ELSEVIER

Journal of Alloys and Compounds 434–435 (2007) 121–125

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

A glance on the glass-transition phenomenon from the viewpoint of devitrification

Dmitri V. Louzguine-Luzgin*, Akihisa Inoue

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Abstract

The formation of a supercooled liquid region and devitrification behaviour of metallic glasses on heating are discussed in relation with the glass-transition phenomenon observed using differential scanning and isothermal calorimetries as well as X-ray diffraction and transmission electron microscopy (TEM). One of the most clear sequences of the glassy ↔ supercooled liquid phase transition is the change of the devitrification behaviour and the kinetics of the devitrification reaction in Al-based and some other alloys after the transition from the glassy to the supercooled liquid state. The significant variation in the devitrification behaviour and thermodynamic parameters indicate the difference between the glassy and the supercooled liquid phases.

Keywords: Glassy alloy; Glass-transition; Supercooled liquid; Devitrification

1. Introduction and target setting

The glass-transition phenomenon in metallic glasses has been studied extensively since they were first fabricated [1–3]. Structurally, glassy and liquid states are quite similar but as compared to a glassy solid state, liquid has zero value static shear modulus. Several theories of glass-transition have been put forward [4,5] and one of the most successful explanation is the mode-coupling theory [6]. A thermodynamic aspect of the glass-transition process has been pointed out by Kauzmann [7]. However, an important question which is still not completely answered is: Do glassy and liquid phases belong to the same phase, just observed at different temperatures, or the liquid–glassy phase transformation and vice versa (called glass-transition) indeed does take place? Three kinds of approaches have been formulated ([4,8–10], for example, among the other sources):

1. Glassy phase is just a frozen liquid, and thus, glass-transition is a kinetic phenomenon and no thermodynamic phase transformation takes place.
2. Glass-transition may be a second-order transformation as follows from the shape of the curves for the thermodynamic parameters, for example; specific volume or enthalpy, which exhibit a continuity at the glass-transition temperature while their derivatives like $\partial V/\partial T$ or $\partial H/\partial T$ exhibit a discontinuity (in a certain approximation) at the glass-transition temperature.
3. Glass-transition may be a first-order transformation as follows from the free-volume model.

At the same time, the abrupt change of the thermodynamic parameters during a first-order transformation is not obviously necessary. For example, it is not the case if the local chemical composition changes upon phase transformation, or in the case of displacive transformation.

A large number of the recently collected experimental data motivated us to have a closer look at the glass-transition phenomenon in metallic glasses from the viewpoint of devitrification of the glassy phase on heating.

2. Experimental details

The experimental procedure can be obtained from any of our previous works devoted to devitrification of metallic glasses [11], for example; in details the ingots of Al- and Cu-based alloys were prepared by arc-melting mixtures of pure elements in an argon atmosphere. Cu-based alloys are bulk glass formers while Al-based ones can be produced only as melt-spun ribbons. From these ingots, ribbon samples were prepared by a melt spinning technique. The structure of the samples was examined by X-ray diffractometry with monochromatic Cu Kα and synchrotron radiation as well as transmission electron microscopy (TEM). The phase transformations on heating were studied by differential scanning

---

* Corresponding author. Tel.: +81 22 215 2592; fax: +81 22 215 2381.
E-mail address: dml@imr.tohoku.ac.jp (D.V. Louzguine-Luzgin).

0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.08.146

calorimetry (DSC) at a heating rate of 0.67 K/s and by differential isothermal calorimetry.

3. Glass-transition on cooling and heating in co-relation with devitrification behaviour

The slope of the enthalpy (H) of a liquid as a function of temperature curve, which is the specific heat capacity at constant pressure (C_p) per mol, changes in the certain temperature interval. The variation of the enthalpy on cooling is schematically shown in Fig. 1(a). The glass-transition on cooling takes place in the temperature range between the conditional beginning of glass-transition ($T_{\mathrm{bg}}^{\mathrm{C}}$) and the finish of glass-transition ($T_{\mathrm{fg}}^{\mathrm{C}}$) temperatures which can be treated as a glass-transition region. The intersection of the two slopes $\mathrm{d}H/\mathrm{d}T$ gives an intermediate point which is called a glass-transition temperature $T_{\mathrm{g}}^{\mathrm{C}}$ attained at a certain cooling rate as glass-transition temperature is cooling rate dependent.

