15]. Using these functions the plot of $\Re$ versus temperature was created and is expressed in Fig. 1(c). An intersection point of two slopes indicates the glass-transition temperature of 1200 K.

The equi-volume (isochoric) temperature approach to determine the reduced glass-transition temperature (T_{rg}) shown in Fig. 1(a) and an ab initio molecular dynamics simulation [11] demonstrate that an ideal T_{rg} of pure Ni may be as high as ~0.6–0.7, which is an extremely high value for a pure metal. In general, bulk glassy alloys are formed at the compositions with high T_g/T_l (T_g glass-transition temperature, T_l liquidus temperature) ratio exceeding approximately 0.6 [16].

A few words must be said about the definition of T_g. The glass-transition phenomenon is characterized by the specific heat capacity (C_p) change and change in the volumetric thermal expansion coefficient as one can observe in Fig. 1(a). An arbitrary glass-transition point is defined as a temperature at which viscosity of

* Tel.: +81 22 217 5957; fax: +81 22 217 5956.
E-mail address: dml@wpi-aimr.tohoku.ac.jp

0925-8388/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2012.09.057

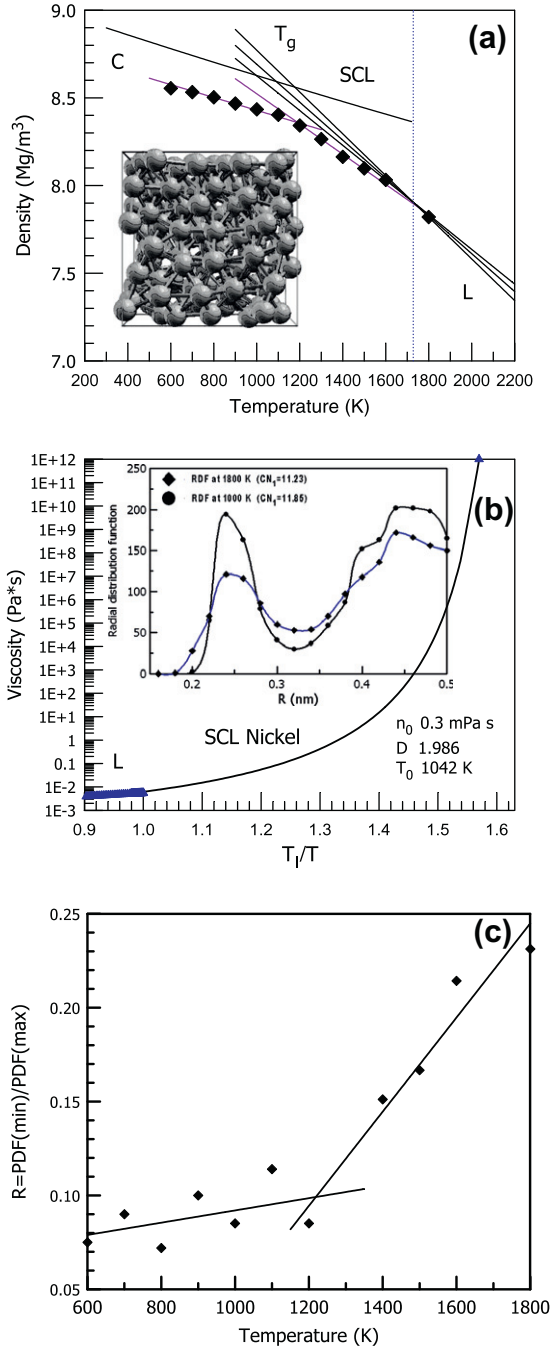

Fig. 1. (a) Solid lines – density versus temperature diagram for Ni according to literature data. Diamonds represent the results of ab initio MD simulation. Several plots for liquid Ni represent data from different literature sources. The insert – atomic structure of Ni cell obtained in an MD simulation at 1000 K. The dotted line represents the liquidus temperature. The data for (a) is taken from Ref. [11] with permission from AIP. (b) The viscosity of liquid Ni as a function of temperature fitted considering *Tg* of 1100 K. The insert – RDFs for liquid and glassy Ni at 1800 and 1000 K, respectively. (c) $\Re$. parameter versus temperature plot.

a liquid reaches 10^{12} Pa s on cooling, while the transition takes place in a temperature interval [17]. For some materials this value belongs to the glass-transition region defined by C_p measurement, but it is not the case for other materials [18]. In the present work the glass-transition region is related to the area of change in the thermal expansion coefficient from a relatively high value characteristic of a liquid phase to a relatively low value for a solid glassy phase as shown by the diamonds in Fig. 1(a). Such a change of the thermal expansion coefficient on glass-transition was clearly demonstrated in many works, see for example, Ref. [19].

