

## Contents

Preface .....	vii
Historical notes .....	ix
I. Nanomaterials based on metals.....	1
I.1. Technology of nanocrystalline-structured materials obtained through glass-transition of amorphous metallic alloys <i>Nikola Nikolov</i> .....	3
I.2. Severe plastic deformation (SPD) – technology for bulk nano- crystalline metals and layers <i>Anguel Baltov</i> .....	37
II. Nanomaterials based on polymers .....	49
II.1. Polymer nanocomposites of epoxy resin and multiwall carbon nanotubes: processing-structure-properties relationships <i>Rumiana Kotsilkova, Evgeni Ivanov, Ekaterina Krusteva</i> .....	51
III. Modeling of nanomaterials and nanostructures .....	91
III.1. Analytical modeling of nanocomposites stiffness <i>Ludmila Parashkevova, Nikolina Bontcheva, Vitali Babakov</i> .....	93
III.2. Continuum approach in nanomechanics <i>Anguel Baltov, Ana Yanakieva</i> .....	133
III.3. Equilibrium shapes of fluid membranes and carbon nano-structures <i>Vassil Vassilev, Petar Djondjorov, Mariana Hadzhilazova, Ivailo         Mladenov, Jan J. Slawianowski</i> .....	153
III.4. Numerical modeling of nanocrystalline metallic materials obtained by glass-transition or severe plastic deformation <i>Nikola Nikolov, Anguel Baltov</i> .....	185
III.5. Hierarchical modeling of biological nanocomposites <i>Svetoslav Nikolov, Helge Fabritius, Martin Friák, Dierk Raabe</i> .....	199
IV. Experimental nano- and micromechanics .....	225
IV.1. Micro- and nanometrology <i>Vassil Kavardzhikov, Dessislava Pashkouleva</i> .....	227
IV.2. Mechanical characterization of layers and thin films via nanoindentation and numerical simulations <i>Roumen Iankov, Sabina Cherneva, Maria Dacheva, Dimitar Stoychev</i> .....	261
IV.3. Experimental nano and micro mechanics of nanostructured materials <i>Evgeni Ivanov, Irena Borovanska, Boryana Milosheva, Rumiana         Kotsilkova</i> .....	287

## Technology of nanocrystalline-structured materials obtained through glass-transition of amorphous metallic alloys

Nikola Nikolov\* e-mail: [n.nikolov@imbm.bas.bg](mailto:n.nikolov@imbm.bas.bg)

\*Institute of Mechanics, Bulgarian Academy of Sciences

### Abstract

Forms of existence of metallic matter attainable in nanoscale are treated. Design, production and identification of such kinds of amorphous and nanocrystalline forms are described. Specific features related to the chemical contents of Zr- and Hf-based metallic alloys and the corresponding technologies ensuring obtaining the forms pointed out are discussed, mathematically modeled and optimized in order to achieve large glass forming ability. In a brief historical review the discovering of such types of alloys and the development of methods and techniques for their production are traced.

Keywords: *Amorphous and nanocrystalline metallic alloys, glass-transition and crystallization temperatures, mathematical models, optimizations*

## 1. Introduction

### 1.1 Nanocrystalline structured metallic alloys

At present, the amorphous- and nanocrystalline-structured materials attract the attention of science, industry and the market, respectively of researchers, producers and merchants, owing to the opportunity to be designed and manufactured with their unique properties. This opportunity could be realized through advanced technologies ensuring the success of atomic-level operations and corresponding control.

Thereby, the research and elaboration of nanocrystalline metallic alloys are basically inspired by the recent development of experimental devices and production technologies. On the other hand, the industry imposes requirements arising from some specific applications of such kind of materials. Therefore, during research, in some cases the scientific achievements have a driving role, and in other cases the design requirements get the driving role. The applications of nanocrystalline metallic materials are provoked by their specific properties, as high hardness and high elasticity, combined with high yield and tension-pressure strengths, corrosion resistance, *etc.* Their specific applications are undertaken in some areas, where the other conventionally structured materials are not applicable indeed. For the properties pointed out, the metallic structure in atomic level is crucially determinative. Roughly seen, the recent technology development needs new knowledge, methods and instrumentations for outside purposive nano-scale manipulations during formation of configurations between the atoms of metallic chemical elements. In

this way, new atomic configurations different from the conventional crystalline lattices could be formed with the aim to determine the corresponding properties.

