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Structure and properties of nanomaterials produced by severe plastic deformation

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Abstract In recent years, a number of methods for refining the structure of metals by severe plastic deformation (SPD) have been developed. Some of those methods permit grain refinement to a nanometric level. These methods include, among others, high pressure torsion (HPT), equal channel angular pressing (ECAP) and hydrostatic extrusion (HE). The aim of this paper was a more detailed description of these methods and presentation of exemplary applications of these methods for structure refinement and improvement of mechanical properties of chosen materials. The results obtained in the present study show that the microstructures of the materials subjected to SPD studied in this work displayed considerable refinement, characterised by the formation of nanosized grains. Such a refinement resulted in increased tensile strength and hardness of the SPD materials studied in this work. In view of the results obtained on a large number of metals and alloys, a conclusion can be drawn that SPD could become an attractive way of processing materials for variety of applications.

Key words nanocrystalline metals • severe plastic deformation • nanostructure • mechanical properties

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Introduction

Nanometric dimensions of microstructure elements were utilised to obtain new material properties for a long time. For example, nanometric particles of carbon black have been used for over a hundred years for rubber vulcanisation and nanometric precipitations of metastable phases in Al alloys enabled a significant increase of strength of these alloys. However, a rapid increase of interest in this field has been noted from the moment of appearance of a review paper on the subject of nanocrystalline materials (NCM) by Gleiter [5], who was the first to propose a method of producing metal nanoparticles through their deposition from gaseous phase, and is one of the main precursors in this field. At present, four techniques are applied for producing bulk NCM:

a) consolidation of nanocrystalline powders, produced by various methods;
b) physical, chemical and electrochemical deposition;
c) crystallization of amorphous materials;
d) severe plastic deformation.

Each of the methods mentioned above has its advantages and limitations and the level of technological advancement is still too low for industrial applications of bulk NCM. In the powder methods the main problem is consolidation of these materials. Currently used deposition methods are mainly limited to producing layers on the surface of conventional materials. The crystallization of amorphous materials can only be used in the case of materials prone to amorphization and the obtained structures of materials are specific: nanocrystalline precipitations in the amorphous matrix. Moreover, the amorphous materials are usually in the form of thin ribbons, which restricts their potential application.

A group of methods enabling fabrication of nanocrystalline materials without any of the aforementioned flaws are methods of severe plastic deformation, due to which relatively large elements, yet characterized by lack of porosity, can be produced.

Large deformations can be achieved through various technological processes, e.g. rolling. However, it was the Bridgman concept [3] of high pressure deformation of materials, that enabled development of a method of high refinement of materials structure to a submicron or even nanometric scale due to plastic deformation [27, 37]. In recent years, a number of methods for refining the structure of metals by severe plastic deformation (SPD) have been developed. Some of those methods permit grain refinement to a nanometric level. These methods include, among others, high pressure torsion (HPT) [3], equal channel angular pressing (ECAP) [28], hydrostatic extrusion (HE), accumulative roll-bonding (ARB) [26], repetitive corrugation and straightening (RCS) [7], long-term shot peening of the metallic material surface [18], (which leads to a nanostructure in the surface layer), cyclic extrusion compression (CEC) [9, 25] or multiple alternate forging [35]. The most prospective out of the aforementioned methods of grain refinement through severe deformation seem to be HPT, ECAP and HE. The aim of this paper was a more detailed description of these methods and presentation of exemplary applications of these methods for structure refinement and improvement of mechanical properties of chosen materials.

High pressure torsion

High pressure torsion (HPT), as a method of severe deformations, was proposed by Bridgman already in 1952 [3]. However, for obtaining nanostructured metals and alloys it has been used for a dozen or so years.

Figure 1 presents schematically the idea of this method. Generally speaking, the method consists in pressing a thin disk of a material between two punches and, subsequently rotating one of them. Friction between the sample and punch is high enough for large deformation of material to occur.

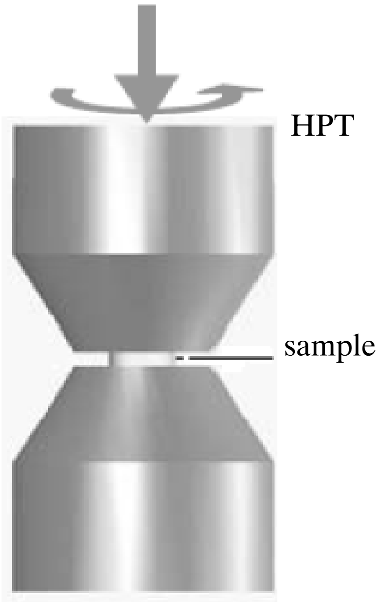

Fig. 1. Schematic illustration of high pressure torsion.

