A Versatile Method for Nanostructuring Metals, Alloys and Metal Based Composites

G Gurau¹, C Gurau¹, L G Bujoreanu² and V Sampath³
¹“Dunărea de Jos” University of Galati, Faculty of Engineering, Domnească Street, 47, RO-800008, Galati, Romania
²Faculty of Materials Science and Engineering, “Gheorghe Asachi” Technical University of Iași, Blvd. Dimitrie Mangeron 61A, 700050 Iași, Romania
³Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai-600 036, India

E-mail: carmela.gurau@ugal.ro

Abstract. A new severe plastic deformation method based on High Pressure Torsion is described. The method patented as High Speed High Pressure Torsion (HSHPT) shows a wide scope and excellent adaptability assuring large plastic deformation degree on metals, alloys even on hard to deform or brittle alloys. The paper present results obtained on aluminium, magnesium, titan, iron and coper alloys. In addition capability of HSHPT to process metallic composites is described. OM SEM, TEM, DSC, RDX and HV investigation methods were employed to confirm fine and ultrafine structure.

1. Introduction

Ultrafine grained (UFG) and nanoscale metals and alloys have been of significant interest to research community due to their exhibited physical and mechanical properties accurately enhanced, not achievable in their coarse-grained counterparts [1-3]. Since the discovery of the production of UFG microstructures, in the early 1990s, using the ‘‘top-down’’ approach several publications dealing with pure metals and alloys have been appeared [4]. These techniques refer to imposing severe mechanical strains to a bulk solid with a relatively coarse grain size and processing the solid to produce a UFG or nanoscale microstructure [4]. Severe plastic deformation (SPD), among every production technique of bulk nanostructured materials (BNMs) proved to be a powerful tool for manufacture of nanostructures of different metallic materials down to ultrafine grain range, leading to remarkable combination of properties [1,5]. As much as, through variation of SPD processing parameters materials manifest various properties resulting from a wide range of grain sizes (below 1 μm), phase composition grain boundaries and interfaces evolve [6,7]. In this context, many methods have been developed to produce bulk fine-grained materials have been using very diverse SPD techniques such as: accumulative roll bonding (ARB) [8, 9], equal channel angular extrusion (ECAE) [1-13], high pressure torsion (HPT) [6,14,15,16], local canning compression [17,18], pure shear extrusion (PSE) [19] and so on. These procedures are capable of introducing large plastic straining (in excess of Von Misses strains of 1) and cause significant microstructural changes in bulk crystalline solids [20].

One of the most common and widely used methods of severe plastic deformation, used to obtain BNMs is high pressure torsion. High pressure torsion is a severe plastic deformation process, able to drastically reduce grain size, down to nanostructure or amorphous level, in bulk materials [21]. HPT,
known ever since 1943, provided a direct demonstration of the ability to employ heavy plastic straining in the production of bulk materials having microstructures with grain sizes in the submicrometer range (under 500µm until amorphous) and with a high fraction of high-angle grain boundaries [21,22,23]. Among methods designed based on the HPT approach, stands High Speed High Pressure Torsion (HSHPT) original technique. Basically this technology is a combination of friction stir technology and High Pressure Torsion. In this article, we present new successfully produced UFG on different types of alloys and comprise ours previous recent published results by means HSHPT processing route. In addition capability of HSHPT to process metallic composites is described.

2. Materials and methods

2.1. HSHPT processing route

HSHPT is a patented, reliable method able to produce ultrafine grained and BNMs, for appreciable types of alloys [23-25]. As HPT, refers to the processing of metals whereby samples are simultaneously subjected to a compressive force and torsion strains, efficient in grain-refinement, contributing to a marked increase of mechanical properties [24-26]. Unlike classic HPT, to which rotations of the superior anvil performs at the low speed, of the order of 10-1 rotation per minute (rpm), in HSHPT technology the torsional stress is performed at high speed of the order of hundreds rpm up to 2000 rpm. The technology involves heat generation by friction between the anvils (a and b figure 1) and the sample (c) due to high pressure (h) on inferior anvil (around 1GPa) somewhat lower than commonly used in HPT and also the shear of the crystalline grains due to rotation of superior anvil at high speed. The HSHPT process is very fast, lasting about 10 s. Because entire HSHPT process is developing in a few seconds, a fast metal flow and thermal transfer takes place on the cold surfaces of the anvils, acquiring fine structure [27]. The HSHPT method has been designed to severe plastic deformation of brittle alloys. This technology is able to perform much larger, with a diameter as large as 45 mm and more complex-shaped specimens [25]. The extent of deformation/plastic strain was estimated using the following relationship: ε=ln(hf/hi); where hi and hf indicate the initial and final thickness of the sample, respectively [23].

