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ULTRAFINE-GRAINED MATERIALS

Production, properties and application prospects of bulk nanostructured materials

R. R. Mulyukov · R. M. Imayev · A. A. Nazarov

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Abstract Fundamental mechanisms of grain refinement during equal-channel angular pressing (ECAP) and multiple isothermal forging (MIF) are analyzed and compared. Based on this analysis, deformation methods of nanostructuring are classified into severe plastic deformation and mild plastic deformation methods. It is demonstrated that MIF is a versatile method allowing for a production of bulk and sheet nanostructured semi-products with grain size down to 50 nm and applicable to various metals and alloys. Novel mechanical properties of bulk nanostructured materials produced by this method are presented. The ways of their structural and functional applications are discussed.

Abbreviations

SPD Severe plastic deformation
ECAP Equal-channel angular pressing
MIF Multiple isothermal forging

Introduction

In the last two decades tremendous research work has been devoted to the development of deformation methods of nanostructuring of materials; these methods are commonly referred to as severe plastic deformation (SPD) methods [1, 2]. Deformation methods exploit the very common phenomenon of accumulation of dislocations and formation of a misoriented substructure. This process occurs at both low and elevated temperatures, but its behavior and consequences are fundamentally different in these two extreme cases. At present equal-channel angular pressing (ECAP) and its modifications are very intensely studied [3]. Normally, this method is based on the formation of deformation microstructures at low temperatures. Meanwhile, the method of multiple isothermal forging (MIF), which is based on dynamic recrystallization [4–7], is less common, although it seems very promising for practical applications.

In the present paper, we analyze the fundamental differences between the two methods capable of producing bulk nanostructured materials, ECAP and MIF, and show that the latter has many important advantages and a high potential for industrial applications. The mechanical properties of MIF-nanostructured materials will be presented and some pilot products produced out of these materials will be demonstrated.

Comparative analysis of ECAP and MIF

Despite a large number of structural studies the mechanisms of grain subdivision during deformation treatment are still not well understood. Nevertheless, very general regularities of different SPD processes have been established that allow one to make some conclusions on their efficiency in nanostructuring different samples of metals and alloys.

First, let us consider ECAP. Numerous studies of the substructure development during low temperature deformation of metals by ordinary methods such as cold rolling and die compression show that the main mechanism of grain subdivision is the formation of microbands, which

R. R. Mulyukov · R. M. Imayev · A. A. Nazarov (✉)
Institute for Metals Superplasticity Problems, Russian Academy of Sciences, 39 Khalturin Street, Ufa 450001, Russia
e-mail: nazarov@imsp.da.ru

normally lie on the planes of maximum shear stress [8, 9]. ECAP is a deformation process with a changing strain path that allows varying this process. The change of deformation path in ECAP is done by rotations of a sample between its successive passes through the die. After the first pass, microbands parallel to the plane of intersection of the channels (shear plane) are formed [10]. Subsequent passes with a rotation of the samples to 90° (routes B_A and B_C according to the common classification) result in microband boundaries in oblique planes, which intersect with the previously formed boundaries to form closed fragments that evolve to equiaxed grains. Due to this, the routes B_A and B_C result in the most rapid formation of an equiaxed structure in terms of the number of passes [11]. However, as well known, each substructure is a response of the material to a particular straining, and a change of the strain path always tends to destroy the old substructure and form a new one typical to the new path [8]. Therefore, when using the routes with a rotation of samples one has a partial destruction of previously formed boundaries, and an accumulation of misorientations occurs more slowly than during monotonic straining. Due to this reason, the routes B_A and B_C lead to a formation of an equiaxed nanostructure with dominantly low-angle GBs [11]. Most evidently this is seen at a comparison of two extreme routes A and C, which use no rotation and a rotation to 180°. In the former case the structure is developed continuously and highly misoriented elongated grains are formed, while the latter case results in an equiaxed structure with predominantly low-angle boundaries [11].

Due to these fundamental reasons and to a large friction between the samples and channel walls, ECAP is a fairly power-consuming process and does not take the full advantage of deformation methods of nanostructuring.