Of all the methods of grain refinement through severe plastic deformation mentioned in the introduction, the HPT method allows to obtain perhaps the highest grain refinement. This method has been used to deform many materials, from pure metals to brittle intermetallic phases [10, 23, 38]. The advantage of the method is high refinement of structure and the possibility to process brittle materials. The disadvantage is a low volume of the sample and non-homogeneity of the material processed by this method. The HPT process yields discs in which the material deformation degree and, so, the material microstructure depend on the distance from the disc center. In the central part of the disc, the deformation is the smallest. Therefore, microstructure of the specimens will differ from one another depending on the disc part in which it was observed. It results in considerable differences in the properties between the central part of the disc and the rest.

Figure 2a presents the macroscopic image of a specimen of 316L steel processed by HPT. Figure 2b presents the microstructure of this specimen obtained

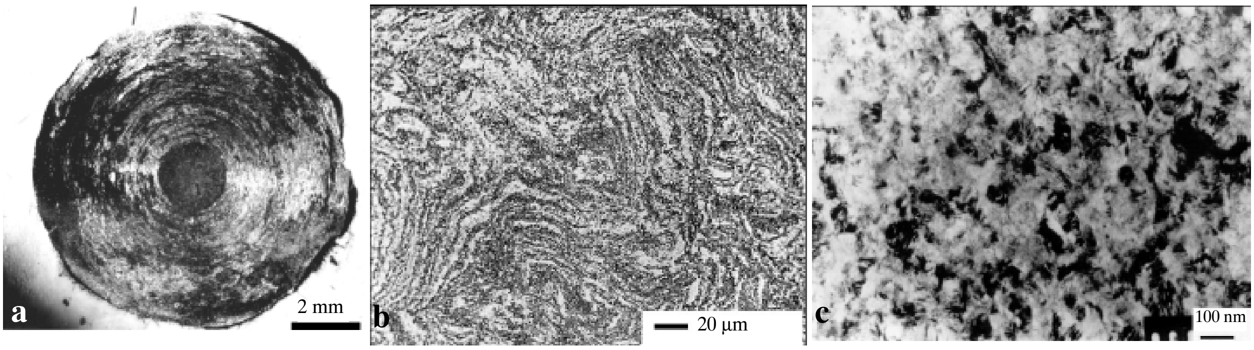

Fig. 2. 316L steel processed by HPT: a – macroscopic image of the specimen; b – microstructure of the specimen revealed by light microscopy; c – nanostructure of the specimen reviled by transmission electron microscopy.

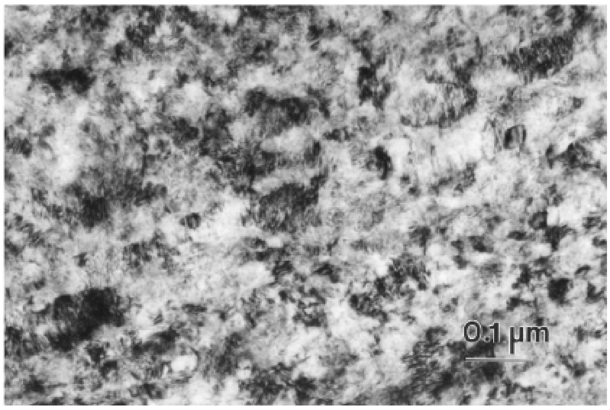

Fig. 3. An example of nanostructure of Ni$_3$Al processed by HPT.

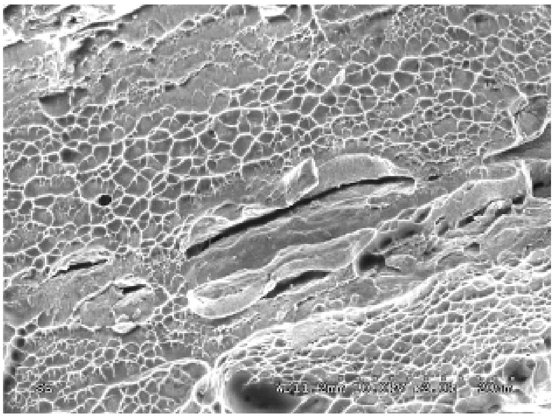

Fig. 4. An example of microcrack produced in austenitic steel during high pressure torsion [4].

by light microscopy and Fig. 2c by transmission electron microscopy. The photographs reveal that the material microstructure homogeneity differs very much depending on the magnification.