![Figure 1. Principle scheme of HSHPT machine.](image-url)
The HSHPT machine is powered by a 15 kW AC electric motor (figure 1d) operated by an EATON SVX024AI-4AI1 frequency converter via PLC XC 200. The force variation is recorded with Hottinger Spider 8 system (figure 1e, 1f and 1g). Also the process temperature and displacement of lower anvil are monitored with a temperature sensor CT laser radiation pyrometer T2 MHCF OPTC and 5LMO LiU5X3 displacement magnetic-inductive sensor.

2.2. Materials

In order to identify the potential for severe plastic deformation of the HSHPT technology, various samples of metals and alloys were manufactured in the flat and coned discs or rings. Technical grade metals such as cooper, aluminium, magnesium were selected in the tests. Based on the results of previous works shape memory alloys (SMAs) group were systematically investigated, since offer a myriad of possibilities for different applications in the industry, based on unique properties: shape memory effect (SME) and the superelasticity (SE). Cu-Al-Ni SMA, Ti-Ni with slightly different composition and, consequently, different transformation temperatures were studied, Fe-Mn-Si-Cr SMAs and Ni-Co-Fe-Ga magnetic SMA have been the main subject of research. The new research direction consists of producing composite multilayers by the HSHPT method. HSHPT process can be used to produce multilayers coherent and well-bonded inasmuch as is similar to stir friction method. In this context we perform Cu/Al and NiTi (SME) /NiTi (SE) composites.

Microstructural observations were realized on the as-cast, extruded or rolled state, as well as the HSHPT-processed alloys specimens, described above, and subjected to different degrees of deformation. Samples were prepared for primary microstructural examination by optical microscopy (OM) as well as scanning electron microscopy (SEM). The samples were cut, enclosed in cold mounting resin, and polished using standard metallographic techniques; the samples were then etched using a typical solution for each alloy system.

The OM examination was carried out using an OLYMPUS BX51 microscope equipped with a video camera and the QCapture software package. A Zeiss microscope was used for the SEM studies. The microstructural analysis of the samples by TEM was carried out using a Tecnai 20G2 transmission electron microscope operating at a voltage of 200 kV and equipped with an EDX spectrometer. Thin foils from HSHPT-processed specimens were prepared using an electrolyte with 90vol% of methanol and 10vol% of perchloric acid. The phase identification was carried out using an X-ray diffractometer (Bruker AXS D8 Discover) equipped with a Cu Kα radiation source. The transformation temperatures of the specimens processed were determined by differential scanning calorimetry (DSC TA Q20). A heating/cooling rate of 50°C /min in the range of 0 to 250°C was adopted for the experiments. Room temperature Vickers microhardness values were determined using an indenter under a load of 0.98067N (HV0.1) applied for 10s.

3. Results and discussion

3.1. Cu-Al-Ni SMA

The HSHPT technology was developed for plastic deformation of severe brittle polycrystalline Cu-Al-Ni shape memory alloys, attempted to improve the ductility by grain refinement. The presence of coarse grains of extruded billets, larger than 200µm are shown in Figure 2a does not recommend it for severe deformation. The maximum pressure applied was 0.7GPa. The strain levels applied was between 0.7 and 3.62. The HSHPT discs were achieved up to 29mm in diameter. The SPD occurs in about 20s. Figure 2b present elongated grains in case of 1.7 deformation degree. As shown in Figure 2c, subjecting the alloy to HSHPT processing to a logarithmic strain of 3.5 the coarse austenitic grains have completely been replaced by flowlines.

The room temperature TEM micrographs show a heavily deformed microstructure of the HSHPT processed alloy incorporating a logarithmic strain of 1.7. In figure 3 martensite plates and stress fields are clearly visible for extruded initial sample.
Figure 2. Optical micrographs of Cu-13Al-4Ni: a) extruded; severely plastic deformed by HSHPT logarithmic strain of: b) 0.7; c) 2.5.