The analysis of the thermal expansion curves allowed to derive a new parameter $\delta = \alpha_l * \rho_l (T_m - 298)/\Delta\rho_{s-l}$ [20,21] where α_l is the volumetric thermal expansion coefficient of the liquid alloy, ρ_l is the density of a liquid measured at a certain temperature, usually close to the melting temperature (T_m) and $\Delta\rho_{s-l}$ is the density difference between the solid and liquid phases. The influence of thermal expansion coefficient of a solid α_s is much smaller than that of the liquid and is excluded for convenience. The δ criterion indicates how fast a metal/alloy can reach the glass-transition temperature, while it does not provide information on the stability of the resulted glass against crystallization.

Another important parameter is the stability of the supercooled liquid or metallic glass against crystallization. The correlation observed between the critical cooling rate for glass formation R_c, liquid fragility index (m), and T_{rg} [22] explains the low glass-forming ability (GFA) of a pure metal even if it has a high T_g. This is intuitively clear because according to the Angell plot [23] strong liquids, as a rule, have a higher viscosity above T_g, and thus, should be less prone to crystallization for kinetic reasons, which, however, does not include the thermodynamic aspects related to the driving force in terms of the Gibbs free energy difference. If we assume that the viscosity of a liquid should rise steeply when the liquid Ni volume approaches that of the FCC crystal, take 1100 K as T_g for Ni when the viscosity reaches about 10^{12} Pa s and fit the viscosity of the equilibrium liquid Ni together with the point at T_g by VFT equation ($\eta = \eta_0 exp[D*T_0/(T-T_0)]$) [23,24] (where η_0, D and T_0 are the fitting parameters), we obtain the fragility parameter $D = 2$ (Fig. 1(b)). Thus, liquid Ni is more fragile than any metallic glass-former known so far, as according to [25], most fragile metallic glasses have $D = 6$. It indicates that pure Ni, as a very fragile liquid, should be very unstable against crystallization, though its GFA is higher than that of Cu (Ni has a lower critical cooling rate), which has a lower δ parameter [20].

The above-mentioned factors limit the applicability of the T_{rg} concept to metallic glasses, and indicate that a parameter combining both T_{rg} and stability of the supercooled liquid against crystallization linked to its fragility must be taken into consideration.

Nevertheless, as can be seen from Table 1, metals, which were found to vitrify easily [26], i.e. Ni, Fe, Co, V have a relatively large δ parameter and a large activation energy for the temperature dependence of viscosity (E) above 40 kJ/mol in the equilibrium liquid state. Most of the data is from Ref. [10].

It is also interesting to note that T_g predicted by the point of equal volume for liquid and crystalline Fe of about 1200 K [20] is very close to that found in the MD simulation [27] by monitoring the dependence of the size of the largest cluster formed by mutually penetrating and contacting icosahedrons.

The width of the supercooled liquid region (ΔT_x) (defined as $T_x - T_g$ where T_x is the onset crystallization temperature) as indicator of the stability of the supercooled liquid against crystallization also correlates quite well with the glass-forming ability [28]. There is also a good correlation between the alloy system complexity, critical diameter of the sample and ΔT_x [29]. The parameter $\gamma = T_x/(T_g + T_l)$ [30] takes into account both T_{rg} and ΔT_x criteria.

One should also mention a topological criterion λ [31], the thermal conductivity of a molten alloy λ_l [32], electronegativity difference between the constituent elements ΔEN [33], σ [34] and many other parameters [35]. For example, the addition of Zr or Sc substituting for Y reduces the effective ΔEN values among the constituent elements and increases ΔT_x of an Al–Y–Ni–Co alloy [36]. The importance of an efficient atomic packing for the formation of metallic glasses was shown recently [37,38]. However, a comparative study of the GFAs of the binary Si–Ni and Ge–Ni as well as ternary Si–Ni–Nd and Ge–Ni–Nd alloys showed that the principles for