Properties of the Amorphous Alloys.
An Elementary Introduction.

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I. Introduction

Thermo-physics of the amorphous phase was established on the base of experimental observations concerning substances which, when cooled from high temperature range where liquid state seems natural, formed preferentially disordered solid state of structural elements, even in case of relatively slow cooling. These are mainly organic liquids, oxide systems and polymers. In case of such substances formation of crystalline phase in low temperature range is improbable, if possible at all. We name them *strong glass-formers*.

Metallic glasses themselves have always been known, mainly in the form of thin layers or films formed intentionally or not on massive object surfaces. Metallic glasses became a separate subject of scientific studies when intentional formation of more massive, separated forms like ribbons, droplets and bars became possible. Nevertheless, in comparison with the "classical" amorphous phases alloys and metal-nonmetal systems remain much weaker glass-formers. To understand how glass is formed in such materials, the knowledge of physical-chemistry of the strong glass-formers remains indispensable.

II. What is the "amorphous" or "glassy" state of material. Basic thermo-physical description

A glassy state of material may be recognized as a special kind of liquid, in which diffusion is so slow that the internal relaxation process leading to the equilibrium state is much, much longer than the time available for experimental observations. In case of many relaxation processes this concerns the slowest one [Ang1995], [Ang1996], [Leu1972]. The basic concept concerning thermo-physical characterization of the amorphous or glassy state of material is the observation of the relaxation time of different parameters in the direction of equilibrium. The other process leading to the equilibrium, opposite to the relaxation of amorphous structure, is crystallization. A good glass-former must reveal low energetic states of different molecular structures, dens-packed but non-crystalline, separated by high energetic barriers. What is more, the number of the molecules indispensable for the formation of crystalline embryo in a good glass-former should be much larger than necessary for the local relaxation process [Leu1972]. If two parameters are introduced -: nucleation relaxation time τ_{nuc} and equilibrium (non-crystalline) relaxation time τ_{eq}, the following relation should take place [Leu1972]:

$$\tau_{nuc} >>> \tau_{eq} \qquad (1)$$

Processes which may proceed from the liquid state down to the glassy state are schematically presented in Fig.1. First, in cooling, at temperature T_{ca}, a strong decrease in the long distance kinetic movement of the molecules take place, and the molecules start to move only in the limited local volumes named *cages* [Leu1972].

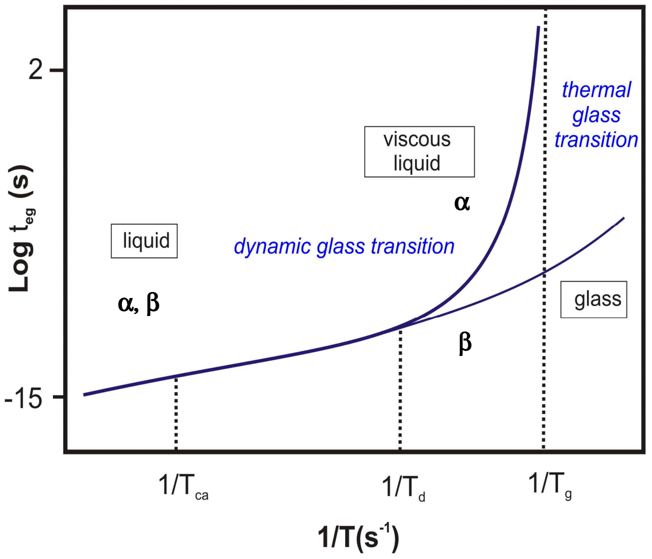

Fig. 1. Schematic presentation of the relaxation time τ_{eq} of the good glass-former structure versus reversed temperature. Characteristic temperatures T_{ca}, T_d and T_g as well as two types of relaxation processes α and β are distinguish for a glass-former (see text). ([Leu1972]).