Mechanical elements possessing such atomic structures, but also produced through corresponding special technologies, are distinguished with characteristics exceeding in times these of the same mechanical elements produced conventionally. Such mechanical characteristics could be a high elastic modulus, low Poisson's ratio, high strength limits, *etc.* The achievement of some characteristics of metallic materials given in advance in respect to definite mechanical elements depends on the exploitation requirements. Consequently, before the manufacture of special mechanical elements, corresponding needs of the development of devices, methods of design, synthesis, testing and studying of nanocrystalline materials arise, as well as techniques for control and conduct of the metallic structures forming.

## 1.2 Basic topics of the mechanics of nanocrystalline metallic materials

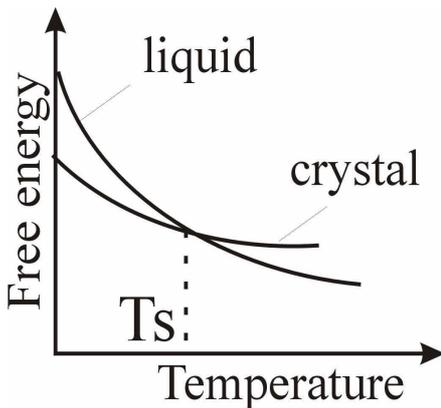
Even though the solid mechanics is an old scientific area, in the field of nanostructured metallic materials and corresponding technologies its development is still provoked by topics, such as: mechanical behaviour of amorphous and nanocrystalline materials depending on different multiple scales and fracture mechanisms; derivation and verification of corresponding proper realistic models of mechanical behaviour generalized in meso- and macro-levels depending on material structure and chemical content; realizing observations on the deformation processes without initiation and growth of material damages together with enlargement the knowledge of reliability in complex stress-strain states. These topics could be explored by development of new experimental equipment, new inventive experimental methods and improved mathematical models, as well as interaction with each new enlarging scientific field concerning similar common topics.

A multitude of other requirements could be pointed out, but for each of them the simplicity of modeling should be important to struggle with the complexity. Usually, only few material characteristics among many are directing the general deformation behaviour. Besides, usually they are closely related to the numerous precise characteristics of technological production regimes. The aim is such material and technological characteristics to be identified and reduced as representative ones in rationally derived but simple models. On these ideas the present Chapter is concentrated. It touches the frontiers between the Solid Mechanics, Material Science and Chemistry.

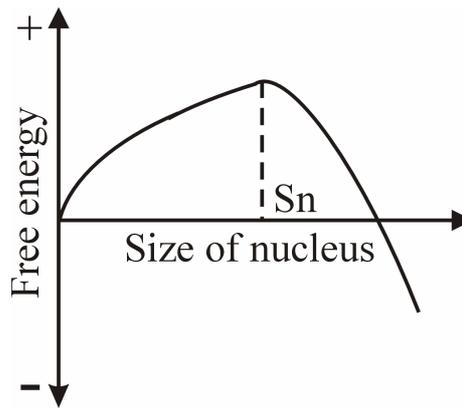
## 2. Crystallization process in metals

Under conventional technological conditions, usually assumed as ambient temperature 20°C and normal atmospheric pressure 948hPa, the process during transformation of metallic alloy from liquid aggregate state to solid aggregate state is called crystallization if the atomic arrangements are performed in long distances compared to the atomic radii, crystal lattice is formed and crystals are nucleated and grown [1]. In principle, each body or process in nature, including transformation processes, aims to achieve a more stable state with lower internal energy. At equilibrium theoretical crystallization temperature  $T_s$ , the two free energies of liquid state and solid state are equal, Fig. 1. The Helmholtz free

energy is defined as  $F \equiv U - TS$ , where  $U$  is the internal energy,  $T$  is absolute (Kelvin) temperature and  $S$  is the entropy. In both aggregate states the metal appears in equilibrium, Fig. 1. To start crystallization, the process should be developed to decreasing free energy, Fig. 2, *i.e.* it is necessary the system to be led to a temperature lower than this of crystallization. The difference between the two crystallization temperatures, theoretical and actual, is called overcooling.



