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STRUCTURAL EVOLUTION OF THE NiTi/NiFeGa SMART HYBRID MATERIAL DURING SEVERE PLASTIC DEFORMATION

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High speed high pressure torsion (HSHPT) a patented new approach is proposed to fabricate nanocomposites. The goal of this work is to investigate the NiTi/NiFeGa bilayer hybrid material with nano- and submicrocrystalline structure under the influence of HSHPT. Apart from the grain refinement, the effectiveness of the joint are revealed scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The mechanical properties of the composite layers in bulk and after severe plastic deformation are investigated. Bi-layered composite disks consisting of NiTi shape memory alloy and NiFeGa - Heusler type alloy, exhibit thermoelastic structural martensitic transformation. Submicrocrystalline structure is formed in the both layers of the hybrid material. It is also ascertained significant hardening of each layer of the hybrid as a result of HSHPT. The results highlight market differences between the bulk and the hybrid and the role of severe plastic deformation on martensitic transformation.

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1. Introduction

Bulk submicrocrystalline materials produced by severe plastic deformation (SPD), have been extensively explored due to their superior mechanical properties [1-3]. Among various methods to fabricate submicron metallic materials is high speed high pressure torsion (HSHPT). This method is amid the most effective methods that can refine coarse-grained structures to ultrafine-grained (UFG) and nanocrystalline (NC) materials [4-6]. The grain refinement processes to UF (< 1000 nm) and NC (< 100 nm) are fairly sophisticated needing the long-range redistribution of different components in alloy. This SPD technology lead to exceptionally high strength and hardness and low-temperature superplasticity even in the case of very brittle at low temperature, large grain size or in as-cast state alloys.

Shape memory alloys (SMAs) are a class of intermetallic materials capable to remember their previous shape when subjected to variation of thermo-mechanical certain stimuli [7] based on a diffusionless reversible martensitic transformation (MT). Through this class, NiTi is the most attractive one, for excellent shape memory effect and pseudoelasticity. Most SMA devices are produced from NiTi being used in many fields [8]. NiTi is characterized by good corrosion, wear and fatigue resistance, as well as biocompatibility [9]. A special class of shape memory alloys is that of Heusler alloys. Families of Heusler type alloys, that undergo a MT, such as Ni-Fe-Ga [10, 11], Co-Ni-Ga [12], Ni-Mn-(Ga, Al, In, Sn) [13, 14, 15], have been extensively studied due to the applications their properties offer, such as the magneto-caloric effect, magneto-resistance effect, magnetic field induced strain. The Ni-Fe-Ga Heusler alloys drawn much attention because of the practical advantage of its better ductility which is associated with the presence of a second γ face-

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centered cubic (fcc) phase. [16, 17].

Metallic composite materials have attracted attention latterly due to their special properties. In fact, many researchers have studied various composites with SMAs as matrix with high mechanical strength, fracture toughness and damping performance or superior superelasticity [9], [18-25]. In view of this, SMA/Heusler composites seem to possibly own outstanding mechanical and physical properties. NiTi/NiFeGa bilayer hybrid material with nano- and submicrocrystalline structure may offer new opportunities for applications as miniaturized active elements for sensors, actuators as well as in MEMS devices and other functional devices [26, 27]. And it is expected that such type of composite is in favor to develop state-of-the-art structures having simultaneously shape memory and magnetic properties.

SPD technique are very promising not only for improvement of functional properties of SMAs by reducing the grain size but recently are developed for fabrication of bimetallic composite [28]. HSHPT severe plastic deformation machine that combine stir friction and high pressure torsion technology demonstrate capability to bond submicron metallic alloys.

The goal of this article is to investigate bi-layered composite disks consisting of NiTi shape memory alloy and NiFeGa, Heusler type alloy by HSHPT technology. One such a hybrid composite may simultaneously exhibit ferromagnetism and thermoelastic martensitic transformations by combining the excellent shape memory effect of the NiTi alloy with the NiFeGa specific magneto-structural properties.