Grain refinement is not accompanied by a high density of lattice defects as can be seen in figure 3 b. but finer twins and needles are accompanied by numerous stacking faults. Parallel-banded of two martensite plate variants that spatial intersecting are notable. These morphologies are referred to as twin type martensite: $\gamma_1'$ (2H) orthorhombic predominantly after SPD and $\beta_1'$ (18R) monoclinic, confirmed by XRD investigations [27].

Figure 3. TEM images of Cu-13Al-4Ni alloy a) extruded b) martensite morphology.

The alloy processed by HSHPT shows reversible martensitic transformation without the necessity for post-deformation annealing and phase transformation stability after 10 thermal cycles. Due to microstructural refinement the microhardness increases by nearly 50%.

3.2. Ti-Ni SMA

All selected Nickel–Titanium (Ni–Ti) alloys of two different near-equatomic chemical compositions (Ni-rich and Ti-rich) subjected to severe plastic deformation by means of HSHPT exhibit unique shape
memory effect (SME) or superelasticity (SE) quickly after deformation without any post-deformation heat treatment. The DSC and in situ XRD studies confirm reversible martensitic transformation in modules severe plastic deformed [28]. The rotation speed applied was 1795 rpm and the maximum force was about 120kN. The torsion time for Ni-Ti samples varied between 7 to 19 seconds determining different degrees of refining of the crystalline grains. The strain levels applied was between 0.92 and 3. The HSHPT modules were achieved up to 45mm in diameter as against those manufactured by means HPT usually about 10 mm in diameter.

For Ni rich Ni-Ti, in the case of the deformation degree of 0.92 (figure 4a) the austenitic grains are finer than few micrometres, equiaxed and distributed almost uniformly. The microstructure of Ni-Ti alloy after HSHPT processing with 1.52 deformation degree is characterized by the obviously elongated grains with waved grain boundaries (figure 4b).

![Figure 4. Optical micrographs of Ni-Ti severely plastic deformed by HSHPT logarithmic strain of: a) 0.92; b) 1.52.](image)

After subjecting the alloy to the HSHPT processing to a logarithmic strain of 0.92, the grains exhibit apparent grinding. Inside the B2 austenite grains appear especially randomly oriented twins (figure 5a). The refinement of the grain size is more evident after increasing degree of deformation as shown in figure 5b. In discs subjected to a logarithmic strain level of 2.33 the individual grains or grain boundaries were no longer observed being outside the range of detection by standard SEM observation. The sample reveals only large precipitates and lines of one martensite plates variant.

![Figure 5. SEM images of Ni-Ti severely plastic deformed by HSHPT logarithmic strain of: a) 0.92; b) 2.33.](image)

TEM micrographs of the Ni-Ti sample that was subjected to a deformation level of 1.71. Figures 6a and b highlight the heavily deformed microstructure showing a complex strain contrast, having no
preferred orientation, lattice defects such as dislocation accumulated in clusters, dislocation tangles and high density of dislocations, also residual stress field can be find. Figure 6c shows multiple fine twins and variants with parallel orientations of $\beta 19'$ martensite with a monoclinic crystal structure.

![Figure 6. TEM images of Ni-Ti severely deformed with logarithmic strain 1.72 highlighting areas of different structural morphologies.](image)

The hardness of HSHPT processed specimens is increased with increasing of the deformation degree up to 180%, being essentially homogeneous along diameter [28].

### 3.3. Fe-Mn-Si-Cr SMA

HSHPT Fe-Mn-Si-Cr modules can behave as actuators, being able to generate compensation strokes or constrained recovery forces.

![Figure 7. Optical micrographs of Fe–Mn–Si–Cr alloy (a) cast state and (b) after severe plastic deformation by HSHPT of 2.3.](image)
A superelastic-like response was obtained during compression loading-unloading to coned-disk spring shape modules, obtained from as cast state alloy (figure 7a) by means of HSHPT procedure [29]. The presence of ε (hcp) stress-induced in samples severe plastic deformed was confirmed by OM (figure 7b), SEM (figure 8), TEM (figure 9) micrographs and XRD patterns, too [23, 25]. The distorted SPD alloy microstructure can be seen in Figure 7b, revealing only the dark contrast of the triangular morphology of ε-HCP martensite.