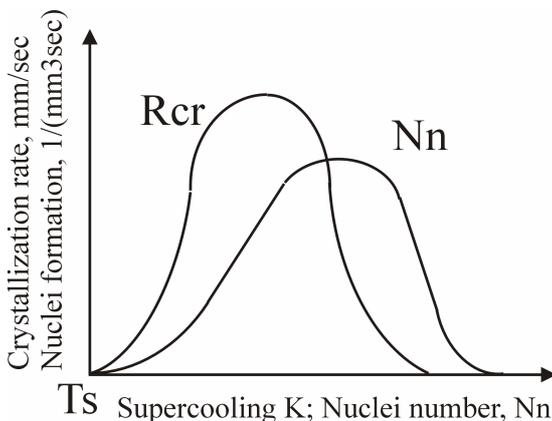
**Figure 1.** Free energies of liquid and crystalline states



**Figure 2.** Size of nucleus depending on the transformation of Free energy

The crystallization process consists of two subprocesses: formation of crystallization nuclei, or nucleation, and growth of crystals based on these nuclei, Fig. 3.

At given crystallization temperature and cooling rate, the sizes of formed nuclei  $S_n$  depend on the rate of crystal growth  $R_{cr}$  (mm/sec), or crystallization rate, and the rate of nuclei formation  $R_n$  ( $\text{mm}^{-3}\text{sec}^{-1}$ ), or nuclei number  $N_n$ . With high values of  $R_{cr}$  and low  $R_n$ , for example low cooling rates, a small number of larger crystals are formed. With low values of  $R_{cr}$  and high  $R_n$ , *i.e.* high overcooling, a large number of smaller crystals are formed.



**Figure 3.** Crystallization process

Finally, in conformity with the C-curves of Thaman [1], if an opportunity occurs to overcool the liquid without crystallization, then  $R_{cr}$  and  $R_n$  become equal to zero. The molten metal (the melt) retains its structure of liquid aggregate state not transformed. This structure remains amorphous and not crystallized, with corresponding possibility to form nanocrystals and to be manipulated technologically according to its properties given in advance.

But the liquid metals and their alloys are feebly disposed to such a supercooling and do not achieve such amorphous state easily. Salts, silicates and organic substances show the opposite trends being more disposed to supercooling. The ordinary silicate solid glass is a supercooled viscous liquid. Such a state appears amorphous and characterizes with absence of regular order in the atomic arrangements like that in a determined ordered crystal lattice. The structure of conventional metallic alloys in micro-level characterizes by the well-known ordered crystal lattice, for example BCC, FCC, HCP, *etc.* [1]. In difference, the structure of nanocrystalline metallic alloys contains atoms ordered in different nano-sized unique glassy structures, and atomic configurations which are different in metal-metal type alloys (including Mg-, Lanthanide-, Ti-, Hf-, Be-Zr-based ones), metal-metalloid type alloys (including Fe-, Co- Ni-based ones), and Pd-metalloid type alloys (including Pd- and Pt-based ones) [2]. The unique glassy structure can have high liquid/solid interfacial energy and low atomic diffusivity, and requires long-range atomic rearrangements for crystallization to proceed, thus producing high stability of supercooled liquid that allows to form bulk glassy alloys.

### 3. History

For the first time, in September 1959, in Caltech, **Duwez** and his coworkers obtain metallic amorphous structure. An amorphized Au-Si-structure of Gold (Au) and Silicon (Si) is obtained by rapid quenching [3]. It is reported that for some metalloids, which bonding may actually be more covalent than the metallic, such amorphous configurations have been retained in solid state by cooling the melt with sufficient rate, so as to prevent formation of equilibrium crystalline structures. Until then, highly disordered arrangements of atoms similar to that of liquid state have never been observed in solid metals and alloys, except for thin films deposited at very low temperatures. The necessary cooling rate is of the order of  $10^6$ K/s and the time interval is from 0.1 to 1 millisecond. Such kind of metallic amorphous alloys are called conventional. Shortly after that, **Cohn** and **Turnbull** found that the content of such alloy is close to the eutectic points in the phase diagram [4]. This simple condition facilitated and opened the researches in the field of metallic glasses. During the early 60s, **Turnbull** and coworkers reported similarity between the amorphous metallic alloys, ceramic alloys and silicate glasses. Glasstransition is established in rapidly quenched Au-Si-based amorphous alloys, as well as in Pd-Si and Pd-Cu-Si-systems synthesized by Duwez and coworkers earlier [5].