2. Procedure and materials

The NiTi Ni rich SMA alloy ($Ni_{50.3}Ti_{49.7}$) commercial available was selected for the present study. The $Ni_{57}Fe_{18}Ga_{25}$ alloy were prepared by arc melting under argon protective atmosphere from high purity elements, and subjected to a thermal treatment in high vacuum for 25 h at 1223 K, followed by a quenching in iced water. The alloys were cut into specimens of suitable dimensions and subjected to SPD by HSHPT technique. To enable structure refinement concurrent with bonding of layers, SPD parameters were selected: the rotational speed of the upper punch was selected at 900 rpm, the initial pressure applied from the bottom punch was 20 bars. The pressure levels recorded were under 1GPa. The microstructural examinations were carried out on a Zeiss scanning electron microscope to study the grain structure and the quality of joints. EDX investigations were carried out to determine the chemical composition across the width and joints of the bi-layered composites. The microstructure was also studied by using a transmission electron microscope (Tecnai 20G2) operating at a voltage of 200 kV. The hardness was measured using a Vickers microhardness tester under a load of 0.98067N (HV0.1) applied for 10s.

3. Results and discussion

Fig. 1 illustrates the morphologies of severely plastic deformed $Ni_{50.3}Ti_{49.7}$/ $Ni_{57}Fe_{18}Ga_{25}$ observed under the scanning electron microscope. The micrographs of the bi-layered composite show a distinct interfacial region as well as each of the two layers fine structure. As can be seen in Fig.1a, the interfacial area is continue and uniformly extended along the shear direction. The interface between NiTi and NiFeGa is identifiable but show no evidence of atomic diffusion or intermetallic phases. This observation was confirmed by EDX line scan analyses (Fig.4). Withal, the quality of the bonding is visible. The microstructural aspect of both layers is congruent with refinement expected after severe deformation by HSHPT. The pronounced grain refinement can be easily seen in micrograph focus on NiTi dark layer (Fig.1b). This layer reveals a highly deformed austenite microstructure which are dense with equiaxed darker area. There, near bonding area, is a homogenous distribution of spherical second-phase particles throughout the structure. The particles is prevailing $NiTi_2$ (composed of 55.59 at% of Ti and 44.41 at% of Ni) as is determined from SEM-EDS point analysis. The NiFeGa layer are denser and nearly homogenous (Fig.1c). The deformed $Ni_{57}Fe_{18}Ga_{25}$ layer shows a martensitic matrix with no evidence of grain boundaries which is in good agreement with the following TEM microstructural characterization from figure 6b-d. The ϒ second phase, with face centered cubic (FCC) type structure, is present describing flow lines.

SEM-EDS point analysis was performed in 5 areas belonging to the both layers (Fig.2). Despite SEM-EDS is a semi-quantitative technique, it is still possible to observe the tendency of percentage layers composition after HSHPT deformation, as presented in Table 1. There can be observed that the atomic percentage of Ni and Ti are always similar through the NiTi SMA layer (Fig.2 points 3 and 4). The NiFeGa layer shows characteristic dual-phase features: a martensitic phase with fine structure that constitute the matrix and somehow orderly islands of second phase.