Among the materials studied by the present authors, the most spectacular grain refinement was observed in the case of intermetallic phase Ni$_3$Al. An example of Ni$_3$Al microstructure processed by HPT is shown in Fig. 3.

In this case grain refinement was from 0.6 mm (in the initial state) to 20 nm after HPT [11]. However, this grain refinement was obtained only at some distance from the specimens centre. In the central part of the specimens we observed coarse grained microstructure [20, 23]. It is also interesting to note that after deformation by HPT the samples retained monolithic, although pure Ni$_3$Al (in the absence of boron doping) is a very brittle material. During and after HPT process some macro- and microcracs can arise, what is presented in Fig. 4 (this figure presents fracture surface of the specimen of 316L austenitic steel processed by HPT). The presented fracture surface was obtained after tensile test. It is typical ductile fracture surface, but on this surface also small flaw is visible. This means that during HPT some flows and materials discontinuities can be produced.

Despite some disadvantages, the HPT method provides an extremely high grain refinement, which allows investigations of materials with microstructure not possible to obtain by other methods. Our research results for various materials subjected to deformation by the HPT method are presented in Table 1 [4, 10–12, 20–23, 31, 38].

Equal channel angular pressing

Equal channel angular pressing – ECAP (also named as equal channel angular extrusion – ECAE), proposed by Segal [28], has been growing in significance in recent years. In the case of this method, the obtained grain sizes are larger than in the case of HPT, but also the volume of the processed material is larger. Billets of 60 mm diameter and 300 mm length are obtained [6, 24, 36].

ECAP consists in pressing of billet, usually with circular or square cross-section, through an angular channel, bent at an angle – usually of 90°. The sample is pressed into the channel by a punch and pressed out by a next sample. Pressing of the sample through the angular channel for several times allows accumulating severe deformations in its structure.

Figure 5 presents a schematic rule of material deformation by the ECAP method.

At room temperature, ECAP can mainly be applied to pure metals. Numerous works have been published concerning ECAP of FCC metals, such as: Al, Ni and Cu. Less data is available for BCC, e.g. Fe [32–34] and CPH metals, such as, e.g. Ti [30]. In the case of alloys, heating of tools or billet is usually needed. For the process conducted at elevated temperatures, grain refinement can be obtained in hard to deform refractory alloys and even in brittle intermetallic phases [2, 29]. However, grain size for materials deformed at high temperature exceeds several µm. Interesting results have been obtained for Al alloys. In this case grain size reaches a value of about 200–500 nm, thus it also exceeds the boundary value of 100. However, these

Table 1. Mean grain size and mechanical properties of the materials processed by HPT

Material	Total equivalent strain $\varepsilon_{eq} = 2\pi nR/(L\sqrt{3})$	Grain size Initial, d_i [µm]	Final, d_f [nm]	Vickers hardness HV$_{0.2}$	Tensile strength [MPa]
Fe armco	~240	57	134	470	1100
Pure Ni$_3$Al	~200	600	20	900	–
Pure Ni	~120	120	240	–	1200
Stainless steel 316L	~240	20	55	630	1340

Where: ε_{eq} – equivalent strain, n – number of the stamp rotations, R – distance from the rotation axis, L – thickness of the specimen.

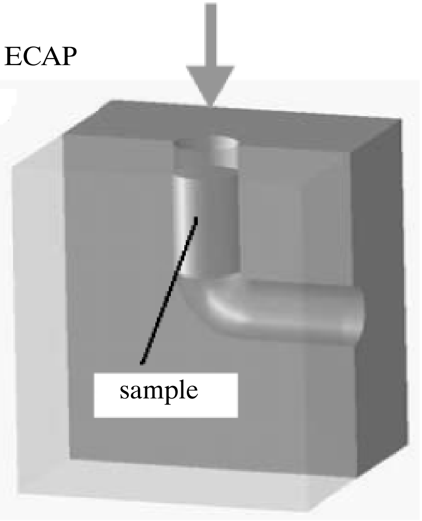

Fig. 5. Schematic explanation of ECAP.

materials obtain, due to grain refinement, a new property, the so-called low-temperature "fast superplasticity". For conventional superplasticity, the required deformation rates are in the range of 10^{-4}–10^{-3} s. In the case of ECAP-ed Al alloys, the superplasticity is achieved at a deformation rate 3–4 orders of magnitude higher and at a temperature of 100–200°C lower than for the "conventional" one [14]. This gives broader perspectives of applications of these materials to manufacture products formed by superplastic deformation.