The micrograph shown in figure 8a reveals two variants of fine martensite plates on surface relief of samples with 2.21 logarithmic strain. As evident in Figure 8b, the individual grains or grain boundaries in discs subjected to a logarithmic strain level of 3.0 were outside the range of detection by standard SEM observation.

The TEM analysis of the alloy after HSHPT subjected to a logarithmic strain level of 0.9 and 1.53 highlighted grain refinement down to 50 nm with two predominant variants of ε-HCP martensite and numerous stacking fault (figure 9a and b). Also ascertain the presence of a high density of dislocations characteristic of cold severe plastic deformation, were not found in this alloy processed by HSHPT. No post-deformation annealing was required after HSHPT processing for actuator applications.

**Figure 8.** SEM micrographs of Fe-Mn-Si–Cr alloy after severe plastic deformation by HSHPT to a longitudinal logarithmic strain of: (a) 2.21 and (b) 3 (transversal cross section).

The maximum force inflicted was approximately 120kN. The processing time varied between 2 and 11 s for the Fe-based alloy. The strain levels applied was between 0.15 and 3. The HSHPT modules exhibited maximum 35 mm diameter having thickness of 0.18 mm.

**Figure 9.** TEM images of the Fe–Mn–Si–Cr after severe plastic deformation by HSHPT to logarithmic strain: a) 0.73 and b) 1.53.
3.4. Ni-Co-Fe-Ga SMA
An ongoing research on magnetic Ni–Fe–Ga alloys points out that by using HSHPT severe plastic deformation method the magnetic properties are improved on the strength of promoting the formation of the β phase martensitic. There is effect of the deformation on decrease of γ phase which obstructs the formation of the β phase. The γ phase were highly deformed elongated long the flow lines (Figure 10 a) and waved (figure 10 b).

![Figure 10. HSHPT ‘ed Ni-Co-Fe-Ga magnetic SMA a) Optical and b) SEM micrographs.](image)

3.5. Cu/Al multilayers composite
The initial copper specimens possessed average grains size of 159μm, and the average grains size of aluminum 56 μm (figure 11a and 11b) respectively. HSHPT is able to bring about Cu/Al composite by 2 to 11 layers, showing coherent, efficient bonding with fine structure (figure 11c and 11d)).

![Figure 11. I OM micrograph of: a) Al; b) Cu; c) HS HPT processed multilayers Cu/Al composite cross sections (c) seven layers and d) highlighting Al layers by metallographic etching](image)
During SPD, large copper clusters (average size of about 10μm) moved deeply into the aluminum matrix, markedly for all Cu/Al composites, showing a homogeneous distribution, with clear boundaries, slightly elongated along the radial direction. A remarkable increase in the Vickers microhardness (up to 16 time compared to the initial state) was noticed for all the multilayers composites, regarding of the numbers of layers as a consequence of the microstructural refinement achieved by HS HPT method. SPD occurs quickly within 2-5s relying on number of layers. The discs diameter was up to 45 mm.

3.6. Ni-Ti (SME) /Ni-Ti (SE) multilayers composite

SEM and OM micrographs of Ni-Ti (SME) /Ni-Ti (SE) multilayer after HSHPT processing is shown in Figure 12 a and b. It is observed, even if the number of layers increase at 24, the interface between the layers is straight and adherent. This multilayer composite has potential for use in MEMS.

![Figure 12. HS HPT processed multilayers NiTi (SME) /NiTi (SE) composite cross sections (24 layers): a) SEM and b) OM.](image)

4. Conclusion

1. SPD processing by HSHPT technique, leads to the occurrence of significant grain refinement down to ultrafine range until the nanocrystalline range, in various metals and alloys like: aluminium, magnesium, titan, iron and copper. The process can be applied even for brittle and hard deformable alloys. SMAs group benefit of this technique based on improved properties: shape memory effect (SME) and the superelasticity (SE).

2. Among methods designed based on the HPT approach, stands High Speed High Pressure Torsion (HSHPT) original technique being a combination of friction stir technology and High Pressure Torsion.

3. HSHPT is a promising and reliable method for achieving semi-products with rotational symmetry, whose dimensions exceed those of the HPT samples by four times depending on system alloy.

4. The capability of HSHPT to process multilayers metallic composites is described.

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