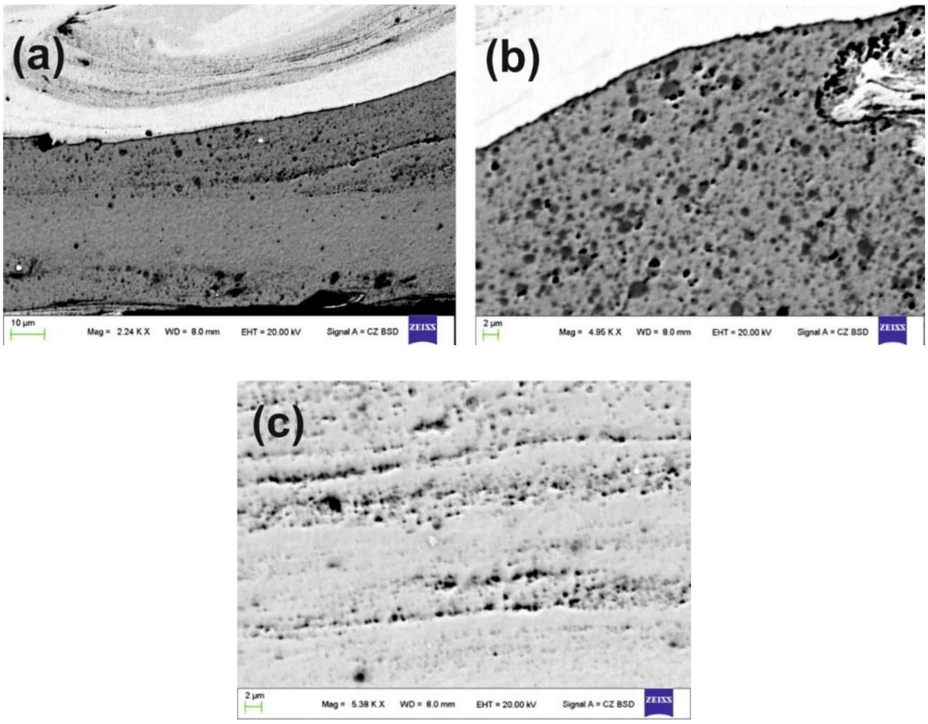

Fig. 1. Cross-sectional secondary electron images of NiTi/NiFeGa composite: at interface (a), focus on NiTi (b) and on NiFeGa (c).

Table 1 shows the composition content of the $Ni_{57}Fe_{18}Ga_{25}$ alloy on the matrix and second phase in points denoted with 1, 2 and 5 from Fig. 2. The Ni content is about the same in all location on the surface of Heusler alloy.

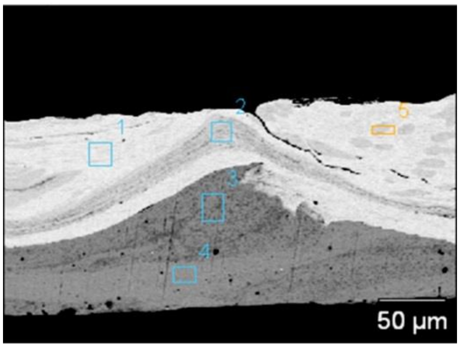

Fig. 2. EDX patterns of scanned area from composite (a) and (b) chemical composition on points denoted in (a).

The martensitic matrix displays a richer content in Ga but leaner in Fe, as compared to the second-phase precipitates Additionally, visible islands of second-phase, are clearly identified into the NiFeGa alloy layer (Fig. 2). In some areas of this layer the islands are elongated on the plastic deformation curves and in others remain equiaxed.

Table 1. Composition of the Ni57Fe18Ga25 alloy on the matrix and second phase

Point	Ti-K	Fe-K	Ni-K	Ga-K
1	-	15.74	54.74	29.52
2	-	20.46	54.24	23.79
3	44.62	0.43	53.88	-
4	45.85		54.15	-
5	-	19.80	55.66	24.53

Fig. 3 shows the representative microstructure of bi- layered composite comprising the interface between NiTi and NiFeGa, and the corresponding EDX mapping of chemical element distribution for the interface.