What concerns processes of the structural reconstruction, two types of them may be distinguished: α type involves cooperative movement of the large amount of molecules while β type involves only limited number of molecules, leading only to the local rearrangement. Below temperature T_d, the time scale for the α type relaxation, - τ_α increases greatly, while relaxation time τ_β of the β type process increases slowly. The temperature T_d at which both relaxation times scales start to behave in different ways is named *temperature of the dynamic glass transition.* If temperature is lowered below T_d the thermal (or calorimetric) glass transition temperature T_g is achieved. In that temperature kinetics of the molecular movement

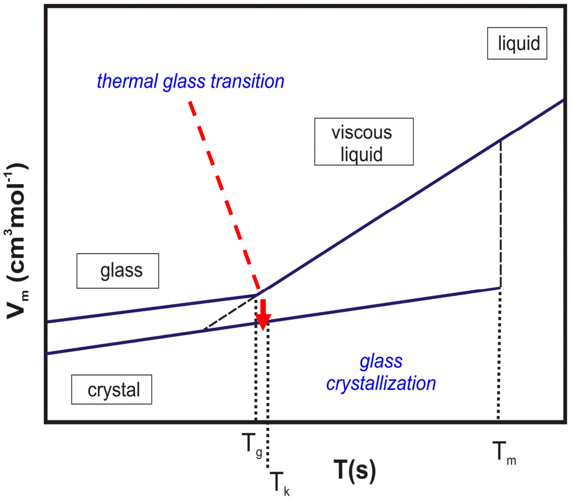

Fig. 2. The chracteristic volume V_m changes in the range of the existence of the phases: glass, crystalline and liquid. Schematic presentation on the base of experimental results for the PdCuNiP glass [Bat2007].

are further limited and the time necessary for the relaxation process is much larger than available for any experiment in a laboratory [Leu1972][1]. At temperatures below $T_{g,}$ the "liquid" phase reveals characteristic features of the solid state, with constant thermodynamic parameters and is named *glass* [Leu1972].

Another characteristic behavior of the liquid phase transforming into glassy state concerns the evolution of the characteristic volume (Fig.2) [Bat2007]. Fig.2 presents experimental results concerning Pd-based metallic glass. As is visible, in the range of supercooled liquid the characteristic volume decreases continuously until T_g temperature is achieved. The characteristic volume in the glassy state is larger than in the crystalline state, but smaller than in the liquid state. What really decreases is the average free volume for the molecules vibrations. Also, some excessive free volume v_f remains frozen in the glassy state. This results in some excessive configuration entropy ΔS_{ex} production and in large increase of the structural relaxation time τ_{eq}. The viscosity, the other very important parameter increases while heat capacity decreases. The Doolittl formula connects viscosity with the free volume in the glassy state [Zep1996]:

$$\eta = A\exp[\frac{\gamma v^*}{v_f}] \qquad (2)$$

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[1] Relaxation time of the Si based glass may be approximately estimated to be in the range of 2x10^{23} years [Leu1972]

where: γ- is a parameter, about 0.5, $v^* = v_{WS} - v_0$ – the difference between Wigner-Seitz cells volume at temperatures T and T_0, v_f – is a free volume [Bat2007], [Zep1996].

Another important formula given by Adam-Gibbs connects viscosity of the liquid state with the configurational entropy S_c [Bat2007], estimated by the difference between liquid and crystalline states entropy ΔS:

$$\eta = A \exp\left[\frac{C}{TS_c}\right] \qquad (3.1)$$

$$S_c = \Delta S = \int_{T_K}^{T} \Delta C_p d \ln T = \Delta S_m - \int_{T}^{T_m} \Delta C_p d \ln T \qquad (3.2)$$

where: - T_K – names Kauzman temperature, - T_m – is melting temperature, - ΔS_m – excessive entropy in the liquid state, in relation to the crystalline state, at temperature T_m.

Examples of the values of some thermodynamic parameters of the metallic glasses are given in Tab.1 [Bat2007].

