Formation of amorphous states in Ti_{50}Ni_{25}Cu_{25} alloy subjected to severe plastic deformation: Nanoglass issue

V Yu Slesarenko¹, D A Gunderov²,³, P G Ulyanov¹, R Z Valiev¹,²
¹Saint Petersburg State University, 28 Universitetskii pr., Saint Petersburg 198504 Russia
²Institute of Physics of Advanced Materials, Ufa State Aviation Technical University, 12 K. Marx str., Ufa 450000 Russia
³Institute of molecule and crystal physics RAS. 151 Prospekt Oktyabrya, Ufa 450075 Russia
E-mail: sl.slesarenko@gmail.com

Abstract. Peculiarities of structure and mechanical behaviour of amorphous Ti_{50}Ni_{25}Cu_{25} alloy were the focus of this research. Amorphous melt-spun ribbons and bulk crystalline samples were subjected to high pressure torsion (HPT) in order to modify their structure and mechanical behaviour. Some properties of obtained SPD-processed samples were compared with initial state with the help of x-ray diffraction (XRD), differential scanning calorimetry (DSC) and nanohardness tests. It was shown that according to XRD no nanocrystallization occurs during HPT of melt-spun ribbons yet at the same time high density of shear bands might be formed in the alloy. Due to the formation of shear bands with the excess free volume the decrease of hardness and crystallization temperature were observed in the alloy. Analysis of structural data and mechanical behaviour allowed us to assume, that SPD processing of melt-spun Ti_{50}Ni_{25}Cu_{25} alloy might lead to the formation of structural state similar to the new kind of noncrystalline state – “nanoglass” state.

1. Introduction
One of the most effective methods for modifying structure and properties of alloys is severe plastic deformation (SPD) [1; 2]. It was already shown [3; 4] that SPD methods, for instance high pressure torsion (HPT) may be used to produce amorphous or amorphous-crystalline alloys. At the same time, amorphous state, obtained by SPD, has some features in comparison with amorphous state, obtained by melt spinning technique. For instance, it was shown that in amorphous SPD-processed alloys crystalline debris may remain in amorphous matrix [4] and, moreover, according to [5; 6], nanocrystallization may occur during severe plastic deformation. In order to prevent such nanocrystallization and obtain homogeneous amorphous state it is necessary to choose special regimes of SPD.

Furthermore, just several years ago the new kind of noncrystalline materials, called “nanoglasses”, was revealed [7]. Structural state of nanoglasses may be characterized as amorphous, but they have some features in structure, that leads to the significant difference of the physical properties and mechanical behaviour in comparison with amorphous state. Nanoglasses consist of amorphous nanoclusters (size about 5 nm), separated by amorphous interfaces [7; 8]. First nanoglasses were
produced mainly by inert-gas condensation or magnetron sputtering. These techniques can be used only to obtain very small volumes of the materials. At the same time, there are several premises, which allow one to assume, that nanoglass state may be produced by means of SPD. For example, it was shown that relatively high density of shear bands is formed during SPD [9]. Under conditions when nanocrystallization is suppressed, these shear bands may result in the atomic structure changes and the obtained structure may be similar to the “classical” nanoglasses. As far as SPD may be used to obtain bulk nanostructured materials, it is important to study a possibility of the producing the bulk nanoglasses using the SPD methods. The global goal of this and following works is to produce nanoglass state by SPD. In this particular article some preliminary results are presented to determine the direction of the following studies.

2. Experimental procedure
Several amorphous states of Ti₅₀Ni₂₅Cu₂₅ alloy were studied. A few sets of samples were obtained using different techniques. Samples from the first set were produced by melt-spinning. Then some of these samples were subjected to HPT on 10 rotations of Bridgman anvils under pressure of 8 GPa at the room temperature. The rotation speed was 1 rotation per minute. Hence, these samples were produced on the base of amorphous melt-spun ribbons. For comparison, third set of samples was obtained by HPT under the same conditions but from the initial crystalline state.

To study structure of produced samples as well as physical and mechanical properties several techniques were used. The structure of the samples was investigated by X-ray diffraction under the Co and Mo radiation at Bruker Phaser D2. To reveal mechanical properties, nanoindentation tests were performed at nanohardness module of SPM Integra. As far as some peculiarities of amorphous state may influence crystallization behavior, thermal effects were investigated by heating up to 550 °C with a heating rate of 20 °C/min in the chamber of NETZSCH DSC 204F1 Phoenix differential scanning calorimeter.