Our own research results for various materials subjected to deformation by the ECAP method are presented in Table 2.

Hydrostatic extrusion

Hydrostatic extrusion (HE) is one of the methods that allows us to obtain large strains in one pass or in several passes. In this method, the sample is located in a container and surrounded with a pressure transmitting medium (Fig. 6). The piston compresses the medium until the sample starts to extrude. The material flows on the film consisting of hydrostatic medium and a lubricant. As a consequence, the friction between the sample and the die is negligibly small. This results in the unique features of hydrostatic extrusion, which are: (a) very high strain rates and (b) homogeneity of deformation. From the application point of view, the main advantage of this method is the possibility to obtain large volumes of products in the form of rods and wires, which can have complex cross-sections, as well as small tubes.

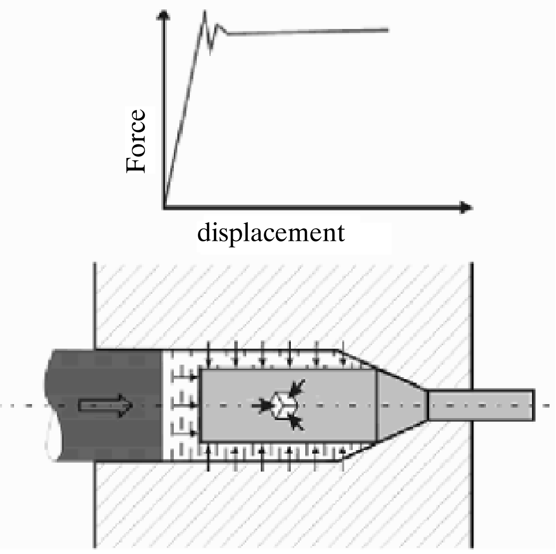

Fig. 6. Schematic presentation of hydrostatic extrusion process.

Recently, this method has been used to grain refinement in various metallic materials such as aluminium alloys, titanium, copper and stainless steel [1, 13, 15, 16]. In this paper, the efficiency of HE with regard to different materials is considered.

Table 3 summarises the mean grain size in various materials processed by HE. An analysis of the data presented in the table shows that titanium is the most outstanding example of grain refinement in the process

Table 2. Mean grain size and mechanical properties of the materials processed by ECAP

Material	Total equivalent strain	Grain size		Vickers hardness $HV_{0.2}$	Tensile strength [MPa]
		Initial, d_i [μm]	Final, d_f [nm]		
Fe armco	~10	57	180	320	1220
Pure Cu	~16	37	260	140	440
Pure Ni	~8	21	360	300	990

Table 3. Mean grain size and mechanical properties of the materials processed by HE

Material	Total equivalent strain $\varepsilon_{eq} = 2\ln(\Phi_i/\Phi_f)$	Grain size		Vickers hardness $HV_{0.2}$	Tensile strength [MPa]
		Initial, d_i [μm]	Final, d_f [nm]		
Pure aluminium	3.8	1	600	50	200
Pure copper	5.6	37	260 (subgrains)	120	410
Pure titanium	3.8	21	80	270	1075
Stainless steel 316L	1.4	microtwins	nanotwins	540	1215

Where: ε_{eq} – equivalent strain, Φ_i and Φ_f – initial and final diameter of the extruded rod.