Tab.1. Examples of the values of thermodynamic parameters of metallic glasses [Bat2007]. T_m - melting temperature, T_g - glassy temperature, ΔS_m - excessive entropy at T_m, ΔC_p^g - change of the C_p in glass transition, m - fragility index. T_g was determined with the heating rates 20 or 10 K/min (marked.*).

Alloy composition	**T_m (K)**	**T_g (K)**	**ΔS_m ($Jmol^{-1}K^{-1}$)**	**ΔC_p^g ($Jmol^{-1}K^{-1}$)**	**m**
$Cu_{47}Zr_{34}Ti_{11}Ni_8$	1144	673	10.1	13.4	59
$Fe_{40}Ni_{40}P_{14}B_6$	1177	663	10.0	21	
$Mg_{65}Cu_{25}Y_{10}$	730	410	11.84	15.7	45
$Pd_{77,5}Cu_6Si_{16,5}$	1020	620	8.0	13,2	
$Pd_{43}Cu_{27}Ni_{10}P_{20}$	790	576*	9.11	16.5	65
$Pd_{40}Ni_{40}P_{20}$	884	578*	10.6	16.3	46
$Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$	937	620	8.75	21	42
$Zr_{46,75}Ti_{8,25}Cu_{7,5}Ni_{10}Be_{27,5}$	1000	635		17	34

III. Glass transition

During cooling of the liquid phase in case of a glass-forming material the temperature range may be experimentally observed in which the liquid phase structure is frozen in place of the crystallization. The observation depends on the cooling rate and physical-chemistry of the liquid phase [Ang1996]. At the same temperature range the change in some thermodynamic parameters like: heat capacity, viscosity and thermal expansion coefficient is observed. Such a temperature range is known as the *glass transition range* . *Glass transition* may proceed during cooling of the liquid phase, as well as during heating of the metallic glass [Ang1996].

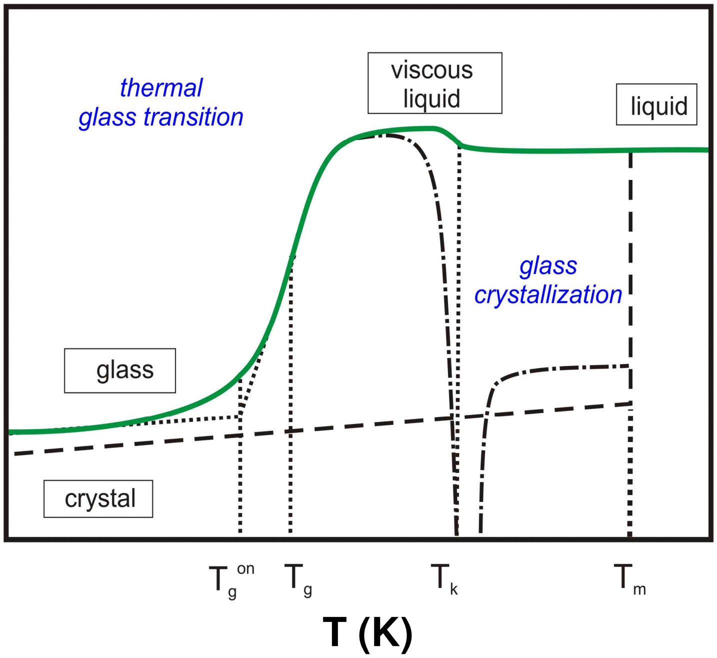

Fig. 3. Specific heat behavior in the glass transition range. Continuous line – C_p of the glass which transforms after glass transition directly into the liquid phase during heating, broken line – C_p of the equilibrium crystalline phase transforming at T_m into the liquid phase, broken/dotted line – change of the C_p of the metallic glass which crystallize at temperature T_x above glass transition. Glass transition temperatures are marked a) in the inflection point- T_g, and b) at the onset point - T_g^{on} .