The efficiency of grain subdivision during monotonic deformation including the route A ECAP can be increased by increasing the mobility of GBs that facilitates a local migration of transverse GBs with a subsequent formation of an equiaxed structure [12]. Recovery and recrystallization processes are very important for a transformation of the deformation substructure to an equiaxed, low-energy granular structure, which is stable during the subsequent deformation. The studies show that dynamic recrystallization occurs already at room temperature during ECAP in low melting point metals (for example, in Cu) [13]. In metals with high melting point, recrystallization is expected to occur at moderately elevated temperatures. This means that depending on the deformation temperature, the formation of a nanostructure during ECAP can occur by one of two main mechanisms: either by the formation of deformation induced boundaries due to an intersection of microbands at low temperatures or by dynamic recrystallization at low temperatures. Apparently, these mechanisms determine which kind of deformation methods of nanostructuring one can refer the ECAP to: that is, SPD at low temperatures and a mild deformation treatment employing the recrystallization at relatively high temperatures.

Second, let us consider MIF. This method takes full advantage of dynamic recrystallization for the grain refinement down to the nanosize [4–7]. For this, one had to work out a route which would combine three requirements that are not readily met by a single process: a significant reduction of the temperature of isothermal deformation, retention of the technological plasticity of material at these low temperatures, and a guarantee of a uniform development of dynamic recrystallization over the sample volume.

To work out a process route for obtaining a nanostructured state in a particular material, one carries out preliminary studies using model samples. Deforming cylindrical samples by compression at various temperatures and strain rates, one determines the dependence of the size of recrystallized grains d on temperature T and strain rate $\dot{\varepsilon}$ and the strain-rate-temperature conditions in which the formation of a uniform fine-grained microstructure is favored. The principal requirement here is to obtain a uniform structure, at least in the central part of the sample. As a rule, a highly uniform microstructure is formed at temperature-strain rate conditions of superplasticity, when the size of grains formed does not exceed $d = 10$–15 μm [14], i.e., at fairly high temperatures and modest strain rates. The dependence $d(T, \dot{\varepsilon})$ provides also information on the conditions in which nanosized grains are formed. These are relatively low temperatures and high strain rates. However, during deformation in these conditions a partially recrystallized, highly non-uniform microstructure is formed in the central part of a sample. To avoid this, deformation is carried out with a step-by-step decrease of temperature.

Figure 1 illustrates the principal scheme of MIF that has been designed and is under use at IMSP RAS. The forging is done in temperature-strain rate conditions chosen by preliminary studies. The scheme of deformation facilitates a uniform distribution of strain over the sample volume [15]. Eventually, the uniformity of recrystallization process and, therefore, of the microstructure obtained is determined by a correctly chosen strain rate, temperature, and scheme of forging. MIF is done up to a complete recrystallization of the sample's volume. The grain size obtained is determined by Zener–Hollomon factor [16].

One should point out several important issues concerning the method. As one can see from Fig. 1, MIF is associated with low contact friction provided that the sample is not strained to very high strains per pass. After each cycle a sample attains a form close to the initial one. Due to the grain refinement the technological plasticity of a material increases. If one deforms it without changing the strain rate or temperature in the next cycle, one may find it

