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Fundamentals of titanium nanocrystalline structure creation by cryomechanical grain fragmentation

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ABSTRACT

The evolution of the CP titanium microstructure at deformation by rolling at the temperature of 77 K in the range of 0.06–3 true strain has been investigated using light microscopy, transmission electron microscopy and X-ray analysis. Role of deformation twinning as the main mechanism responsible for the fragmentation of grains and formation of the bulk nanocrystalline state is determined. We discovered a three-stage character of the grain refinement with increase in cryorolling reduction. It corresponds to stages of twinning process development. The limit of grain refinement in the processing of nanocrystalline titanium using the method of cryomechanical grain fragmentation is ~ 40 nm. It is due to a low probability of occurrence of twins in the grains with a size less than ~ 100 nm. The coincidence of the grain size and the crystallite size (coherent scattering regions) indicates that grains have a sufficiently perfect internal structure. It demonstrates that dislocations known to be a source of lattice distortion cannot be accumulated in nanoscale grains. It was shown that cryomechanical grain fragmentation (CMGF) is the effective method of processing a bulk nanocrystalline titanium (as well as zirconium). The mechanical properties of titanium have been characterized in three structural states: coarse-grained, ultrafine-grained and nanocrystalline.

1. Introduction

The unique properties of nanostructured materials, like high strength, are determined by their structural state with the grain size as its basic parameter. It can be reduced to several nanometers by application of special technological processes. Unalloyed titanium possesses a set of important structural and functional properties, but its application is restricted in most cases because of its low strength. Use of special deformation technologies, as an alternative to hardening by alloying, permits us to form a bulky structural state with submicron/nanosize grains retaining both chemical composition and initial metal density, improving the functional properties of the material at the same time. The deformation structures of this state can be obtained with severe plastic deformation (SPD) techniques of [1–4]. Equal-channel angular pressing (ECAP) is the most-used one of SPD for ultrafine-grained materials preparation (the average grain size is 200 nm < d < 1 μm). Sometimes, the ECAP is followed by additional cold working to ensure more efficient refining. The technological variety [4] also includes other frequently used SPD methods, such as high-pressure torsion [5], accumulative roll bonding [6], rolling extrusion [7], and asymmetric rolling method [8]. The SPD methods are, however, not free from certain disadvantages, such as severe limitation on the size and shape of workpieces, unobtainable nanocrystalline states with grains d < 100 nm in bulky workpieces (especially in pure metals) and a very sophisticated equipment. These factors hamper significantly the practical potentialities of the methods.

The type of the structure formed by plastic deformation is determined by the activity of deformation modes (dislocation slipping and twinning) at selected temperatures and the deformation process. Titanium is a metal with HCP lattice and complex mechanism of plastic deformation. At room temperatures slip can proceed in titanium in several crystallographic planes – prismatic $\{10\ \bar{1}\ 0\}$, basal (0001) and pyramidal $\{10\ \bar{1}\ 1\}$. However, slip develops along the close-packed directions $< 11\ \bar{2}\ 0 >$ ($< a >$ - direction) in the basal plane and it does not involve the grain size variation along the $< c >$ - axis. The activity of these slip systems affords only four independent modes of deformation. Meanwhile, according to the Mises criterion, five independent shearing systems are necessary to ensure plastic deformation holding the material continuity. At higher temperatures this requirement can be met due to the active pyramidal slip $\{10\ \bar{1}\ 1\} < 11\ \bar{2}\ 3 >$. At low temperatures (below ~ 200 K) the critical shearing stress in the basal and pyramidal planes increases significantly and only prismatic slip $\{10\ \bar{1}\ 0\} < 11\ \bar{2}\ 0 >$ is operative [9]. Twinning becomes particularly important.

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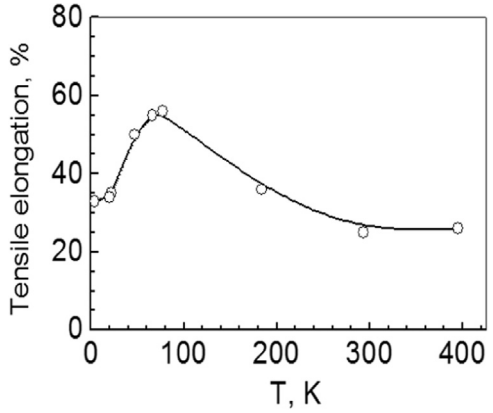

Fig. 1. Temperature dependence of tensile elongation of coarse grained CP titanium VT1-0.

Five types of twinning planes are active in titanium at the liquid nitrogen temperature (77 K) [9–11]. The diversity of twinning systems is favorable for developing secondary and tertiary twinning both inside the primary twin lamellae and for local stresses relaxation in the twin-matrix accommodation areas [12]. Grain fragmentation by twins also enhances plasticity by increasing strain hardening rate and thus hindering the localization of plasticity. These factors contribute appreciably to the plasticity of polycrystalline titanium. It was found the combination of prismatic sliding and twinning leads to a significant increase in ductility in the temperature range 60–150 K [12,13]. In particular, the elongation to failure (δ) of commercial purity titanium at T = 77 K almost twice higher than at room temperature, reaching ~ 55% (see Fig. 1) [12,13].