The glass-transition on heating (symbol (H)) takes place in the temperature range between the conditional beginning of glass → supercooled liquid transition ($T_{\mathrm{bg}}^{\mathrm{H}}$) and finish of glass-transition ($T_{\mathrm{fg}}^{\mathrm{H}}$) temperatures (area of change of slope) as monitored by the deflection of the DSC curve in Fig. 1(b) on heating. As it is difficult to detect the deflection point related to the beginning of change of slope this temperatures ($T_{\mathrm{bg}}^{\mathrm{H}}$) and ($T_{\mathrm{fg}}^{\mathrm{H}}$) are called conditional. As shown in the insert there is also a slight overshoot in C_p because the heating rate is much lower than the cooling rate upon the rapid solidification. The formation of a supercooled liquid is clearly observed in Fig. 1(b). On heating this state exists between $T_{\mathrm{fg}}^{\mathrm{H}}$ and devitrification temperature known as T_x. $T_{\mathrm{bg}}^{\mathrm{H}}$ is often treated as the glass-transition temperature in the literature. The $Cu_{55}Hf_{25}Ti_{15}Pd_5$ alloy (here and elsewhere throughout the paper all alloy compositions are given in nominal at.%) was taken for representation in Fig. 1(b) and (c) as it shows quite a large supercooled liquid region.

The glass-transition phenomenon was also monitored on heating by XRD measurements. Q is wave vector corresponding to the center of mass of the first diffraction maximum at room temperature (Q_0) and current temperature (Q_{T}) measured after completion of the structural relaxation process on heating (the sample was preliminary heated up to $T_{\mathrm{bg}}^{\mathrm{H}}$ to complete the structural relaxation) as is expressed in Fig. 1(c). It is postulated that $\Delta(Q_0/Q_{\mathrm{T}})$ scales with the linear size changes $\Delta(L_{\mathrm{T}}/L_0)$ provided that the interatomic interactions on thermal expansion are elastic [12]. The linear thermal expansion coefficient related to $\mathrm{d}(Q_0/Q_{\mathrm{T}})/\mathrm{d}T$ derivative changes within the glass-transition region from 1.4×10^{-5} to $4 \times 10^{-5}\,\mathrm{K}^{-1}$. These values correspond to that of the solid [13] and liquid metals/alloys [14], respectively.

As it was shown in the previous works the supercooled liquid has the physical properties different from that of the glassy phase [15]. This results in a difference in the devitrification reaction proceeded from a glassy and a supercooled liquid phase in several glass-forming alloys provided that the nucleation and growth transformation mechanism is observed. One of the most clear consequences of the glassy ↔ supercooled liquid phase transition is the change of the devitrification behaviour and the kinetics of the devitrification reaction in Al–Y–Nd–Ni–Co and Al–Y–Ni–Co glassy alloys on crystallization from the glassy and the supercooled liquid state [16,17]. Table 1 shows the influence of the transformation temperature in the isothermal mode on the type of the devitrification (crystallization) reaction. The samples were annealed isothermally at the temperature around