The glass transition is kinetic in character and characterized by T_g temperature, commonly determined with the differential scanning calorimetry (DSC). The same temperature relates also to the rapid change of heat capacity and viscosity, the last one in the range of 10^{10} poises [Bat2007]. The shape of the endothermic effect observed with the DSC may be different in different cases, sigmoidal or more complicated. It is also dependent on the thermal history of the sample, for example low temperature relaxation of the glass structure may change the shape of the heat effect connected with glass transition [Bat2007]. The C_p changes in the glass transition range are shown schematically in Fig.3, in which the continuous line marks C_p changes if during heating, glass transforms into liquid phase without crystallization. Broken/dotted line shows C_p changes for the glass which crystallizes at temperature T_k. In this case C_p reveals discontinuity at the temperature range of crystallization. However, heat capacity of the resulting nano-crystalline phase is commonly slightly higher than C_p of the equilibrium crystalline phase. Broken line in Fig. 3 presents C_p of the equilibrium crystalline phase, formed in cooling, up to the melting temperature T_m. Two different common definitions used for T_g determination in literature, are also marked in Fig.3.

IV. Microstructure of the metallic glass

There are some important elements in the theory of the microstructure of the metallic glass. The first is the idea of the free volume. Originally, it was based on the model of the liquid microstructure[2], in which molecules may move in some limited free volume v_f. It is a *cage*, some average volume not occupied by its nearest neighbors. Only, when the additional free volume $v > v_f$ is available as a result of thermal fluctuations, the particular molecule may move into it [Ega2008]. Cooling of the glass–forming liquid to the state of glass leads to the freezing of the structure, together with the excessive free volume v_f, at temperature higher than glass transition temperature T_g[3]. In low temperature range, total volume decreases but because there is no relaxation, the free volume is preserved, but thermodynamically unstable [Ega2008]. The free-volume theory explains many experimental observations in glasses but remains not completely realistic. Both the methods of molecular dynamics modeling and experimental results proved the collective and diffusional character of the atomic movement, rather than individual, in the structure of metallic glass [Ega2008], [Li2009].

The other important element in the model of the metallic glasses structure are atomic clusters possessing deformed structure, crystalline or quasi-crystalline, of the dens-packed character [Lou2009]. After application of the methods of pair-distribution function PDF and reversed Monte-Carlo simulation [Fan2009] the model of the glass structure was achieved in which three different types of volume were distinguished, depending on the atomic bonding distances and strength of the different components. The following structural elements were defined:

1. atomic clusters revealing strong, directed bonds,
2. free volumes between them with weak bonding,`
3. the transient volumes with decrease of the directional bonds strength.

Such elements of the structure are schematically shown in Fig.4A. The atomic bonds in clusters are much shorter than in crystals or quasi-crystals, of similar symmetry. As a result of the clusters formation the internal energy of glass decreases, also strong, directional bonds act against crystallization, both factors stabilizing the glass structure. In the range of the glass transition, the bonds in the transient volumes weaken, what leads to the separation of the

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[2] Theory of M. Cohen and D. Turnbull, eg. J. Chem Phys. 34 (1970) 3038-3041.

[3] Temperature T_f known as "*fictive temperature*".

strongly bonded clusters by the free volume and results in the transformation of the glass into a supercooled liquid [Fan2009]. The average size of clusters may be quite large - 2-3 nm, as was shown with use of the high resolution microscopy in case of the Pd-Ni-P glasses [Hir2007].

