Application of the hole theory of liquids to the stability of some metallic glasses

Recently, it was shown [1] that the hole or free volume theory of liquids is capable of explaining the bahaviour of metallic glasses. In this short communication, we will show an equation giving the hole formation energy as a function of glass transition temperature, T_g, valid for some metallic glasses, based on the hole theory of liquids and assuming the iso-free volume at T_g; furthermore, we will briefly discuss the stability of some metallic glasses. T_g is experimentally determined as the temperature where specific heat exhibits an abrupt rise and/or as the temperature where the thermogram shows an endothermic change of slope in differential scanning calorimetry.

Assuming that a liquid has a quasi-crystalline lattice, empty "sites" in the liquid are called holes, and they have the same characteristics as vacancies in crystalline solids. The total volume, V_T, due to holes is given by [2]:

$$V_T = V_0 + N'\Delta v, \qquad (1)$$

where Δv denotes the smallest volume of a hole and is approximated to the "free volume", representing the unfilled space between atoms in the liquid, V_0 is the hypothetical volume at $T = 0\,\mathrm{K}$ in the crystalline state, and N' is the number of holes in a gram-molecule of liquid.

The number of holes at a particular temperature T is statistically given by: $N' = N \exp(-U/kT)$, where U is the energy for formation of "hole", N the number of atoms in the liquid and k is the Boltzmann constant. Thus, Equation 1 reduces to:

$$V_T = V_0 + N \exp(-U/kT)\Delta v. \qquad (2)$$

When the liquid is quenched at an appropriate rate to transform into the galssy state, a particular number of holes is "frozen-in" at T_g.

The "relative free volume", f_T, is defined as:

$$f_T = (V_T - V_0)/V_0, \qquad (3)$$

therefore, the "hypothesis" of an iso-free volume state [3], i.e. $f_T = \text{constant}$ ($\cong 0.025$) at all temperatures below T_g, leads to a proportional relationship between U and T_g:

$$U = (3.688 + \ln N\Delta v/V_0)RT_g, \quad (\mathrm{cal\,mol^{-1}}). \qquad (4)$$

The validity of the iso-free volume hypothesis has widely been accepted for polymeric and inorganic materials [3, 4].

Fig. 1 shows the plot of the hole formation energy U against the glass transition temperature T_g, depending on the value of $N\Delta v/V_0$ which represents the product of the relative free volume, f_T, and $\exp(U/kT)$; the figure also shows the experimentally determined values of U and T_g for palladium-, platinium- and gold-based metallic alloys by Ramachandrarao *et al.* [1]. They determined U from the plot of $\Delta\alpha \cdot T_g$ against U/RT_g, where $\Delta\alpha$ represents the change in the coefficient of thermal expansion α at T_g for the glasses, and

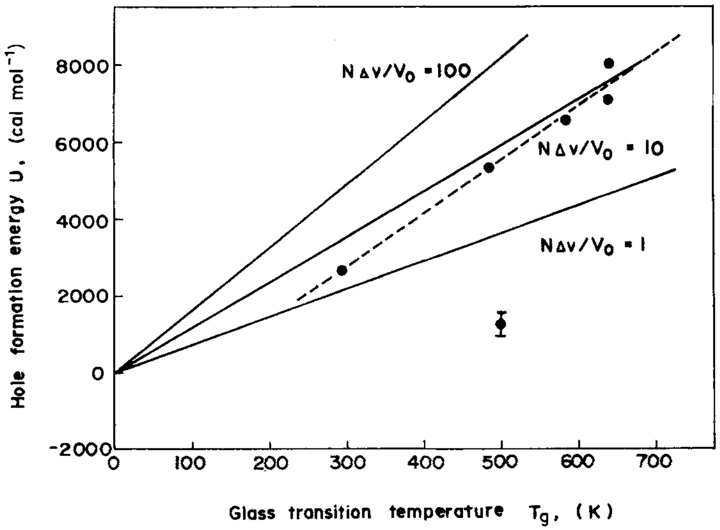

Figure 1 Plot of the hole formation energy, U, against the glass transition temperature, T_g, depending on the value of $N\Delta v/V_0$; the figure also indicates the experimentally determined values of U and T_g for palladium-, platinium- and gold-based metallic alloys by Ramachandrarao *et al.* [1].