The development of amorphous metals advances during the early 70s after development of the process of melt-spinning. The melt-spinning enables cooling the melt rapidly to ribbons with thickness from 10 to 50 micrometers. That is realized through the melt flowing on a wheel. At that time most alloys developed are two-componential, with

composition close to the eutectic. In the same period, **Chen** and coworkers applied a simple method of casting through suction of the melt [6]. Using significantly low cooling rates, they have obtained a rod Pd-Cu-Si-sample with diameter 1mm. Compared to the ribbon thickness, this sample could be treated as a bulk.

After 1982 **Drehman, Kui, Greer, Turnbull** conducted experiments on Pd-Ni-P-melts using fused boron oxide in order to suppress the crystal nucleation [7; 8]. These experiments reveal that if the heterogeneous crystal nucleation is suppressed, the alloy is able to form samples with millimetric sizes at cooling rates 10K/sec.

During the late 80s, in Sendai, **Inoue** and coworkers found exceptional amorphization ability in La-Al-Ni and La-Al-Cu-based alloys [9]. Fully amorphous samples with thickness a few millimeters are obtained by casting in copper molds.

Thereafter, such four- and five-component alloys are investigated and elaborated with critical cooling rates below 100K/sec. Similar alloys containing a rare-earth metal, partially replaced by the alkaline Magnesium (Mg-Y-Cu, Mg-Y-Ni, and others) are also developed [10] together with the Zr-based (Zr-Al-Cu-Ni) ones [11]. These amorphous alloys demonstrate that the bulk formation of amorphous alloys is not limited to the Pd- and Pt-based alloys only. Later, based on these elaborations wide class bulk amorphous alloys are synthesized. Not for no long, the noble metals remain to be important basic elements in these new systems. Some alloys, such as Zr-Al-Cu-Ni possessing exceptional amorphizing abilities, contain the transition elements only. The large Glass Forming Ability (GFA) is due to the enhanced aptitude to dense packing through multitude of elements because in the system alloys there exists a wide choice of atoms with proper sizes to fill up the free volumes in the free packed disarranged structures [12].

Shortly after the Tokyo group, in Caltech, **Peker** and **Johnson** report an exceptional multicomponent amorphous alloy with content  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  [12; 13]. This alloy appears as one of the best glass formers, and maybe it set up limits in the multicomponent effect for dense packing in the Zr-based amorphous alloys.

The GFA improved through multitude components is also related with the decreasing free energy in the alloy systems because of the effect of mixed chemical entropy. That could be explained by the “principle of mixing”, i.e. “more introduced elements, decreasing possibility of the alloy to choose a stable crystalline structure and increasing possibility of amorphizing” [14].

After 1990, the elaborations in the field of the so called bulk (or massive) amorphous alloys (metallic glasses) advance. The bulk amorphous alloys show cooling time range from 1 to 100 sec and more. Some multicomponent alloys have exceptional ability to amorphization commensurable to this of silicate glasses. They form supercooled melts, which are relatively stable and therefore proper for investigations of the atomic diffusion. Contrariwise, the conventional amorphous alloys crystallize below the glasstransition temperature. Because of that they can only be investigated below this temperature. The thermal manipulation of bulk amorphous alloy, e.g. annealing in the supercooled liquid region under chosen temperatures and for given time, makes possible to obtain nanocrystalline atomic-structured materials with unique specific properties, such as high strength, hardness, elastic energy, viscosity, wear- and corrosion resistances, magnetic properties, magnetic penetration, reflecting ability, large ability to stamping, and others. The listed properties determine the specific applications of these materials in consumer/household

goods, sport accessories, in machine-building, fine-mechanics, medicine, aircraft, space technique, *etc.*

A presentation of the recent achievements, as well as applications and possible directions of future investigations in the field of amorphous alloys susceptible to formation of nanocrystals can be found in [15-17]. As an area, where the future efforts could be directed, the development of universal basic models could be pointed out. Such models could provide possibilities for predicting the nanocrystalline alloy compositions, limits of supercooling, glass transition and other thermal properties, and for identification of thermo-dynamical, geometrical, electronic, chemical and kinetic parameters, correlation between the nanostructure and chemical content with different properties and behaviour. From this point of view, the prediction of nanomaterial properties and corresponding deformation behaviour is outlined as one of the leading scientific directions in the field of nanocrystalline metallic alloys. The mathematical modeling and optimization of the thermal characteristics of bulk amorphous alloys could be an instrument to assist the advance in this direction. The derivation of mathematical models will give opportunity to identify values and discover relations between chosen characteristics of GFA and technological regimes. Finding such opportunity only through real experiments is a long and expensive process, which could be often recompensed with unsuccesses or failures.