Grain refinement by twin lamellae and high ductility were the physical basis of our production technology of bulk nanocrystalline state by the method of cryomechanical fragmentation of grains (CMGF). In essence, CMGF is an extension of the standard methods of plastic metal working (drawing, sheet-, strip-, shape- rolling and so on) at the low temperatures. One of the CMGF techniques (rolling at the liquid nitrogen (77 K) [14]) was successfully used to prepare the first bulky nanocrystalline titanium with a unimodal structure ($10 < d < 100$ nm) and average grain size ~35 nm. On the other hand, a combined application of cryodeformation and annealing allows to vary a submicron grain content in a nanocrystalline matrix, i.e. to form a bimodal structure.

Note that recent a investigations report that are concerns with Ti microstructure refinement through cryodeformation – pressing in the channel press mold [15,16] and cryorolling [17].

Here we report the results of studies on the relationship between the evolution of the twin microstructure and the parameters of nanostructural titanium produced by cryorolling to large degrees of reduction. It is shown that cryomechanical grain fragmentation is an efficient method to form a bulky nanocrystalline state in twinning-prone titanium. It revealed the existence of limiting average grain size in nanocrystalline titanium obtained by using CMGF method. The physical nature of this fact is explained by a decrease in the propensity to twinning with decreasing grain size. The reliability of the experimental results is based on complex investigation of size characteristics of microstructural elements by light and electron microscopy and the X-rays diffraction analysis. Mechanical properties of titanium have been characterized in three structural states: coarse-grained, ultrafine-grained and nanocrystalline.

2. Materials and methods

The experiments were carried out on commercial-purity titanium fabricated in the form of 4 – 16 mm thick sheets. In the as-supplied materials the grain size was ~ 15 μm and changed to ~ 20 μm after annealing at 670 °C for 45 min. The concentration of the main impurities were (mass %) Fe – 0.06; O – 0.11; N – 0.02; C – 0.01; H – 0.005. To obtain the nanocrystalline state in the metal the initial grains were fragmented by repeated rolling in the laboratory rolling mill at the rate ≈ 35 mm s^{-1} and the per-pass compression ~ 0.1–0.3 mm at the liquid nitrogen temperature. The true compressive strain at rolling $e = \ln(t_0/t_e)$ (here t_0 and t_e are the initial and final thicknesses, respectively) varied within $|e| \sim 0.06 - \sim 3$. The reduction ratio $|e|$ was measured with an accuracy of 10–15%.

Average grain size at the starting low cryostrain ($e < 0.3$), when grains have a micrometer size, was estimated by optical metallography. Microstructural investigations were made on the sample surface parallel to the rolling plane. The grain size in this case was calculated as the average value of random linear intercept (the stereometric metallography method) [18]. The term "grain size" means the effective size of the structural elements surrounded by high angle boundaries (misorientation above 15°). These are original grain boundaries, twin boundaries and their fragments. The crystallographic orientations of the slip, primary and secondary twinning planes using GM-2 goniomicroscope were determined (as in [20]).

Deformation microstructure after application of strain has been studied with a transmission electron microscope EM-200 at the accelerating voltage of 175 kV. Samples for TEM studies were cut by the electric spark method and thinned with sanding paper to a thickness of ≈ 0.3 mm. Further thinning until the hole appearance was performed by double jet electropolishing in electrolyte at 233 K (perchloric acid dissolved in methyl and butyl alcohol in a ratio of 1: 6: 10 vol parts, respectively). Bright-field images are more suitable for the analysis of relatively "large" structural elements - with a grain size of not less than 500 nm. Grain boundaries in the ultrafine materials with smaller grains become unclear. Dark-field regime of microscope operation is better for their quantitative analysis. Grain size d is defined as a diameter of a circle with area equal to TEM dark field image area of the grain. Dark-field microscopic images were obtained by cutting out fragments in three closely spaced diffraction rings {10 $\bar{1}$ 0}, (0002) and {10 $\bar{1}$ 1} in the selected area diffraction pattern by aperture diaphragm. Grains on dark field negatives were sorted by size in order to plot histograms with 800–1300 counts. The average grain size was defined as a coordinate on the x-axis center of gravity of a plane figure.

Sizes of coherent-scattering region (CSR) or crystallites were determined by X-ray diffraction. Its analysis was performed on a DRON-2.0 in the emission of copper anode with a nickel filter at room temperature at θ–2θ scanning scheme using a collimating slit in a continuous mode with automatic recording on the computer. The subsequent data processing was carried out using computer programs. General view of the diffraction patterns has been obtained by recording the intensity in the range of angles $30° < 2\theta < 110°$ with scanning step 0.1°. Crystallite sizes were measured from Hall plots with Cauchy or Gauss function fits to describe the shape of the profile line [19,20]. Instrumental line broadening was considered by recording a reference sample (coarse grained aluminum). X-ray diffraction patterns were obtained from the sample surface parallel to the rolling plane without additional treatment.

The mechanical properties were determined in experiments under quasi-static uniaxial tension, at a nominal rate of deformation $\dot{\varepsilon} \approx 2 \times 10^{-4}$ s^{-1}. Tensile samples in the form of double blades with a working area of 0.6 × 5 × 25 mm, were prepared using a strip of appropriate thickness in the rolling direction using a punch.

3. Results

3.1. Twin microstructure evolution. Metallographic analysis

From initial stage of deformation ($|e| \sim 0.06$) at 77 K intragrained titanium substructure is characterized by a number of twins on a background of randomly distributed screw dislocations [21]. This is due