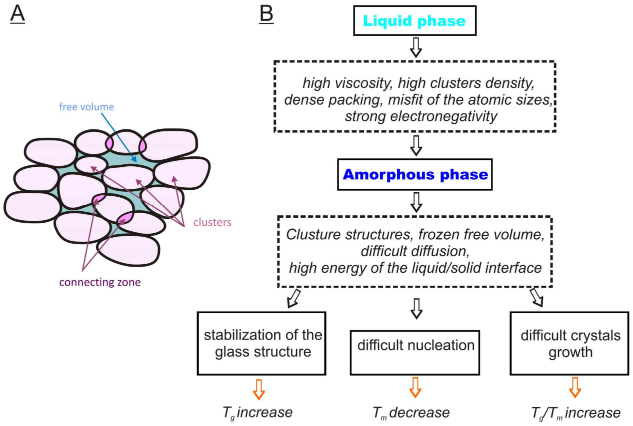

Fig. 4. A) schematic presentations of the characteristic elements of the metallic glass microstructure; B) relations between microstructure and properties of the glass-forming liquids and metallic glasses required for the large glass forming ability (see text) (by [Ino2004]).

V. Basic conditions for metallic glass designing

Designing of the alloys revealing high glass-forming ability requires compositions which strong tendency for the amorphous phase formation, with the structure of the dense but random atomic packing and high energy of the liquid/solid interface., The decreased tendency for nucleation and crystallization is also important [Ino1998], [Mir2004]. These conditions may be achieved by the composition of elements which reveal difficulties in topological rearrangement to form a long distance order. Inoue given following simple principles of the glass-former design [Ino1998], [Li2009], later completed by Egami [Ega2003]:

- many different components should be used,
- differences in the atomic radii of components should be as large as possible,
- interaction between large and small atoms should be strong,
- interaction between small atoms should be repulsive.

The second and third conditions explain why the increase in the glass forming ability is quite often increased by the addition of a non-metallic component. The last condition was added against formation of the clusters seldom from the small atoms. All above conditions may be divided in two groups, the first one concerns increase of the liquid phase stability against crystallization, the second decrease tendency to the nucleation, crystallization and growth of the crystals in the solid state [Ino2004]. Schematically the conditions for a good-glass former design and high thermal stability of the glass are shown in Fig.4B.

VI. Fundamentals of mechanical properties of metallic glass

In macroscopic scale and at room temperature metallic glasses reveal a large range of elastic deformation (typically abort 2%), while the plastic deformation range is insignificant, especially in the tensile experiments. The plastic deformation may be both homo- and heterogeneous. The homogenous one proceeds in high temperature range, heterogeneous in low temperature range. The ranges of both types of deformations in relation to temperature and deformation rate are shown schematically in Fig.5. The heterogenic type of deformation is connected with localization and accommodation of the deformation in shear bands followed by the catastrophic fracture [Liu2005], [Nie2008].

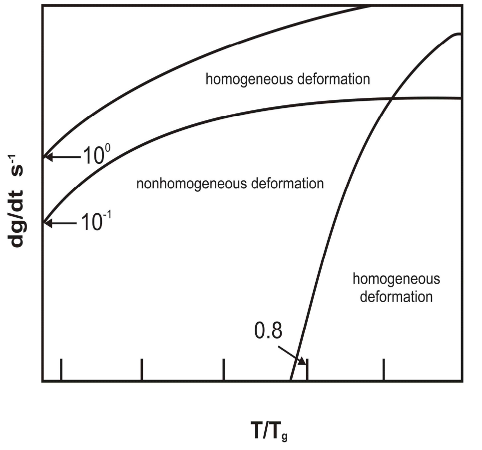

Fig. 5. Schematic map of the plastic deformation modes in dependence on the deformation rates and temperature [Sch2004].

The asymmetry between flow stress and strength in the tensile and compression tests is also characteristic of the metallic glasses [Nie2008]. Yield criterion in the case of metallic glasses has the form of the Mohr-Coulomb formula [Nie2008], [Wri2001]:

$$\tau_y = \tau_0 + \alpha\sigma_n \tag{4}$$

Where: τ_y means shear yield stress, τ_0 –a constant, α - characteristic material parameter, σ_n – stress normal.