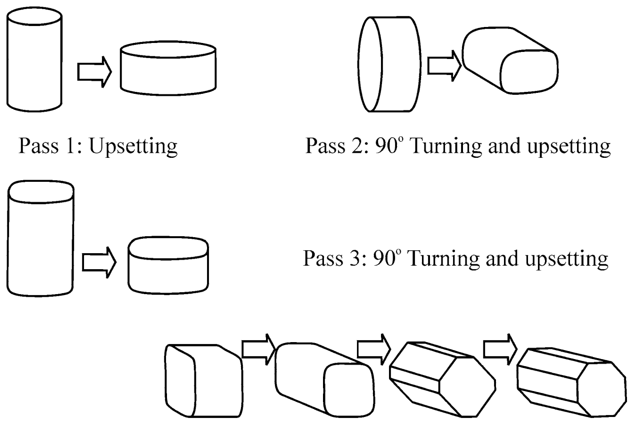

Fig. 1 A schematic representation of multiple isothermal forging

will flow superplastically and this is indeed often observed [14]. A decrease of the temperature in the next cycle maintaining the strain rate provides a further reduction of the grain size. An even larger increase of plasticity allows a further decrease of temperature in the next cycle and thus obtaining a fully recrystallized microstructure with an even smaller grain size. Thus, MIF with a stepwise reduction of temperature allows one to refine the grain size down to the nanometers range avoiding fracture. The final forging temperature is determined by the dependence $d(T, \dot{\varepsilon})$. The number of cycles, temperature decrement between the cycles, ΔT_i, the whole temperature fall between the first and last cycles, ΔT, and number of passes in each cycle depend on the material and its initial microstructure. The key issue is to provide a uniform recrystallized microstructure after each cycle. Non-recrystallized volumes of material retained at higher temperatures are inherited at lower temperatures, since further deformation is localized in recrystallized fine-grained volumes. This results in a bimodal microstructure with spatially separated fine-grained and coarse-grained components.

MIF allows introducing more deformation energy into material than ECAP can, since the energy expenses to overcome friction are much less in the former case. Due to this fact, MIF allows one to obtain bulkier semi-products. Another advantage of MIF making it a technologically attractive method is that it allows for nanostructuring of materials by the use of ordinary pressure equipment and very simple technological setup.

In its essence, MIF is not an SPD method but a mild deformation-thermal treatment of materials. From the fundamental point of view its advantage is that dynamic recrystallization allows one to fix the granular structure formed at each cycle such that further deformation does not destroy this structure but continues the grain refinement. Due to this, more effective nanostructuring is achieved by this method than by SPD.

Processing of alloys by MIF

Titanium alloys

Preliminary studies of the effect of hot and warm deformation on the microstructure and mechanical properties of a series of Ti alloys (VT1-0, VT6, VT8, VT9, VT30) have been done on model samples to determine the temperature-strain rate conditions for (a) obtaining uniform fine-grained structure and (b) formation of nanosized grains and subgrains [4, 6, 15, 17–20]. These data served as basic information for the development of methods for production of nanostructured billets of these alloys. Consider the technological route of the fabrication of bulk and sheet nanomaterials of large dimensions on an example of Ti alloy VT6 (Ti–6Al–4V).

The studies have shown that the most favorable initial structure for a uniform recrystallization process in this alloy is a thin plate-like $(\alpha + \beta)$-structure [15]. This structure is formed during preliminary thermal treatment consisting of cooling the billets in water after heating in a temperature interval of β-phase. Other types of structure such as thick plate-like and coarse-grained equiaxed grains lead to a localization of recrystallization processes.

To fabricate bulk nanostructured samples of VT6 alloy a hot-forged bar with diameter $\varnothing = 230$ mm was used. The temperature of complete $\alpha \Rightarrow \beta$ transformation was equal to $T = 995$ °C. Studies of the macrostructure in the sample's cross section revealed structural heterogeneity consisting in a wide grain size distribution (the size of β-grains between $d = 600$–1,000 μm) and even larger regions with the size 2–4 mm having similar crystallographic orientations as revealed by similar etching depths.

Prior to deformation treatment the samples cut from the bar were held in β-phase field ($T = 1{,}010$ °C, $t = 2$ h) and cooled down in water. The fine lamellar microstructure obtained by this thermal treatment is presented in Fig. 2a.

Further treatment of the samples was done by a multiple cycle MIF according to the scheme of Fig. 1 in the temperature interval of $(\alpha + \beta)$-phase field, $T = 700$–600 °C = (0.50–0.45)T_m (T_m is the melting temperature) at average strain rate $\dot{\varepsilon} = 10^{-3}$ s^{-1}. The accumulated true logarithmic strain was at least $\Sigma e = 3$. For these conditions, the largest VT6 samples that could be deformed on a hydraulic press with load $P = 16$ MN available at IMSP RAS had a diameter $\varnothing = 200$ mm and length $L = 300$ mm and a mass more than 40 kg. The temperature interval of forging ΔT depends on the initial microstructure. If in the initial state the material has a