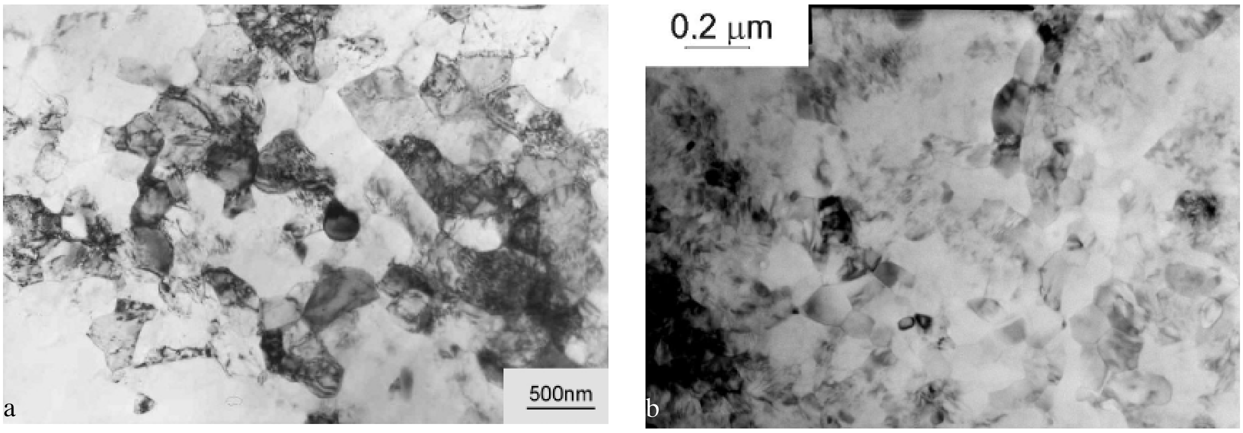

Fig. 7. Microstructure of HE processed 6082 (a) and 2017 (b) aluminium alloys. (True strain 3,8.)

of hydrostatic extrusion. In the case of austenitic stainless steel, the transformation of microtwins into nanotwins was observed, while HE of pure copper results in the microstructure which consists mainly of subgrains. The mean size of these subgrains is about 260 nm. Pure aluminium exhibits the largest size of grains when compared to the other materials examined in the present study. However, a comparison to pure aluminium processed by other SPD methods [8, 17, 19, 38] clearly shows that the mean diameter of 600 nm is in the middle of the data reported in the literature.

The process of HE proceeds in the near adiabatic conditions and, the plastic work is converted mainly into heat. The residual part of plastic work is retained in a material in the form of defects. The heat generated during the process of HE causes a temperature rise, which can result in thermally activated processes such as recovery or recrystallization. On the other hand, the process of HE is very fast (the strain rate exceeds 10^2 s^{-1}) which, on the other hand, offers the possibility to suppress the grain growth phenomena. It should be noted that all the extruded samples used here were water cooled at the die exit.

The processes of recovery or recrystallization occur very easily in materials with high stacking fault energy and low melting point, e.g. pure aluminium. As a consequence, in this material the possibility of grain refinement seems to be very limited. In order to obtain smaller grain size, the processing of materials more resistant to the temperature rise, e.g. aluminium alloys was performed. The study has shown that in aluminium alloys, the final grain size is much smaller than in pure aluminium. The microstructures of HE processed aluminium alloys are presented in Fig. 7 for (a) non-heat treatable 6082 and heat treatable 2017 (b) aluminium alloy. The results clearly show that by HE, the grain size can be reduced to less than 300 nm in the case of 6082 aluminium alloy and even below 100 nm for the 2017 aluminium alloy.

Such microstructure evolution during processing by HE results in the improvement of mechanical properties as is shown in Fig. 8. It should be noted that some materials exhibit excellent mechanical properties, e.g. yield strength more than 1000 MPa for titanium, more than 500 MPa for the 2017 aluminium alloy and 650 MPa for a 7475 aluminium alloy. Such values cannot be obtained by a conventional processing.

From the results obtained in the study of HE processing, the following conclusions can be drawn. First, processing by HE reduces the grain size in metallic materials even to less than 100 nm and this method can be used for the fabrications of nanocrystalline metals. Second, the efficiency of HE, defined as the ability to grain size reduction, depends on a material. In particular, it depends on its susceptibility to recovery and/or recrystallization. (The smaller the recovery/recrystallization rate, the smaller the grain size that can be obtained by HE.) Finally, due to a significant grain refinement, the materials processed by HE exhibit very high mechanical properties.

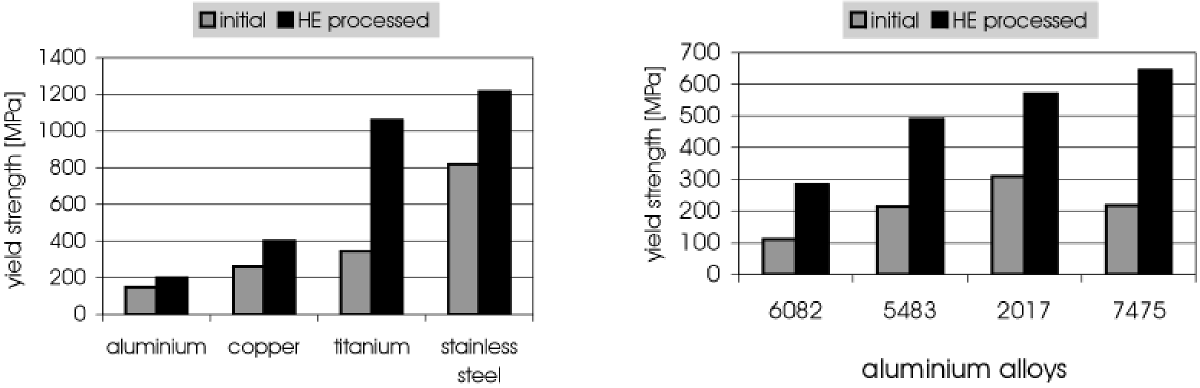

Fig. 8. Mechanical properties of materials processed by HE.

