Properties of Ni-based amorphous ribbons consolidated by high pressure torsion.

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Abstract. Two amorphous ribbons, of compositions (Ni_{56}Cu_{2})Zr_{18}Ti_{16}Al_{3}Si_{5} and (Ni_{36}Cu_{23})Zr_{18}Ti_{14}Al_{5}Si_{4}, were subdued to the similar process of cold consolidation by the high pressure torsion (HPT) method. The first ribbon, that revealed higher thermal stability of the amorphous phase, higher GFA and better mechanical properties like tensile strength, Young modulus and hardness, partially crystallized in the HPT process. The second ribbon, revealing lower T_{g} and T_{x} temperatures, tensile strength and hardness, could be consolidated preserving amorphous structure. Such result suggests that the thermal stability against crystallization was not responsible for the preservation of the amorphous phase in the cold consolidation by the HPT. It rather seemed that a proper relation of the undercooled liquid temperature range to the local temperature increase during consolidation is suggested and it was a decisive parameter.

1. Introduction
The method of high pressure torsion (HPT) was invented for fabrication of the bulk nanostructured materials, quite often revealing extraordinary phase composition, mechanical and magnetic properties [1]. The microstructure produced by HPT is generally metastable, and may relax in a much lower temperatures than in the coarse-grained samples [1]. The HPT method was also successfully applied for consolidation of the powder or milled powder samples [1]. In case of the amorphous materials the method was applied to produce massive samples from the melt-spun ribbons by consolidation at room temperature [2-4]. This application is especially interested for the amorphous alloys relatively easy to achieve with melt spinning methods but hard to prepare in the form of the bulk amorphous samples. The large strains in HPT may induce crystallization in the amorphous matrix [2,3,4]. It is considered that the crystallization is athermal in nature [5]. The crystallization induced by HPT reveals the dependence of the distance to the rotation axis, and on the range of the accumulated shear strain. It also affects the path of the further, thermal crystallization of the remaining amorphous phase [4]. The paper presents results of cold consolidation by the HPT method of two amorphous ribbons of Ni(Cu)-(Zr,Ti)-Al-Si compositions, in comparison with the properties of the as quenched ribbons.

2. Experimental
Two alloys of the compositions (Ni_{56}Cu_{2})Zr_{18}Ti_{16}Al_{3}Si_{5} (Ni-1) and (Ni_{36}Cu_{23})Zr_{18}Ti_{14}Al_{5}Si_{4} (Ni-2),
were made from the components of 3N and 4N purity, by the levitation method, under an argon atmosphere. The alloys were several times re-melted, and shaped. Later the ribbons were prepared by melting in quartz crucibles and spun on the CuCoBe rotating disc 20 cm in diameter. The 19 m/s linear velocity of the disc and 160 mbar pressure of He gas were used. HPT cold consolidation of the ribbons was performed in the following way: the ribbons were cut into 10-12 mm pieces and six parts of each was consolidated in quasi-hydrostatic conditions under the pressure of 6GPa, two full turns were applied. The Bridgman anvils were 8 mm in diameter.

3. Results

3.1. Characterisation of the ribbons
The XRD patterns of the ribbons corresponding to their both sides are shown in figure 1a. The characteristic broad symmetric halos around 25 deg. (Cu Kα radiation was used) were typical for the amorphous microstructure. Also TEM microstructures and electron selected area diffraction patterns (SADP) confirmed the amorphous microstructure (figures 1b,c). The DSC analysis of the thermal stability of the amorphous phase was performed by continuous heating with the rate 0.50 Ks⁻¹. The glass transition temperature \( T_g \) (measured at the inflection point) and primary crystallization temperature \( T_x \) (at the onset) in the ribbon Ni-2 were lower by 32 and 48 K respectively in comparison with the ribbon Ni-1. The enthalpy of crystallization \( \Delta H \) 69 J/g for the ribbon Ni-2 was slightly higher than for the ribbon Ni-1, 66 J/g. The DSC results are presented in table 1. The melting temperature \( T_m \) for both alloys was very similar but the liquidus temperature \( T_l \) of the alloy Ni-1 was much higher, as a result of multi-phase composition (table 1). To compare the ability for crystallization in the solid state the activation energy and \( \Delta G \) at temperature \( T_g \) were determined for both alloys. The activation energy was determined by the Kissinger method and \( \Delta G \), which at \( T_g \) is proportional to the

![Figure 1](image1.png)

Figure 1. a) XRD from the ribbons Ni-1 (two sides) and Ni-2; TEM microstructure and SADP from the ribbons: b) Ni-1, c) Ni-2.