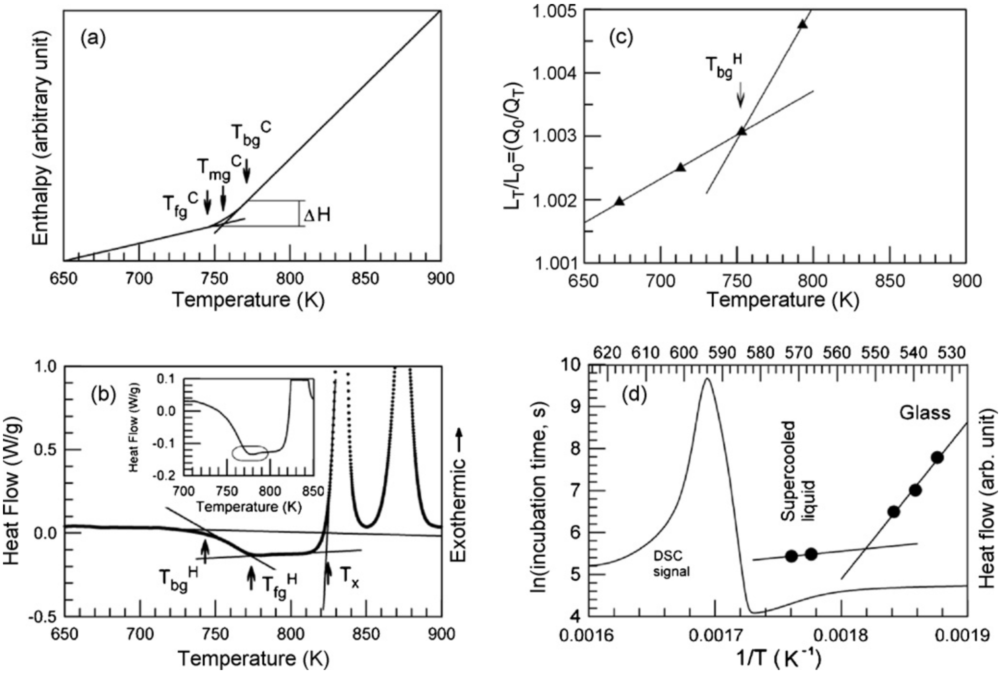

Fig. 1. (a) Specific heat H as a function of temperature (scheme). (b) DSC curve for $Cu_{55}Hf_{25}Ti_{15}Pd_5$ alloy and (c) the ration of X-ray diffraction peak positions Q_0/Q_{T} related to L_{T}/L_0 vs. temperature. (d) DSC trace and Arrhenius plot created using incubation time for phase transformation in $Al_{85}Ni_5Y_4Nd_4Co_2$ alloy.

Table 1
Devitrification of $Al_{85}Ni_5Y_4Nd_4Co_2$ alloy in the vicinity of glass-transition region

Temperature (K)	Features of transformation[a]	Phases	n[c]	$\tau_c - \tau_i$[d] (s)
533	Steady state nucleation interface-controlled growth	α-Al + IM[b]	4	4200–2400
538		α-Al + IM	4	2300–1100
543		α-Al + IM	4	1300–660
563	Non-steady state nucleation diffusion-controlled growth	α-Al + traces IM	3.1	300–240
568		α-Al	2.6	270–225

[a] The features of phase transformations have been taken from the earlier work [17].

[b] Intermetallic compound.

[c] Avrami exponent.

[d] Transformation time as a difference between the time of the completion of the reaction τ_c and the incubation period τ_i (corresponding to the smallest detectable fraction transformed).

T_{bg}^{H} (measured at 1.67 K/s) of 561 K [18]. The transition from the interface-controlled conjoint growth of α-Al and intermetallic compound (IM) to the diffusion-controlled growth of α-Al takes place within the glass-transition region (Fig. 1(d)). Such a behaviour was also observed in the $Al_{85}Ni_7Gd_8$ alloy [19]. It is also found that the complete transition from the formation of α-Al + intermetallic compound to α-Al in $Al_{85}Ni_7Gd_8$ takes place just below T_{fg}^{H} of about 543 K.

The reasonable linearity of the Avrami plot below T_{bg}^{H}, an exact value of the Avrami exponent of 4 and conjoint precipitation of two phases (α-Al + IM) (possibly eutectic-like) argued for the interface-controlled growth with steady state nucleation while the non-linearity of the Avrami plot above T_{bg}^{H} and the Avrami exponent of about 2.6 above T_{bg}^{H} argues for the diffusion-controlled growth at non-steady state nucleation of α-Al [18]. This result is in agreement with the conclusions made in a recent work [20] which indicates that transient non-steady state nucleation [21] is typical from the supercooled liquid above T_{fg}^{H} [22]. At the same time, it has been reported that Fe–Ni–B metallic glass exhibits polymorphous devitrification with a diffusion-controlled growth of $(Fe, Ni)_3B$ compound below T_{bg} while its nucleation and growth above the glass-transition region can be described by the viscose flow [23]. Such a behaviour has not been observed in the above-described Al–RE–TM alloys as they do not suffer polymorphous but eutectic-like transformation below T_{bg}^{H} and primary formation of α-Al above T_{fg}^{H}.

At the same time the amorphous Al–RE–Ni–Co (RE-rare earth) alloys which show no clear glass-transition on heating before devitrification exhibited the same devitrification products [16,17] at different temperatures in the isothermal mode and after continuous heating.

The above-mentioned may indicate that the devitrification products in such alloys inherit the local structure (short-range order) of the glassy (amorphous) solid phase while the glasses devitrifying from the supercooled liquid state may inherit a short-range order of the liquid [24]. The origin of such behaviour may also be connected with the difference in the structure, physical and thermal properties between the glassy phase and the supercooled liquid.