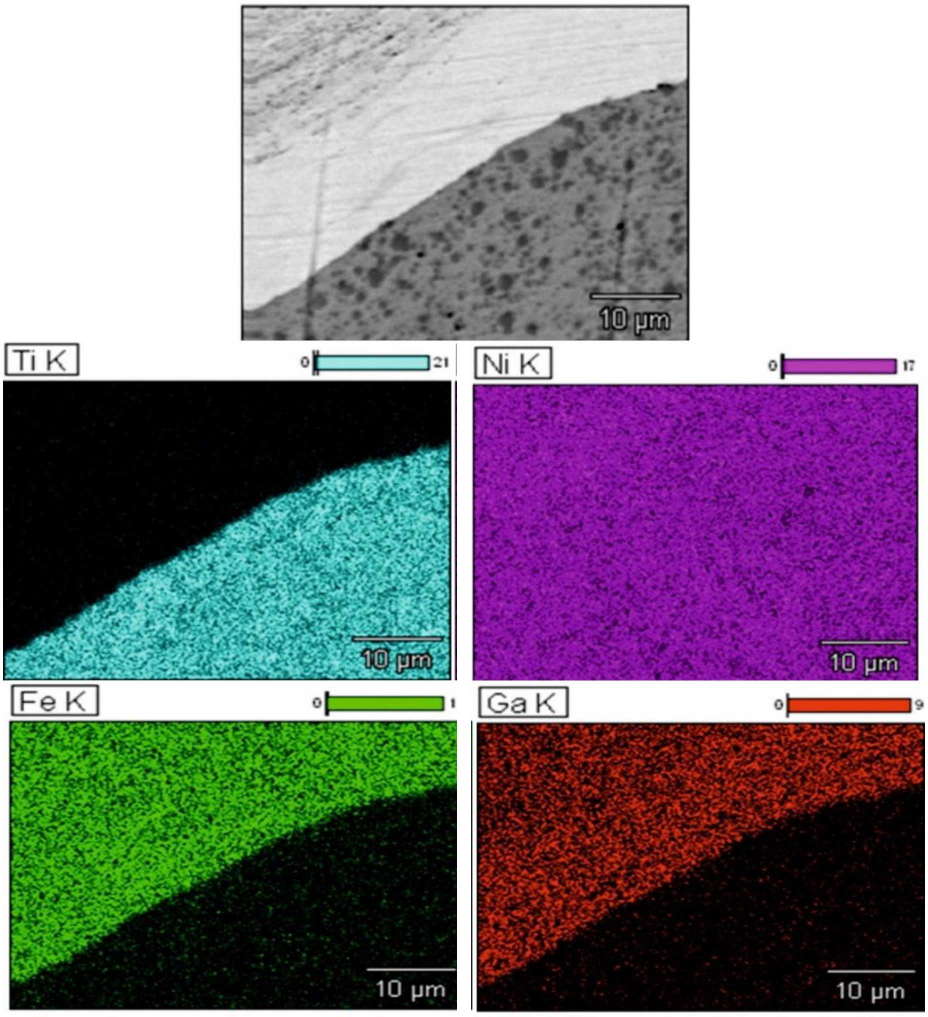

Fig. 3. EDX mapping of chemical element distribution of NiTi/NiFeGa hybrid composite.

As shown in this figure, it is noted that layers are well-bonded metallurgically with no interfacial reaction zone formed between NiTi and NiFeGa in SPD composite. EDX analysis reveals that Ti are presented only in NiTi layer. On the contrary, EDX mapping for Ni highlight its presence spread all over the composite. Furthermore, it is worth noting that the concentration of Ni is not emphasis between the two layers. Additionally, Fe and Ga can be observed clearly just into Heusler alloy layer.

Fig. 4 shows EDX line scan analyses along the full thickness of bi-layer NiTi/NiFeGa composite. SEM-EDS analysis was performed on the entire width of the composite, starting in the NiFeGa material, crossing the fusion zone and finishing on the NiTi base material. In the NiTi dark gray layer only content in Ti and Ni are noticeable. The Ti content decreases sharp on approaching the Heusler alloy layer whilst the Fe and Ga content increases. In the NiFeGa layer no traces of Ti are visible. The line scan during EDX analysis show homogenous elemental distribution in NiTi layer. The NiFeGa layer reveals variation in the Ni, Fe and Ga content corresponding to the dual-phase features.