#### **4. Theoretical and technological bases**

As was seen in the previous section, before 1990, significant numbers of amorphous alloys have been synthesized in search for compositions possessing large Glass Forming Ability (GFA). Only systems based on Palladium and Platinum have been obtained in bulk amorphous states [18]. After 1990, a few systems based on Lanthanum (Ln-), Magnesium (Mg-), Zirconium (Zr-) and Iron (Fe-) with critical cooling rate lower than  $10^3$  K/s have been developed [19]. Among them, the Zr-based amorphous alloys Zr-Al-M (M=Mn, Fe, Co, Ni, Cu) show largest supercooled liquid regions within temperature interval  $\Delta T_x$  nearly 90K defined by the difference between the crystallization temperature  $T_x$  and glass transition temperature  $T_g$  [20]. That region is larger by 20-30K than the one for Pt- and La-based amorphous alloys.

The amorphous alloys with ability for nanocrystallizing, could extend their application through a decrease of the cooling rate needed for their production. Therefore, it is important to know the relative content of chemical elements, which could influence the large GFA. The liquid temperature  $T_l$ , melting (solidus) temperature  $T_m$ , the onset temperature of crystallization  $T_x$  and glass-transition temperature  $T_g$ , as well as their ratios could be measures of GFA. For such a kind of alloy, the difference between the Gibbs free energies in supercooled liquid state and crystalline state is lower than this difference for conventional amorphous metallic alloys [21; 22]. That is equal to a decreasing driving force for nucleation of competitive crystalline phases. Large amorphization ability can be achieved through the stabilization of liquid phases or destabilization of competitive crystalline phases [20-23]. The stability of liquid phases could be realized by an increase of the atomic packing density in liquid state. That could be accomplished through additions of elements with proper qualities and quantities [24].

During heating process, an amorphous bulk metallic body is transformed to super-

cooled liquid state at glass transition temperature  $T_g$ . The stability of the supercooled liquid can be estimated by measuring the temperature region  $\Delta T_x$  before crystallization [25]. In amorphous alloy the presence of that region is due to suppression of the precipitation of crystalline phases and arrest of their growth. Such kind of suppression can result from high energy between the solid-liquid surfaces. The arrest of growth results from the need of reorganization of the alloy components in large distance on the boundary surfaces between both states solid and liquid [26].

The maximal difference  $\Delta T_x = T_g - T_x$  is in a good correlation with other properties, such as maximal density and minimal enthalpy of crystallization [27]. In this way,  $\Delta T_x$  can be regarded as one possibly simplest qualitative criterion for GFA. A large supercooled liquid region of amorphous alloy affords an opportunity for a larger time interval for thermal treatment [22; 28; 29].

Other parameters, which can be assumed as criteria for GFA, are the ratios  $T_g/T_l$  and  $T_g/T_m$  [12]. According to Turnbull, the reduced glass transition temperature  $T_g/T_l$  is among the crucial parameters for GFA in many eutectic compositions. A good GFA is predicted for the values of this parameter approximately  $2/3$  and higher. The high values for both  $\Delta T_x$  and  $T_g/T_m$  suggest large supercooled liquid regions and high stability against nucleation of crystalline phases in the corresponding alloys [30]. In some cases, it is established that the ratio  $T_g/T_l$  is a less precise index for optimal formation of nanocrystals than the difference  $\Delta T_x$  [27]. In other cases, the GFA is more closely related to  $T_g/T_l$  rather than  $T_g/T_m$  [31].

The developed Ln-, Mg-, Zr-, Ti-, Fe-, Pd-, Cu-based systems with GFA and cooling rate lower than  $0.06\text{K/s}$  have values for  $T_g/T_m$  up to  $0.7$  and close to  $0.74$  [31]. For amorphous Fe-based alloys, a tendency to increasing specimen thickness appears with increasing  $\Delta T_x$  and  $T_g/T_m$  [25].