Thus, devitrification behavior of Al–RE–Ni–Co metallic glasses can be classified as follows: (1) If an alloy does not exhibit glass-transition on heating prior to devitrification (crystallization) and exhibits nucleation and growth transformation mechanism then it forms intermetallic compound(s) or IM + nanoscale α-Al. (2) If an alloy does not exhibit glass-transition on heating prior to devitrification and has pre-existing nuclei then it forms nanoscale primary α-Al. (3) If an alloy shows glass-transition on heating and exhibits nucleation and growth transformation mechanism then it forms nanoscale α-Al above T_g and IM + α-Al or IM below T_g.

4. Changes in the activation energies within the glass-transition region

The $Cu_{50}Zr_{30}Ti_{10}Ni_{10}$ alloy which shows formation of an equilibrium oC68 $(Cu, Ni)_{10}(Zr, Ti)_7$ solid solution phase upon devitrification [25] exhibits a completion of the transition to a liquid state at about 740 K (Fig. 2(a)). The isothermal calorimetry traces taken within the supercooled liquid region ($T_x - T_{bg}^{H}$), glass-transition region ($T_{bg}^{H} - T_{fg}^{H}$) and from the glassy phase shown, Fig. 2(b) was used to create an Arrhenius plot (Fig. 2(c)) for the logarithm of incubation time τ versus invert temperature according to the following equation:

$$\tau = \tau_0 \exp\left(\frac{E_n}{RT}\right) \qquad (1)$$

where E_n is an activation energy mostly related to nucleation events, R the gas constant and T temperature. This plot is fitted with two straight lines using least squares method in the high and low-temperature regions, respectively. The intersection of these two lines takes place at a temperature of 730 K (see Fig. 2(c)). This temperature belongs to the glass-transition region between T_{bg}^{H} (∼720 K) and T_{fg}^{H} (∼740 K). The slope of each fit gives E_n of 240 kJ/mol above (liquid phase) and 405 kJ/mol below the glass-transition region (glassy phase). Thus, E_n changes by about two times within the glass-transition region.

Similar data have been obtained for $Al_{85}Ni_5Y_4Nd_4Co_2$ alloy (Fig. 1(d)). The E_n value changes drastically around the glass-transition region (see DSC signal in Fig. 1(d)).

Similar Arrhenius plots were also created for the transformation time in the $Cu_{50}Zr_{30}Ti_{10}Ni_{10}$ glass Fig. 2(d) and the intersection point of two least squares linear fits also gives the glass-transition temperature of 730 K (see Fig. 2(d)). The activation energy values of 280 kJ/mol and 410 kJ/mol are obtained in the high-temperature and low-temperature region, respectively. These activation energy values include both