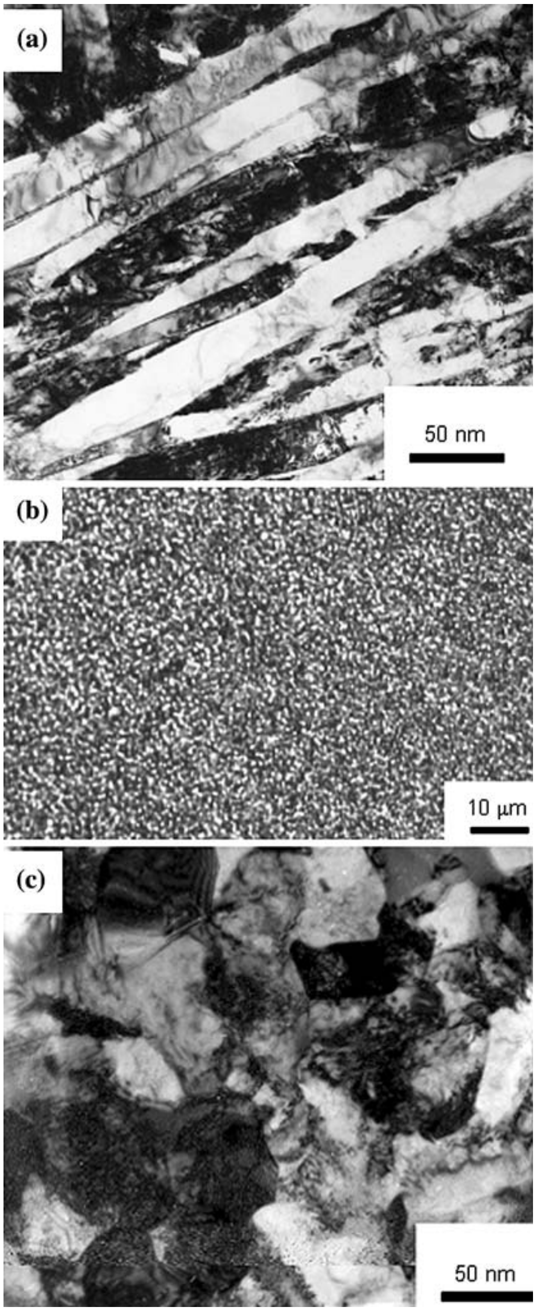

Fig. 2 Microstructure of Ti alloy VT6 after a preliminary thermal treatment in β-phase field as revealed by TEM (**a**) and after MIF as revealed by optical microscopy (**b**) and TEM (**c**)

coarse-grained lamellar structure, the initial temperature must be higher. In VT6 alloy the fine lamellar structure formed after thermal treatment significantly facilitates the subsequent treatment to obtain nanostructure.

The above treatment resulted in a quite uniform microstructure over the whole cross section of the bar. The microstructure is characterized by homogeneously distributed globular particles of α and β phases with an average diameter $d = 400$ nm (Fig. 2b, c).

Figure 3 represents different bulk nanostructured titanium semi-products, which can be obtained by MIF-rods, rolling ingots, disks, and rings.

Versatility of MIF

The above-presented principles of MIF have been successfully used at IMSP RAS to process nanostructured bulk semi-products from several dozen alloys including Ti, Al, Cu, Ni alloys, steels, heat resistant nickel alloys, intermetallics based on TiAl, Ti_3Al, Ti_2AlNb, etc.

Among Ni superalloys, EP962 and Inconel718 have been studied in the most detail [21–23]. To obtain a nanostructure in these alloys MIF should be done in a significantly broader temperature range than for Ti alloys: $T = 1{,}050$–700 °C $= (0.87$–$0.64)T_m$ and $T = 950$–550 °C $= (0.76$–$0.51)T_m$, respectively. It has been shown that in these alloys, despite their different compositions and initial structures, evolution of the structure is similar and consists in a successive formation of microduplex and nanoduplex structures. A nanoduplex structure with the grain/particle size $d = 50$ nm can be obtained using MIF in EP962 alloy and a similar nanostructure with the grain/particle size $d = 80$ nm in Inconel718.