Mechanical testing

For nanocrystalline materials, available very often in small quantities, it is necessary to use special testing methods of mechanical properties. In particular, this is true for materials processed by HPT. In this case, tensile tests can be curried out using microspecimens. On the other hand, such specimens call for special procedures in measurements of yield strength, tensile strength, uniform elongation and elongation to rapture.

In order to compare properties of materials processed by various SPD methods, including HPT, it is necessary to produce microspecimens with a length of 5–10 mm, gauge length of 2–3 mm, and thickness of 0.1–0.2 mm. Testing of such small specimens requires special efforts.

Small specimens require sensitive methods for measuring strain. For example, a 0.2% elongation of a specimen with a gauge length of 2 mm results in a 4 μm displacement. To measure this elongation with an accuracy of ±5%, a measuring device with a resolution of ±0.2 μm is needed. Such a high resolution can be achieved with an electro-mechanical extensometer. A typical small standard extensometer has a gauge length of 5 mm, which permits achieving a resolution of 0.1 μm. If the gauge length of the specimen is below 5 mm, the extensometer is too large to be installed. If this is the case, the extensometer may be fixed to the specimen holders. Knowing the gauge length of the specimen, we can determine its deformation, but the measurements bear a considerable error. This is due to the fact that the strain is localized in stress concentration regions, which in tensile test specimens are located between the holding portion of the specimen and the gauge length. If the specimen deformation is measured indirectly by measuring the displacement of the holders, the flow stress of the material is underestimated and the specimen elongation is overestimated [20, 33, 34]. For this reason, when dealing with small specimen on which an extensometer cannot be installed, the measurements should be performed by optical or other direct methods.

One of such direct methods is the digital image correlation method (DIC). This method allows to measure total and local strains of the tested specimen. Therefore, using this method we can obtain deformation maps of the tested specimen. An example of such a map is presented in Fig. 9.

This figure presents a deformation map of microspecimen of nanocrystalline Fe, produced by sintering of nanocrystalline powder. Such a map is produced in a digital form by processing images of specimen surface. (Sometimes this may require deposition of graphite spray to produce black and white dots on a specimen surface.) Computer code for DIC measures displacements of these dots by comparing images before and after deformation.

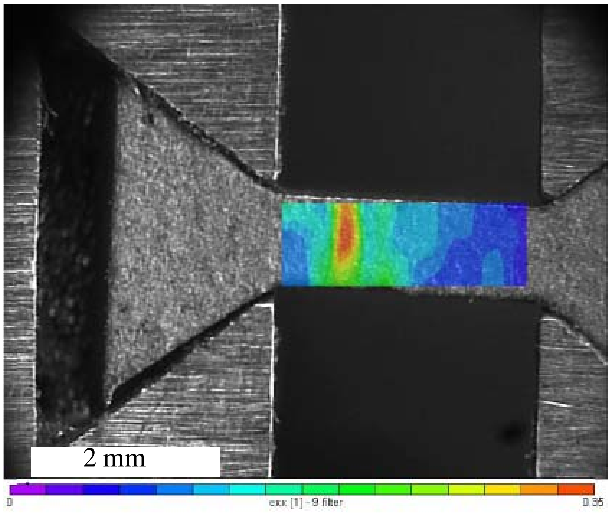

Fig. 9. Deformation map obtained by DIC method. (Specimen of nanocrystalline Fe processed by pulse sintering of nanocrystalline powder. Average strain of the sample 14%, maximum strain, measured on the specimen surface 35%.)

Conclusions

The results obtained in the present study show that there are now a number of severe plastic deformation methods that can be used to refine the structure of metals.

The microstructures of the materials subjected to SPD studied in this work displayed considerable refinement, characterised by the formation of nanosized grains. Such a refinement resulted in increased tensile strength and hardness of the SPD materials studied in this work. In view of the results obtained on a large number of metals and alloys, a conclusion can be drawn that SPD could become an attractive way of processing materials for variety of applications.

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