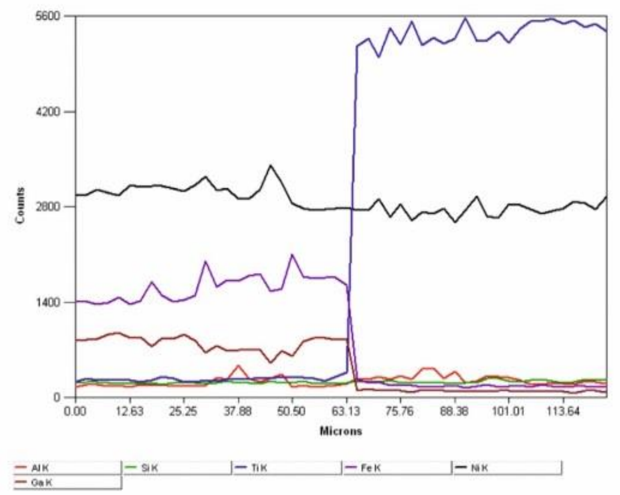

Fig. 4. Line scan by EDX across the full thickness of bi-layer NiTi/NiFeGa composite highlighting the variation of chemical composition at interface.

The martensite matrix is going with rise of Ga content and drop of Fe content. The composite interface appears very well defined. The formation of intermetallic phases reported after other HPT type of process [28] does not occur at this interface. An abrupt increase in the Ti content is noticed on approaching NiTi layer. The absence of intermetallic layer at the NiTi/NiFeGa interface may be attributed to the very short time of deformation. The entire process last less than 10s causing presumably a very low diffusion rates. This even the temperature increases by means of friction developed between sample and anvils during HSHPT. The inherent oxide layers on the surface amid this composite likely is broken down due to shear straining under high pressure induced [28]. However, HSHPT leads to a good contact all along the NiTi and NiFeGa disks on the strength of imposed high pressure. Anyway, the appearance of a slight slope of Fe and Ga content on a distance of 2.5 micrometers near interface demonstrate the mobility of these atoms.

The SEM micrograph and EDX mapping analysis of by-layer composite is commonly used in evaluation of the interfacial zone of composites [29]. SEM-EDX of NiTi/NiFeGa hybrid composite after HSHPT with 2.3 logarithmic degree of deformation confirmed joint produced by this SPD (Fig. 5). More than that no evidence of atomic diffusion or intermetallic phases are observable. The appearance of a clear delineation of the layers without an intermediate layer is highlighted along the whole fusion zone. A sharp interface between layers is visible in all images from Fig.5 based on morphology and chemical composition distribution of the elements. The presence of Ni element is noticeable on each layer. The Ti distribution profile appear just in NiTi layer. Also the Fe and Ga elements distribution profile is only found in NiFeGa layer.