Heterogeneous deformation with the shear bands formation

Some results concerning shear band formations were achieved in the compression test or nano-indentation tests made on the bulk metallic glasses [Liu2005], [Nie2008], [Yan2005]. The process which determines a rate of the shear band formation is the nucleation process. After nucleation a shear band propagates with high speed in the time scale of 10^{-5} s. The whole process of the shear band formation is dependent on the applied load, its type and deformation rate and resulting stresses. Low deformation rate results in the generation of shear bands in the individual way, but above some critical rate many shear bands are generated at the same time and they multiply. [Liu2005]. This behavior results from the lack of the ability of glass to accommodate deformation in separated shear bands at high deformation rates. However, glasses of the same composition may be deformed in a different way, which shows the importance of the physicochemical character of the particular glassy phase. Importance is attached to the type of atoms cohesion forces and a free volume content but also an amount and character of the locally ordered structures, which are present at the clusters boundaries but are misfit to the surrounding structure. These structures play a role of the local structural defects [Ben1997], [Liu2005]. Such a concentrated defect, the size of tens of atoms are named *shear transformation zones* (STZ) [Ara1979], [She2010]. At low temperatures STZs are localized and concentrate stresses resulting from the thermal history of the sample. Increasing stress leads to the STZs grow, to the size of hundreds of atoms, however, they reveal the highest mobility for the small stresses [Neu2009]. At high temperature range STZs are less localized and interact with the local structural fluctuations [Neu2009]. Deformation may be also initiated by the local increase of temperature [Ben1997] [Wri2001], but it is believed that the more important reason for deformation is the increase of the free volume, its dilatation under the stress and a decrease in viscosity in the deformation bands [Flo2001], [Liu2005], [Wri2001], [Yan2005].

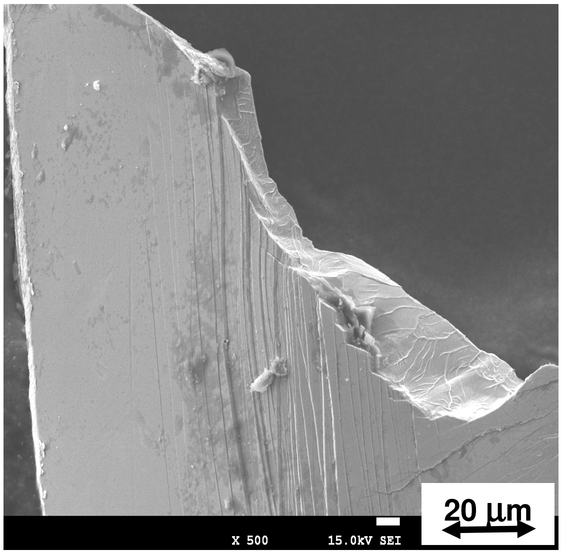

Fig. 6. Scanning electron microscopy image of the shear bands and the fracture surface in case of the NiNbZrTiAl glass. Example of the heterogeneous deformation in tensile test, at room temperature.

Some results concerning shear bands show nanocrystallization inside the bands. This observations were explained both by the diffusion induced by the flow of the material in a shear bands and by the local temperature increase inside them, up to T_g, or even to the melting temperature T_m [Yan2005] [Wri2001].

The measure of the deformability/brittleness of the metallic glasses is supplied by the shear resistance parameter S [Lew2005], [Zha2007], which is defined as:

$$S = \frac{\mu}{B} = \frac{3(1-2\nu)}{2(1+\nu)} \qquad (5)$$

where: – μ– means shear module, - B - volume module, - ν – Poisson number.

The increase of the S parameter, up to the value of about. 0.32, is the limit for the plastic behavior of the metallic glasses.

Propagation of the individual shear bands as well as their multiplication leads to the catastrophic fracture of the sample. However, if accommodation of the deformation may have place in many interacting bands which may also form barriers for their further propagation, the increased macro-scale range of plastic deformation may be observed [Das2005] [She2010]. This observation allows the methods leading to the increased ability of plastic deformation of metallic glasses like preliminary cold rolling or introducing deformation on the sample surface [Yok2001], [Yok2003], [Zha2006].