Nanostructuring of intermetallic compounds which are even much less deformable than superalloys is of high interest. Consider shortly the process for a stoichiometric alloy Ti-25Al containing a single phase α_2 (Ti_3Al) [24]. An ingot of the size $\varnothing 110 \times 150$ mm in the initial state had a lamellar structure with the colony size $d = 200$–300 μm. The ingot was subjected to MIF, in which the drawing step was omitted, in the temperature range $T = 1{,}100$–650 °C $= (0.73$–$0.50)T_m$. The alloy has a good technological plasticity at $T = 1{,}100$ °C, in the two-phase $(\alpha + \beta)$-state. In the first cycle of MIF the microstructure was refined down to $d = 23$ μm. This resulted in a sharp increase of the technological plasticity of material and allowed further treatment to be carried out at a lower temperature, in α_2 ordered phase field. By a step-by-step treatment the temperature was reduced down to $T = 650$ °C and a grain size down to $d = 100$ nm. Further decrease of temperature resulted in a brittle failure of material due to the loss of long-range order.

Mechanical properties of MIF-processed nanomaterials

The most important consequence of nanostructuring is, of course, a significant increase of the strength of material. Moreover, contrary to conventional metal forming processes resulting in a large loss of ductility, the MIF-nanostructuring retains a reasonably high ductility.

As an example, Table 1 presents the mechanical properties of nanostructured Ti alloy VT6 [25]. For a

Fig. 3 Bulk nanostructured VT6 semi-products: rod $\varnothing = 200$ mm, $L = 300$ mm (**a**); rolling preform $200 \times 170 \times 100$ mm^3 (**b**); disk $\varnothing = 320$ mm, $h = 100$ mm (**c**); ring $\varnothing_{ex} = 320$ mm, $\varnothing_{in} = 200$ mm, $h = 80$ mm (**d**)

Table 1 Mechanical properties of differently processed alloy VT6 (Ti-6Al-4 V) at room temperature (ultimate tensile stress σ_u, yield stress $\sigma_{0.2}$, elongation δ, contraction ψ, and fatigue limit σ_{-1})

Processing and grain size	σ_u, MPa	$\sigma_{0.2}$, MPa	δ, %	Ψ, %	σ_{-1}, MPa
MIF, $d = 400$ nm	1,350	1,300	8	60	690
MIF + cold rolling	1,500	1,460	8	55	–
ECAP + extrusion, $d = 200$–400 nm	1,357	1,250	11	32	623
Quenching + aging, $d = 10$ µm	1,050	980	9	35	580

comparison, the data for the same alloy processed to obtain an ordinary fine-grained state and nanostructured by a combination of ECAP and extrusion are presented [26]. As one can see from this table, the yield stress and ultimate strength of the MIF-processed alloy have nearly the same values as the characteristics after ECAP followed by extrusion; after additional cold rolling the properties become even higher. At the same time, the MIF-processed samples have much larger dimensions than those obtainable by ECAP (Fig. 3).

The enhanced strength of the alloy VT6 is retained in the range of exploitation temperatures of this alloy (up to $T = 400$ °C). At higher temperatures one observes an opposite effect, i.e. a sharp decrease of the flow stress and at a certain temperature, superplasticity is observed. The most exciting result is that the MIF-nanostructured alloy can be deformed superplastically at temperatures 200–300 °C lower than the onset of superplasticity of ordinary fine-grained materials [27]. This effect of low-temperature superplasticity has been found to be universal and is observed in the majority of MIF-nanostructured materials including the very brittle intermetallic alloys. For example, Ti-25Al with the grain size of $d = 100$ nm exhibits a superplastic behavior at a temperature as low as $T = 600$ °C with a total elongation $\delta = 780\%$ (Fig. 4a) [24]. One should point out also the fact of non-zero plasticity of this absolutely brittle material at room temperature with an elongation $\delta = 4.8\%$ (Fig. 4b).

Prospects of scaling up and applications of nanomaterials

From the possibility of processing large samples by MIF, its versatility, and enhanced mechanical properties of nanomaterials produced by this method, it follows that MIF is an advanced method for the fabrication of various commercial semi-products of nanostructured materials. For example, bulk billets processed by MIF can be subsequently rolled at relatively low temperatures to obtain sheets. As an example, commercial-size sheets ($1{,}500 \times 500 \times 2$ mm^3) with the grain size $d = 500$ nm have been produced from a slab of nanostructured Ti alloy VT6 [28].