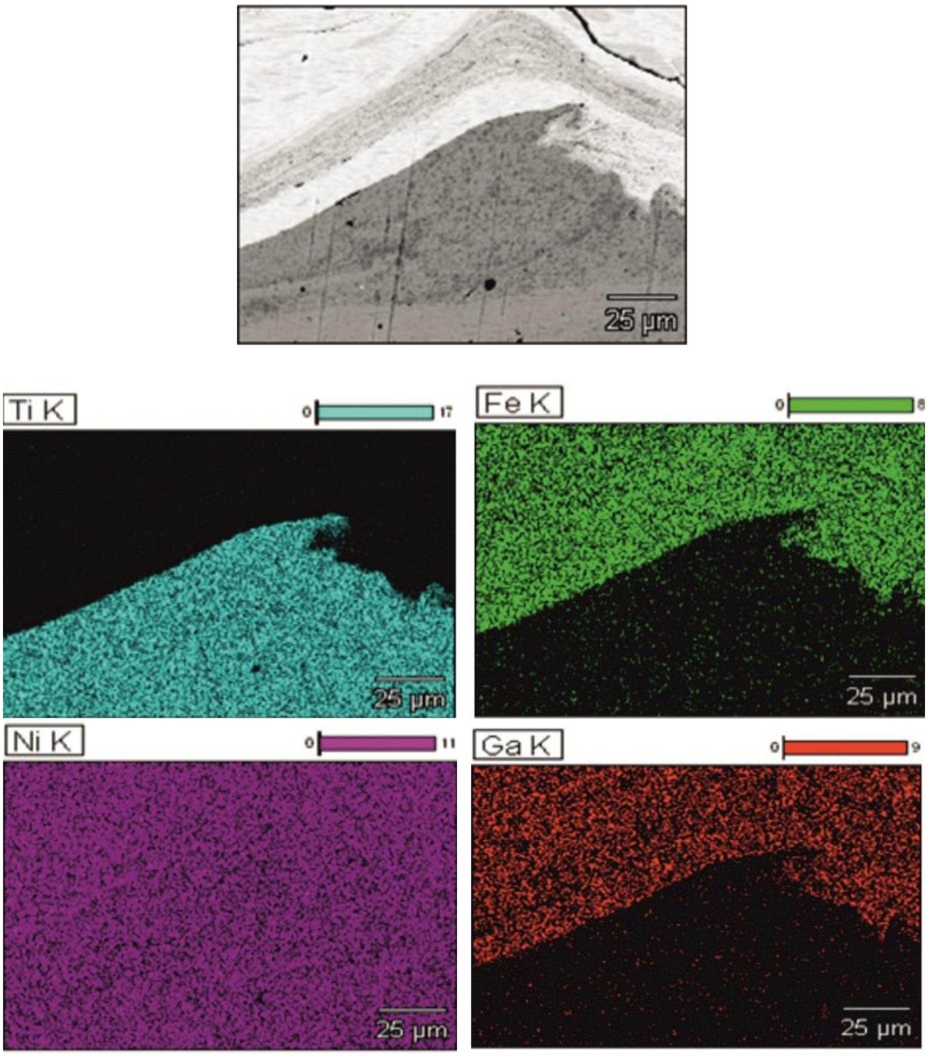

Fig. 5. EDX mapping of chemical element distribution of NiTi/NiFeGa hybrid composite after HSHPT with 2.3 logarithmic degree of deformation.

In order investigate the morphology of NiTi/NiFeGa composite in more detail and confirm the refinement of each layer was performed TEM investigation.

The deformation process introduced by high speed high pressure torsion not only provoked fusion between NiTi and NiFeGa but also refined grain structure. Fig. 6a displays the bright field image of NiTi layer after HSHPT which outlines B2 austenite and dislocation cells specific severe plastic deformation processes. Fig. 6 b-d present the bright field images and SAED pattern of martensite for NiFeGa layer after HSHPT. TEM micrograph from Fig. 6b shows a heavily distorted dual-phase microstructure of martensitic lamellae and ɡ phase of NiFeGa layer. The grains boundaries delineates small grains of about 100nm of fine martensitic twins beside larger ones ultrafine-grains (under 1 µm). The ultrafine grained martensite is surrounded by serrated stress fields as is typical in severe plastic deformation. HSHPT causes the increase of grain boundaries area but not to the same extent of dislocation density as classic HPT method. In the center of image are clearly identifiable zig-zag shape of twin boundaries. Fig. 6c highlights martensite plates twinned and well self-accommodated. As can be seen from the image, the martensite twins are very thin (on the order of 20-30nm). The SAED pattern shows spots of martensitic matrix (Fig. 6d).