Strength of the metallic glass at low temperature range

Mechanical strength of the metallic glass results directly from the physical and chemical properties, like the cohesion strength of the atoms, temperature range of the glass transition, elastic module and thermal expansion coefficient [Nie2008]. Commonly, the strength of

the shear stress is about 0.02 of the shear module μ [Nie2008]. Strength is also connected with the thermal properties and density, so the following formula may be written [Nie2008]:

$$\tau_y \gamma_0 \approx \int_{T_0}^{T_g} \rho C_p \, dT \qquad (6)$$

where: - τ_y – is maximal shear yielding stress, -γ_0=1 –shear stress in the shear band, - ρ- material density. From the formula (6), the following formula for the fracture stress σ_f results:

$$\sigma_f = 55 \frac{\rho_0}{M} (T_g - T_0) \qquad (7)$$

where: - ρ_0 means material density at room temperature T_0, and M- is a molar mass.

It is well established that the linear relation between glass strength and glass transition temperature T_g exists [Nie2008].

Homogenous deformation at higher temperatures

At temperatures above $0.7T_g$ homogenous mode of deformation is observed. This mode reveal very large range of deformation, e.g for the CuNiZrTi glasses - 300-650%, [Kim2007], especially in the temperature range of the supercooled liquid [Nie2001], [Nie2008]. In some sense this kind of glass deformation is similar to the superplastic behavior of the polycrystalline alloys. In case of metallic glasses such deformation is known as *extended plasticity* [Nie2001]. Two temperature ranges are distinguished: from temperature T_h, at which material changes the deformation mode from hetero- to homogeneous to T_g temperature and from T_g temperature to the crystallization start temperature T_x [Nie2001]. In the first temperature range the deformation is small ($\varepsilon < 50\%$) and weakly dependent on the deformation rate [Nie2001]. The homogenous deformation in the second temperature range $T_g < T < T_x$ strongly depends on the temperature and the rate of the deformation In the range of high temperature and moderate rates of deformation, metallic glass behaves like "Newtonian liquid". High deformation rates lead to the modification of this characteristics [Nie2001].

Mechanism of the homogenous deformation results from the high rate atomic diffusion, which is possible due to the free volume evolution, caused by the load and temperature [Nie2001], [Nie2008]. This kind of deformation interpreted as a result of the challenge between two competitive processes of the formation and annihilation of free volume. The first mechanism results from the materials deformation, the second from the structure relaxation [Lee2009], [Wan2010]. The homogenous deformation requires formation of the active volumes, of the size of tents of atoms, similar to the STZs, in the heterogeneous deformation mode [Lee2009]. The extended plasticity depends on the amorphous phase thermal stability, so even glasses of the similar composition may behave in a different way [Kim2007]. Also nanocrystallization is sometimes observed [Kim2007]. It was noticed that increase amount of the clusters in the structure of the glass leads to increase in strength and hardening but also promotes nanocrystallization. On the other hand, crystallization reveals some dependence on the deformation [Kim2007].

Literature

[Ang1995] C.A. Angell; Science 267 (1995) 1924-1935

[Ang1996] C.A. Angell; Solid State Materials Science 1 (1996) 578-585

[Ara1979] A.S. Aragon, Acta Metall. 27 (1979) 47-58

[Bat2007] L. Battezzati , A. Castellero, P. Rizzi; J. Non-Cryst. Sol. 353 (2007) 3318-3326

[Ben1997] V. Z. Bengus, E.D. Tabachnikova, P. Duhaj, V. Oleck; Mat. Sc. Eng. A226-228 (1997) 823-832

[Das2005] J. Das, M. B. Tang, K. B. Kim, R. Theissmann, F. Baier, W. H. Wang, J. Eckert; Phys. Rev. Lett. 94 (2005) 205501

[Ega2003] T. Egami J Non-Cryst Solids 317 (2003) 30-33

[Ega2008] T. Egami: Atomistic theory of metallic liquids and glasses; w: Bulk Metallic Glasses, eds. M. Miller, P. Liaw, Springer 2008; str. 29-32