3. Results and discussion
Figure 1 shows the X-ray diffraction patterns of the produced samples. It is clear that despite the assumption that melt-spun ribbons should be amorphous, several sharp peaks appear on corresponded curve. That allows us to assert that these samples contain not only amorphous phase but also crystalline inclusions. Based on the XRD patterns, volume fraction of crystalline phase in initial melt-spun ribbons is estimated as 10-15 %. At the same time, it is clear that the structure of the melt-spun ribbons subjected to HPT is amorphous because no peaks are observed on the XRD patterns curve. After SPD samples show only one broad peak indicating that all crystalline inclusions, observed after melt spinning, disappear and no obvious crystallization takes place during HPT. As one may see from Figure 1, several peaks, corresponding to crystalline phase, are observed on XRD pattern for crystalline alloy subjected to HPT (curve c). The volume fraction of crystalline phase in these samples may be estimated as 30-35 %. Thus, one may suggest that under chosen conditions HPT of the initially crystalline Ti₅₀Ni₂₅Cu₂₅ alloy leads only to partial amorphization.
Despite the fact that XRD reveals that not all samples are completely amorphous, nanohardness tests were performed to evaluate their mechanical properties. Typical depth-load curve is shown in Figure 2. Nanoindentation shows that average hardness ($H_v$) of initial melt-spun ribbons as well as the samples, subjected to HPT, are about 7-8 GPa. Calculated $H_v$ values for melt-spun ribbon, SPD-processed ribbon and SPD-processed crystalline alloy were 8.1, 7.4, 7.6 GPa, respectively (Table 1). According to Table 1, the hardness of melt-spun ribbon decreases after HPT in comparison with initial state. It is well-known [9] that SPD not only leads to amorphization of crystalline phase, but also causes significant changes in the structure of the amorphous state. During HPT high density of shear bands forms in amorphous phase. These shear bands are characterized by greater free volume in comparison with “regular” amorphous state. Therefore, the decrease of hardness of amorphous alloy after HPT may be caused by formation of regions with excess free volume due to increase of the shear bands density. In addition, from the depth-load curves, the elastic modulus can be also derived to be 83 and 86 GPa for melt-spun ribbon and SPD-processed ribbon respectively (Table 1). At the same time, the elastic modulus of SPD-processed crystalline alloy is lower than for amorphous and its value is equal to 79 GPa. As far as XRD revealed that initial melt-spun ribbon contains the crystalline inclusions and the crystalline phase of Ti$_{50}$Ni$_{25}$Cu$_{25}$ may undergo martensitic transformation during nanohardness tests, the elastic modulus of initial melt-spun ribbon may be slightly understated. As far as increasing of the elastic modulus caused by HPT is relatively small, more accurate measurements are needed to be performed.

**Table 1. Mechanical characteristics of obtained samples**

| Sample                        | Hardness (GPa) | Elastic modulus (GPa) |
|-------------------------------|----------------|-----------------------|
| Initial melt-spun ribbon      | 8.1            | 83                    |
| SPD-processed melt-spun ribbon| 7.4            | 86                    |
| SPD-processed crystalline alloy| 7.6            | 79                    |

It is well-known [10], that kinetics of crystallization and accompanying processes occurring during the heating of amorphous alloys to high temperatures may help one to characterize structural state of alloy. As far as XRD revealed that all obtained samples have diverse structural state, it is logically to expect that melt-spun ribbons and SPD-processed samples would have different crystallization behavior. To study the crystallization process the samples were heated up to 550 °C at the speed rate of 20 °C/min. Figure 3 shows calorimetric curves obtained during heating. The exothermal peak corresponded to crystallization process is clearly seen on the two curves in Figure 3 (curves a, b). A comparison of the calorimetric curves reveals that the crystallization of the initial melt-spun ribbons takes place at the higher temperatures ($T_p=462$ °C) than the crystallization of the melt-spun ribbons subjected to HPT ($T_p=440$ °C). Moreover, the crystallization of melt-spun ribbons occurs in more narrow temperature range in comparison with SPD-processed samples. There are several possible explanations of such crystallization kinetics. Firstly, decreasing of the crystallization temperature after HPT may be caused by formation of shear bands during SPD. As it was mentioned before, significant increase of the density of shear bands due to SPD leads to growth of the value of excess free volume. The broadening of the temperature range of crystallization may also be caused by structural changes occurred during HPT. The shear bands are formed during deformation, but some inhomogeneity in strain occurring at the high pressure torsion may lead for instance, to minor difference in density of shear bands and consequently excess volume in the different regions. As one may see, there is no
obvious crystallization exothermic peak observed in the DSC curve obtained on heating up to 550 °C of SPD-processed crystalline alloy (Figure 3, curve c). At the same time, it is seen that some exothermal processes take place in the temperature range 350 – 550 °C. As far as XRD measurements previously revealed that SPD-processed crystalline sample has got mixed amorphous-crystalline structure, these exothermal processes may be caused by some local crystallization as well as a grain growth and recrystallization of crystalline grains. More detailed study is needed for clarification. At the same time, it is very clear, that SPD conditions should be drastically changed to provide more developed amorphization of crystalline Ti₃₀Ni₂₅Cu₂₅ alloy. This issue also will be studied later.