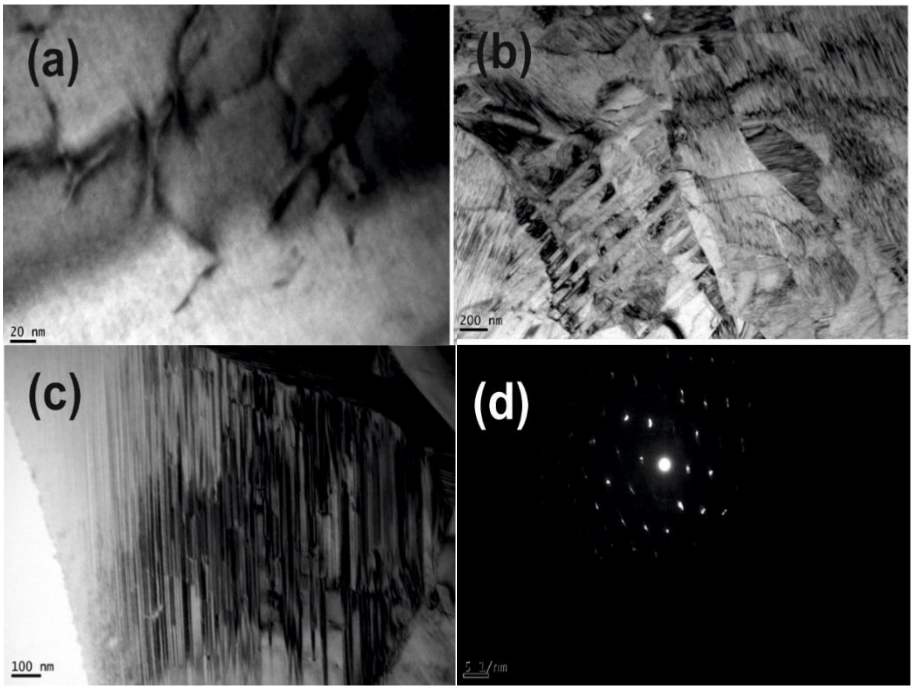

Fig. 6. Bright field TEM after HSHPT of: NiTi layer (a), NiFeGa layer (b) and (c) and SAED pattern of martensite in NiFeGa layer (d).

The hybrid material consisting of NiTi and NiFeGa bonded layers, after severe plastic deformation own sub-microcrystalline structure. TEM observations highlight that NiTi layer exhibits extensive plastic deformation than NiFeGa. This observation is in accordance with results obtained to the Vickers hardness measurement. To our knowledge, data concerning the Heusler alloys deformation by SPD methods are missing. Moreover, is reported the increase of grains size after HPT at high temperature in case of NiMnGa alloy [30].

The differences in mechanical properties of two dissimilar alloys during plastic co-deformation is generally considered to cause instability and fracture in hard layer [31]. It should be mentioned that the hard layer is NiFeGa and act as reinforcement area of composite. This layer show a value of microhardness about 1.75 times as against NiTi layer after HSHPT incorporating 2.3 logarithmic degree of deformation. Our finding points out that applying high degrees of deformation may appear crack initiation in Heusler layer.

4. Conclusions

In conclusion, a bi-layer $Ni_{50.3}Ti_{49.7}$/Ni57Fe18Ga25 composite was successfully processed for the first time by a severe plastic deformation method. The obtained results show that HSHPT at room temperature allows bonding between NiTi SMA and NiFeGa Heusler alloy with high-quality interfaces.

The layers are coherent and a very good joint was found with no interfacial intermediate layer formation. The modules diameter processed by HSHPT varied between 15 and 25mm.

Sub-microcrystalline structure is formed in the both layers of the hybrid material. To our knowledge, data concerning deformation by SPD methods are missing on this Heusler alloy type. The published data about severe plastic deformation reveals that HPT can increase the grains size.

The results indicate the possibility to obtain bi-layer and multilayer NiTi/Heusler alloy composite by HSHPT method. However further work is still on going to produce nanocomposite between NiTi and other Heusler alloys composition. The hybrid nanocomposites NiTi/NiFeGa can be useful as functional component in magneto-thermomechanical systems.

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