[Fan2009] C. Fang, P.K. Liaw, C.T. Liu; Intermetallics 17 (2009) 86-87

[Flo2001] K.M. Flores, D. Suh, R. Howell, P. Asoka-Kumar, P.A. Sterne, R.H. Dauskard; Materials Trans. 42 (4) (2001) 619-622

[Hir2007] A. Hirata, Y. Hirotsu, T.G. Nieh, T. Ohkubo, N. Tanaka; Ultramicroscopy 107 (2007) 116-123

[Ino1998] A. Inoue; Bulk Amorphous Alloys, Preparation and Fundamental Chracteristics; Mater. Sci. Found. 4, Trans Tech Publications 1998, str. 4-8

[Ino2004] A. Inoue, A. Takeuchi; Mat. Sci. Eng. A 375-377 (2004) 16-30

[Kim2007] W. J. Kim; Intermetallics 15 (2007) 282-287

[Lee2009] K.S. Lee, H-J. Jun, S. Pauly, B. Bartusch, Y.W. Chang, J. Eckert; Intermetallics 17 (2009) 65-71

[Leu1972] L. Leuzzi, T.H. Nieuwenhuizen: Thermodynamics of the Glassy State; Series in Condensed Matter Physics, Taylor & Francis 1972

[Lew2005] J.J. Lewandowski, W.H. Wang, A.L. Greer; Phil. Mag. Lett. 85 (2) (2005) 77-87

[Li2009] F. Li, X.J. Liu, H.Y. Hou, G. Chen, G.L. Chen, M. Li; Intermetllics 17 (2009) 98-103

[Liu2005] L. Liu, K.C. Chan; Materials Letters 59 (2005) 3090-3094

[Lou2009] D.V. Louzgine-Luzgin, A.R. Yavari, G. Vaughan, A. Inoue; Intermetallics 17 (2009) 477-480

[Mir2004] D.B. Miracle, O.N. Senkov, W.S. Sanders, K.L. Kendig; Mat. Sc. Eng. A 375-377 (2004) 150-156

[Neu2009] M. Neudecker, S. G. Mayr; Acta Mat. 57 (2009) 1437-1441

[Nie2001] T.G. Nieh, J. Wadsworth, C.T. Liu, G.E. Ice, K.S. Chung; Materials Trans. 42 (4) (2001) 613-618

[Nie2008] T.G. Nieh: Deformation behavior; w: Bulk Metallic Glasses, eds. M. Miller, P. Liaw, Springer 2008, p.147-167

[Sch2004] C.A. Schuh, A.C. Lund, T.G. Nieh; Acta Mater. 52 (20) (2004) 151-154

[She2010] Y. Shen, G. P. Zheng; Sripta Mat. 63 (2010) 181-184

[Wan2010] J. Wang, P. D. Hodgson, J. Zhang, W. Yan, Ch. Yang; Comput. Mat. Sc. 50 (2010) 211-217

[Wri2001] W.J. Wright, R. Saha, W.D. Nix; Materials Trans. 42 (4) (2001) 642-649

[Yan2005] W.H. Yang, F.E. Pinkerton, A. Atzmon; Acta Mat. 53 (2005) 3469-3477

[Yok2001] Y. Yokoyama, K. Yamano, K. Fukaura, H. Sunada, A. Inoue; Materials Trans. 42 (4) (2001) 623-632

[Yok2003] Y. Yokoyama; J. Non-Cryst. Solids 316 (2003) 104-113

[Zep1996] J. Zeppel, F. Sommer; J. Non-Cryst. Sol. 205-207 (1996) 494-499

[Zha2006] Y. Zhang, W.H. Wang, A.L. Greer; Nature Materials 5 (2006) 857-860

[Zha2007] Y. Zhang, A.L. Greer; J. All. Comp. 434-435 (2007) 2-5