Therefore, the comparison of the properties of initial melt-spun ribbons and SPD-processed amorphous and crystalline alloys by several experimental techniques reveals significant structural changes and mechanical properties. Based on the difference of hardness and the crystallization temperatures of melt-spun ribbons before and after HPT one may assume that these changes are connected principally with the formation of high density of shear bands in the amorphous phase. As it was mentioned before, the new kind of materials “nanoglasses” should have a specific structure with amorphous nanoclusters, separated by amorphous interfaces. These very thin interfaces have enhanced free volume in comparison with interior of nanoclusters [7]. On the base of this work, it seems that SPD-processed melt-spun amorphous ribbons have the similar structure. Therefore, one may expect that such alloys are able to demonstrate the mechanical behavior similar to the “classical” nanoglasses, for instance, it is expected, that such alloys should have much greater plasticity in comparison with amorphous state. The accurate measurements are still needed to confirm or disprove this assumption and a detailed study will be carried out in the on-going research.

4. Conclusion
In summary, it was shown that:
1. High pressure torsion of the melt-spun Ti₃₀Ni₂₅Cu₂₅ ribbons leads to their complete amorphization. At the same time 30-35 % of crystalline phase remains in the crystalline Ti₃₀Ni₂₅Cu₂₅ alloy subjected to HPT under the same conditions;
2. HPT causes the decrease of hardness and crystallization temperatures of melt-spun ribbons possibly due to the formation of high density of shear bands;
3. The amorphous structure of the melt-spun Ti₃₀Ni₂₅Cu₂₅ ribbons subjected to SPD displays similarity to the structure of nanoglasses [7] produced by inert-gas condensation, but this assumption needs further in-depth studies.

Acknowledgements

The authors are grateful to Dr V.G. Pushin for preparation of the initial melt-spun ribbons.

The authors acknowledge gratefully the Russian Ministry of Education and Science for the financial support of this study through project № 14.B25.31.0017. The scientific research was performed at the Research Centre for X-ray Diffraction Studies, Interdisciplinary Resource Center for Nanotechnology and Research Center of Thermal Analysis and Calorimetry of St.Petersburg State University.
References

[1] Valiev R Z, Zehetbauer M J, Estrin Yu et al. The Innovation Potential of Bulk Nanostructured Materials 2007 Adv. Eng. Mater. 9 7 527–533.
[2] Valiev R, Islamgaliev R and Alexandrov I. Bulk nanostructured materials from severe plastic deformation 2000 Prog. Mat. Sci. 45 103-189
[3] Huang J Y , Zhu Y T, Liao X Z and Valiev R Z Amorphization of TiNi induced by high-pressure torsion 2004 Philos. Mag. Lett. 84 3 183–190.
[4] Sergueeva A V, Song C, Valiev R Z and Mukherjee A K Structure and properties of amorphous and nanocrystalline NiTi prepared by severe plastic deformation and annealing 2003 Mater. Sci. Eng. A. 339 1 159–165.
[5] Valiev R Z, Gunderov D V, Zhilyaev A P, Popov A G and Pushin V G Nanocrystallization induced by severe plastic deformation of amorphous alloys 2004 Journal of Metastable and Nanocrystalline Materials 22 21-26
[6] Glezer A M, Zaichenko S G and Plotnikova M R Nature of nanocrystallization in shear bands created by megaplastic deformation in amorphous alloys 2012 Bull. Russ. Acad. Sci. Phys. 76 1 54–60.
[7] Gleiter H Nanoglasses: a new kind of noncrystalline materials 2013 Beilstein J. Nanotechnol. 4 517–533.
[8] Andrievski R A Metallic nano/microglasses: new approaches in nanostructured materials science 2013 Physics-Uspekhi 56 3 261–268.
[9] Wang X D, Cao Q P, Jiang J Z et al. Atomic-level structural modifications induced by severe plastic shear deformation in bulk metallic glasses 2011 Scr. Mater. 64 1 81–84.
[10] Inaekyan K, Brailovski V, Prokoshkin S et al. Characterization of amorphous and nanocrystalline Ti–Ni-based shape memory alloys 2009 J. Alloys Compd. 473 1-2 71–78.