| \( T_g \) [K] | \( T_x \) [K] | \( \Delta H_c \) [J/g] | \( \Delta T \) [K] | \( \Delta G \) [J/(Kmol)⁻¹] | \( \Delta E \) [J/(Kmol)⁻¹] | \( T_m \) [K] | \( T_l \) [K] | \( \Delta H_m \) [J/g] | \( T_{g}/T_{l} \) | \( T_{l}/T_{m} \) | \( T_{g}/(T_{g}+T_{l}) \) |
|-------|-------|--------|--------|-----------------|-----------------|-------|-------|--------|---------------|---------------|---------------|
| Ni-1  | 845.0 | 878.4  | 66.2   | 33.4            | 9.65            | 486.4 | 1242.5| 1284.3 | 46.0          | 0.66          | 0.68          | 0.41          |
| Ni-2  | 813.0 | 830.6  | 68.7   | 17.6           | 11.37           | 449.8 | 1241.3| 1262.9 | 52.6          | 0.64          | 0.65          | 0.40          |

force for crystallization [6] was calculated with the equation \( \Delta G = 4\Delta H_m T^2(T_m-T)/[T_m(T_m-T)^2] \) [7] where \( T=T_g \). As is visible from table 1, all the calculated parameters connected to the glass forming ability (GFA) decreased for the alloy Ni-2. The activation energy and the force for crystallization at \( T_g \) exhibited higher tendency for the crystallization in the case of alloy Ni-2. The tensile test and microhardness measurements show that ribbon Ni-1 revealed strength hardness 9.07 GPa and elastic
modulus 120.38 GPa, higher than ribbon Ni-2, which had microhardness and elastic modulus 7.76 GPa and 97.67 GPa respectively.

3.2. Characterization of the cold consolidated samples
The optical microscopy and SEM were used to control the quality of the consolidation along the cross-section perpendicular to the surfaces. It was found that until some distance from the rotation axis the consolidation was not complete while in more distant sections of the samples the consolidation was very good (figure 2). This let to estimate the minimal average strain indispensable for the full consolidation of the material. The equation \( e = \ln(1+(\phi \cdot R/h)^2) \)\(^{1/2} \), where \( \phi \), \( R \), \( h \) are rotation angle in radians, the distance from the rotation axis and local thickness respectively [8] gives the minimal strain for consolidation equal to 4.0±0.1. Microstructure of the consolidated samples was investigated with XRD and TEM. As is visible from figure 3, sample Ni-1 crystallized in some part, retaining predominantly amorphous phase, contrary to the sample Ni-2 which remained amorphous. TEM analysis generally supported the results. The microstructure of the sample Ni-1 was not homogenous. It consisted on amorphous matrix, parts where nanocrystals formed (figure 4a), and the separated crystals of the different phases, of the size about 1-2 \( \mu \text{m} \), which revealed type of dendritic growth (figure 4b). In case of the sample Ni-2 after consolidation the TEM images of the microstructure and SADP’s were from the amorphous material (figure 4c).

The DSC curves comparing glass transitions and crystallization processes of the ribbons and the cold-consolidated samples are shown at figure 5. In case of the sample Ni-1 \( T_x \) temperatures are similar and the \( \Delta H_c \) for primary crystallization is lowered by 10% in comparison with the ribbon. In case of the sample Ni-2 the \( \Delta H_c \) is lowered by 18% and \( T_x \) temperature by 2 K. In spite of the similarities in the primary crystallization effects, the complete crystallization may be slightly different as the secondary crystallization effects differ between cold-consolidated samples and the ribbons. More complicated changes were observed in the case of glass transition. After HPT \( T_g \) increased by 4 K for sample Ni-1, while for the sample Ni-2 decreased by 7.5 K, increasing undercooled liquid range from 17.6 to 23 K in comparison with the ribbons.
4. Discussion

Two amorphous ribbons Ni-1 and Ni-2, different in composition, were subjected to the process of cold consolidation by the HPT with the same parameters. The ribbon Ni-1, that contained less Cu and Al, and more Zr than the ribbon Ni-2, revealed higher thermal stability against crystallization, higher tensile strength, Young modulus and microhardness, partially crystallized during cold consolidation, while the ribbon Ni-2 preserved amorphous structure. Such result suggests that thermal stability is not determining amorphous phase preservation in the HPT process. As the temperature in HPT process may increase due to the friction [9], the relation of the undercooled liquid temperature range to the temperature of consolidation may be decisive. If consolidation takes part in the ΔT range and time and temperature of the process are not enough for the isothermal nanocrystallization, the amorphous phase may be preserved. Additionally lower hardness and Young modulus of the ribbon should support easier consolidation. These conditions were fulfilled rather by the ribbon Ni-2 then Ni-1. The DSC experiments showing changes both in the crystallization process, ΔT range and glass transition temperature of cold consolidated samples, but different for each of them, supports such a mechanism. The results concerning process of crystallization as a result of HPT and differences in the subsequent crystallization of the cold consolidated samples are in a good agreement with other papers [3,4,5].

5. Conclusions

It was shown that in some cases Ni-based amorphous ribbons may be cold consolidated by HPT preserving amorphous microstructure. In most cases however partial crystallization took place. The decisive parameters must be the subject of the further investigations.

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