0022–2461/80/071864–02$02.20/0

R is the gas constant. Their experimental results are described by:

$$U = 13.83T_g - 1400(\pm 290)\ (\text{cal mol}^{-1}). \qquad (5)$$

From the figure, it seems that the value of $N\Delta v/V_0$ is in the range of ~ 10 for the glasses. Furthermore, simple comparison of Equation 4 with Equation 5 gives the following:

$$N\Delta v/V_0 = \exp\,[3.275 - 1400/RT_g];$$

$$N\Delta v/V_0 = \exp\,[6.963U/(U+1400) - 3.688].$$

Thus, the value of $N\Delta v/V_0$ increases almost linearly in the observed T_g range for the glasses with increasing T_g and/or U as indicated in Fig. 2, suggesting that the glass with a high value of T_g and/or U involves the large free volume.

It was found previously [5] that T_g decreases linearly with the volume ratio v_a/v_h for some metallic glasses (v_a: the volume of an atom, v_h: the volume of a hole and approximated equal Δv), where the value of v_a/v_h was estimated from the experimentally observed changes in specific heats at T_g for the metallic glasses. Fig. 2 is considered to be consistent with the previous results and also suggests that T_g (a parameter to characterize the stability of a glass) is closely related to the hole volume of the glass.

It is deduced that the liquid with the larger hole volume, smaller molar volume and smaller number of holes at a fixed quenching temperature, leads to the formation of the metallic glass with a higher glass transition temperature, T_g, i.e. higher stability, by splat-cooling methods with an appropriate cooling rate. This might suggest an interesting analogy with the fact that the pre-precipitation and subsequent ageing processes of super-saturated solid solution are predominantly controlled by quenched-in vacancy concentrations and grouping of several vacancies.

The higher hole formation energy suggests a transport process with a higher activation energy (smaller effective diffusion coefficients), if assuming the Stokes–Einstein relationship between the viscosity η and the diffusion constant D in metallic glasses: $\eta \propto 1/D$, because the viscosity varies in a direct way with the energy for hole formation [1].

It is indicated [6] that some sort of chemical ordering between the nickel and boron atoms that decreases the viscosity and therefore the energy for hole formation, reduces the glass transition temperature and the temperature for crystallization in amorphous $(\text{Fe}_{1-x}\text{Ni}_x)_{80}\text{B}_{20}$ alloys. It is also known that the density of metallic glasses increases by the decrease in volume during crystallization which appears as a decrease in length [7]; this might reflect some sort of annihilation process of "frozen-in" holes during crystallization.

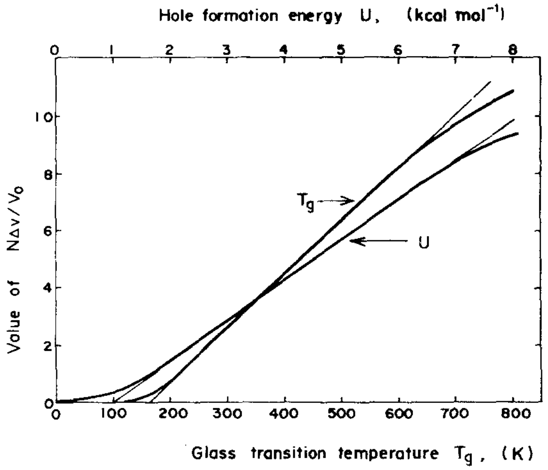

Figure 2 Plots of $N\Delta v/V_0$ against T_g and U, assuming the validity of Equation 5 for the metallic glasses.

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Received 17 October
and accepted 20 November 1979

T. HIRATA
National Research Institute for Metals,
3-12, 2-Chome,
Nakameguro,
Meguro-Ku,
Tokyo