The sizes of bulk and sheet semi-products can be scaled up to any industrial need provided that proper presses and rolling mills are used. Combined with enhanced properties of nanomaterials, this opens fairly good prospects of

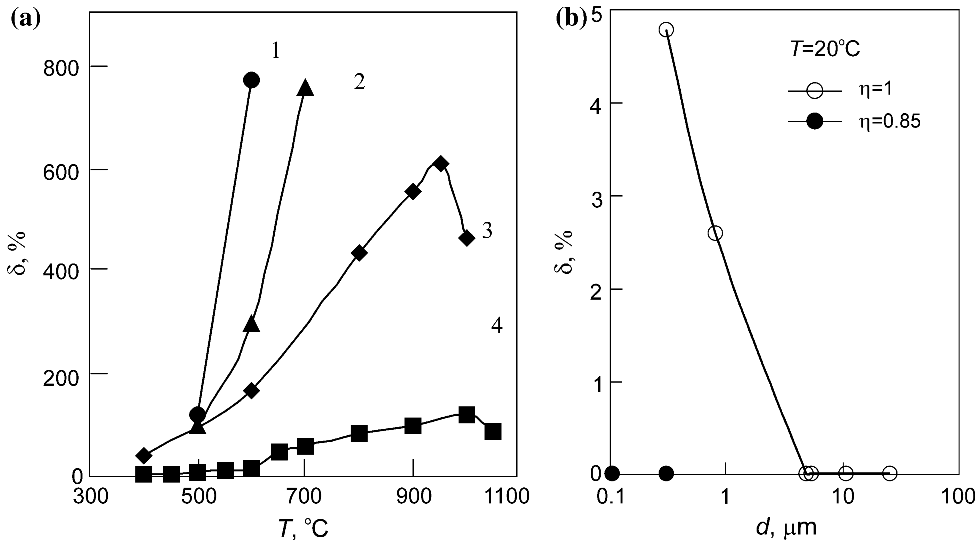

Fig. 4 Elongation to failure δ of Ti-25Al as a function of grain size d ($\dot{\varepsilon} = 6.4 \times 10^{-4}\ s^{-1}$) at elevated temperatures (**a**) (1 − d = 100 nm, 2 − d = 300 nm, 3 − d = 800 nm, 4 − d = 8.5 µm) and at room temperature (**b**); η is the long range order parameter

functional and structural applications of MIF-nanostructured materials.

There are two general ways of possible applications of bulk nanostructured materials.

The first way consists in direct use of nanostructured semi-products in manufacturing of components and structures via, say, cutting. These products will have enhanced strength and fatigue limit and at the same time improved functional properties. For example, nanostructured Ti will be very useful in making medical devices, implants, and both methods, ECAP and MIF, are capable of producing high-quality rod-shaped semi-products for this purpose [26]. The use of nanomaterials as damping materials can simultaneously increase internal friction and strength of damping devices. Nanostructuring allows one to increase the hysteretic properties of hard magnets combined with a high strength and workability. The lowered work function of nanomaterials can be used in the development of efficient electron sources.

The second way is related to the superplastic forming of nanostructured materials. The significantly decreased temperature of superplastic forming makes superplasticity a practically advantageous technology. Using superplastic die forging, forming, and integral technologies based on superplastic forming and pressure welding, figurine-shaped articles can be manufactured. Production of these articles having enhanced exploitation properties is very important for aircraft engine-building, power-engineering, etc.

One of the most important articles of this kind is the hollow blade for gas-turbine engines [29]. The use of nanostructured Ti alloys in the integral technology of pressure welding and superplastic forming of this article allows one to decrease significantly the temperature of process (down to 700 °C and even lower) thus resulting in a significant save of energy and labor and enhancing the properties.

Conclusions

The present analysis shows that one has to distinguish two general approaches to the deformation nanostructuring of materials: severe plastic deformation on the one hand, and mild deformation methods on the other. These methods are based on fundamentally different mechanisms operating at low and high temperatures. It seems useful to analyze the efficiency and application fields of emerging new deformation methods of nanostructuring in terms of this classification. While ECAP and related SPD methods are very useful to produce rod-shaped nanostructured semi-products, multiple isothermal forging belonging to the mild methods seems appropriate for the production of bulky and sheet semi-products with basically unrestricted geometrical dimensions.

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