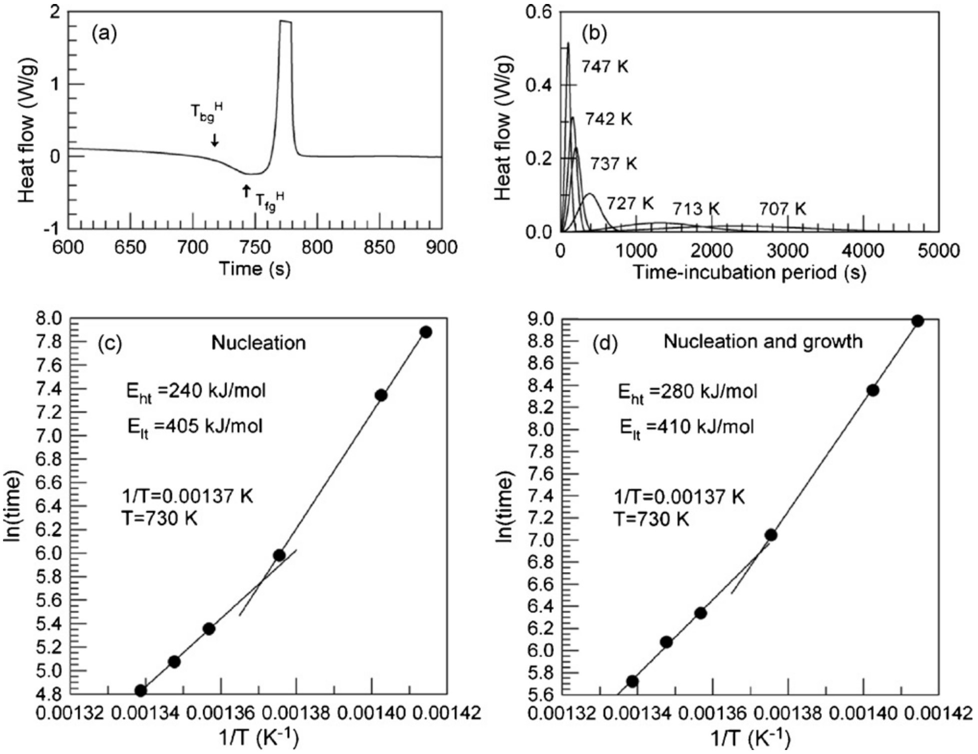

Fig. 2. (a) DSC curve for the $Cu_{50}Zr_{30}Ti_{10}Ni_{10}$ glassy alloy; (b) isothermal calorimetry curves at different temperatures; (c) and (d) Arrhenius plots created using incubation time and reaction time, respectively.

factors: nucleation and growth, and thus, are higher than those obtained mostly for nucleation only from the plot in Fig. 2(c).

The above-mentioned data indicate that the glassy phase may not be a simply frozen liquid but a different type of phase.

5. Possible origin of glass-transition phenomenon

Let us discuss the nature of the glass-transition region consisting of two temperatures T_{bg} and T_{fg}. If it is a phase transformation than the glass-transition may be a first-order type diffusionless phase transformation which takes place within a temperature interval provided that not all but a certain volume of the matrix phase is transformed at a definite temperature between T_{bg} and T_{fg}. The diffusionless character of this transformation implies that the atoms are shifted on the distances smaller than the interatomic distances [26]. One can suppose that the supercooled liquid regions are gradually transformed to the glassy regions upon cooling. This supposition have much in common with liquid- and solid-like cells in free-volume theory [9].

This postulate can be illustrated as follows. Fig. 3(a) schematically shows an atomic structure of an alloy in the glass-transition region between T_{bg}^{C} and T_{fg}^{C}. As in general, the glassy phase has a higher density (lower specific volume) than that of the supercooled liquid. The transformed glassy areas with higher packing density are encircled with dashed line in Fig. 3(a). It is known that the local atomic structure changes insignificantly upon the glass-transition which implies that the atomic shifts are smaller than the average interatomic distance leading to the diffusionless formation of the glassy structure with higher density as shown in Fig. 3(b) and (c). A position shift of a group of atoms (fluctuation) having lower energy may form a local region of a glassy phase having higher density and lower specific volume (see Fig. 3(c)) [27].

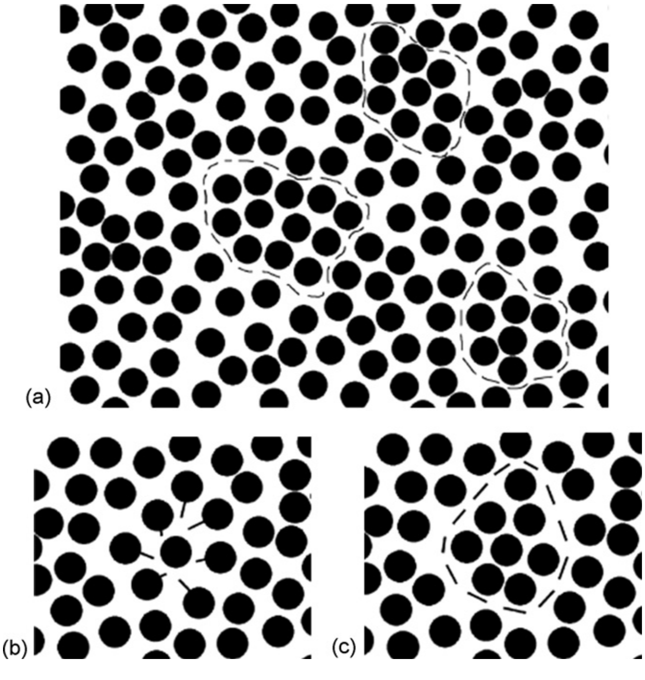

Fig. 3. (a) Schematic representation of the atomic locations in a liquid within the glass-transition region. The glassy areas are marked with dashed lines; (b) and (c) indicate a process of solidification.

At higher heating rate the metallic glass can reach a liquidus temperature, on heating without crystallisation [28], while at slower heating not a diffusionless but a diffusive transformation takes place [29].

The last, the diffusionless transformation can be a natural source of the free volume and stresses, i.e. local regions of the glassy phase which were formed first may not allow the later formed parts to contract to an "ideal" glassy state leading to elastic stresses [30,31]. These elastic stresses generated from the volume differences between transformed (glassy) and non-transformed (supercooled liquid) phases may prevent growth of the glassy regions beyond a critical size, thereby, delaying transformation of the whole volume.