The alloy  $\text{Zr}_{65}\text{Al}_{10}\text{Cu}_{15}\text{Ni}_{10}$  is one of the alloys possessing large supercooled liquid region  $\Delta T_x$ , over  $100\text{K}$  [24]. By additions of other chemical elements, many experimental investigations have been performed with this alloy in order to increase  $\Delta T_x$  and improve the GFA [21; 22; 24; 29; 30 and others]. A significant data base is stored. Applying a properly formulated Design of Experiments, these data could be used for derivation of mathematical models of  $T_g$  and  $T_x$  for Zr-based alloys [31]. Based on such models, the search for optimally increasing  $\Delta T_x$  as a criterion related to large GFA becomes possible. In the following sections, some relations between the atomic radii, atomic percents of additions, alloy mass, and temperatures of glass transition and crystallization for Zr-alloys will be presented and commented.

There exists a chemical similarity between Hafnium and Zirconium [32; 33]. Therefore, preliminary conclusions about possible properties of Hf-based alloys could be drawn on the basis of experimental results and conclusions obtained for Zr-based alloys [32-35]. Successful syntheses of Hf-based alloys  $(\text{Hf}_x\text{Zr}_{1-x})_{52.5}\text{Ti}_5\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}$ , with  $x=0$ ;  $0.33$ ;  $0.5$ ;  $0.66$  is reported in [32]. Linearly increasing density and hardness of these alloys are established with increasing Hf-contents. The conclusion is drawn that Hf-additions decrease the amorphization tendency in these alloys. Beginning with the well known Zr-Cu-Ni-Al glass forming alloy, replacing Zr with Hf and adding Ga in place of Al, a new Hf-based  $\text{Hf}_{50}\text{Zr}_5\text{Ti}_5\text{Cu}_{20}\text{Ni}_{7.5}\text{Al}_{10}\text{Ga}_2$  glass forming alloy has been obtained [34; 35]. It is also established that  $2.5\%$  substitution of Al with Ga increases the alloy vis-

cosity, as well the supercooled liquid region  $\Delta T_x$  with 20K.

Following the theory of amorphous metallic alloys with glass forming ability and similarity of Hf-based and Zr-based alloys, and also based on the theoretical statements referred here, in the next presentation mathematical models of chosen criteria for nanocrystallization of these alloys will be presented in polynomial type [31; 36; 37]. Analyses of the polynomial coefficients are performed. To improve GFA of Hf-alloys, optimal values of Zr-Ti, Ga-Ge-Si-additions together with Pd, Sn, Nd, Y, Ta-additions are found through formulation and solution of a few optimization tasks. Based on the comparisons between both the results modelled [31; 36; 37] and experimental [24; 34; 35; 38] and similarity with those reported in [32; 33], it is concluded that the proposed method could be successfully applied in design of new Zr- and Hf-based amorphous alloys with GFA.

The general prerequisites for obtaining new alloys with large GFA are given by three basic empirical rules [11; 12]. The practice suggests that the obtaining of such alloys principally depends on conducting a great number of experiments with step changing of the alloy contents. Actually, there is no universal method of predicting alloy contents with optimal GFA. Here, the proposed theoretic-mathematical modelling gives some ideas of the choice of additional elements and quantities with aim to reduce and optimize the experimental work and also to enforce the analytical instruments used in this field.

The empirical rules for obtaining large GFA pointed out are well known: (1) multi-component alloy with more than three elements; (2) large difference between the atomic radii of basic elements, more than 18-20%; (3) negative heat of mixing between the elements. At eutectic alloys, their application causes an increase of the density ratio of structure in chemical and topological aspects. As a result, liquids possessing new atomic configurations and multicomponent interactions in short distances are formed. They are basically characterised by:

1. Increase of surface energy on the solid-liquid boundaries, and as a consequence the suppression of the nucleation of crystalline phases happens, Fig. 1-3;
2. Atomic rearrangement causing decrease of atomic diffusion, increase of viscosity and as a consequence the increase of  $T_g$  happens;
3. Need of atomic rearrangement in long distance for beginning crystallisation processes, and as a consequence the suppression of the growth of crystalline phases, decrease of  $T_m$  and increase of  $T_g/T_m$  happen.

Obviously, the alloy components, their atomic parameters and interaction characteristics between them play the principal role. In the previously discussed technology, the large ability to form nanocrystalline metallic structures requires initially to obtain bulk amorphous alloys. That is a result of the high thermal stability of supercooled liquid against crystallization. The stability can be estimated through measurements or calculation of the temperature range of supercooled liquid before crystallization [12; 22; 23]. As it was seen, the temperature range  $\Delta T_x$  is defined by the difference between the recrystallization temperature  $T_x$  and glass transition temperature  $T_g$  [2]:

$$\Delta T_x = T_x - T_g \quad (1).$$