6. Conclusions

The changes of the devitrification pathways in the Al-based glassy alloys and the activation energy values in Al- and Cu-based glassy alloys within the glass-transition region argue that the glass-transition is not just a simple kinetic freezing of a liquid but a phase transformation leading to a different type of phase. It is proposed that the glass-transition may be an analogue of the first-order diffusionless transformation which takes place in the certain temperature interval.

References

[1] W. Klement, R.H. Willens, P. Duwez, Nature 187 (1960) 169.
[2] H.S. Chen, D. Turnbull, J. Chem. Phys. 48 (1968) 2560.
[3] F. Spaepen, Acta Metall. 25 (1977) 407.
[4] S.R. Elliot, Physics of Amorphous Materials, Longman Group, Harlow, 1990, p. 31.
[5] T. Egami, Mater. Sci. Eng. A 226–228 (1997) 261.
[6] E. Leutheusser, Phys. Rev. 29 (1984) 2765.
[7] W. Kauzmann, Chem. Rev. 43 (1948) 219.
[8] A. Van den Beukel, J. Sietsma, Acta Metall. Mater. 38 (1990) 383.
[9] M.H. Cohen, G.S. Grest, Phys. Rev. 20 (1979) 1077.
[10] T.G. Fox, P.J. Flory, J. Appl. Phys. 21 (1950) 581.
[11] D.V. Louzguine, A. Inoue, in: H.S. Nalwa (Ed.), Nanostructured Metals and Alloys, Encyclopedia of Nanoscience and Nanotechnology, vol. 7, American Scientific Publishers, California, 2004, pp. 669–697.
[12] A.R. Yavari, A. LeMoulec, A. Inoue, W.J. Botta, G. Vaughan, A. Kvick, Mater. Sci. Eng. A 34 (2001) 304–306.
[13] Smithells, Metals Reference Book, seventh ed., Butterworth-Heinemann Ltd., Hartnolls Ltd., Bodmin, UK, 1992.
[14] P.F. Paradis, T. Ishikawa, S. Yoda, Appl. Phys. Lett. 83 (2003) 4047.
[15] A. Inoue, Mater. Trans. JIM 36 (1995) 866.
[16] D.V. Louzguine, A. Inoue, Appl. Phys. Lett. 78 (2001) 3061.
[17] D.V. Louzguine, A. Inoue, Mater. Sci. Forum 386–388 (2002) 117.
[18] D.V. Louzguine, A. Inoue, J. Non-Cryst. Sol. 311 (2002) 281.
[19] F.Q. Guo, S.J. Poon, G.J. Shiflet, in: T. Egami, A.L. Greer, A. Inoue, S. Ranganathan (Eds.), MRS Symposium Proceedings on Supercooled Liquids, Glass Transition, and Bulk Metallic Glasses, vol. 754, 2003, p. CC11.6.
[20] U. Köster, R. Janlewing, Mater. Sci. Eng. A 375–377 (2004) 223.
[21] V.A. Shneidman, D.R. Uhlmann, J. Chem. Phys. 109 (1998) 186.
[22] K.F. Kelton, Acta Mater. 48 (2000) 1967–1980.
[23] U. Köster, J. Meinhardt, Mater. Sci. Eng. 178 (1994) 271.
[24] D.V. Louzguine, A. Inoue, Proceedings of 11th International Conference on Rapidly Quenched and Metastable Materials, RQ 11, Oxford, UK, 25–30 August 2002, Mater. Sci. Eng. A 375–377 (2004) 346.
[25] D.V. Louzguine, A. Inoue, J. Non-Cryst. Sol. 325 (2003) 187.
[26] C.M. Wayman, in: R.W. Cahn, P. Haasen (Eds.), Phase Transformations Nondiffusive in Physical Metallurgy, third ed., Elsevier BV, 1983, p. 1032.
[27] D. Turnbull, J. Chem. Phys. 10 (1969) 473.
[28] H.W. Kui, D. Tubnbull, Appl. Phys. Lett. 47 (1985) 796.
[29] A.L. Greer, Science 267 (1995) 1947.
[30] H.S. Chen, H. Kato, A. Inoue, Jpn. J. Appl. Phys. 39 (2000) 1808.
[31] T. Egami, International Symposium on Metastable and Nano Materials, 27–31 August, 2006, Warsaw, Poland, J. Alloys Comp., in press.