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Research on Submicron-Grained Structure Formation in Titanium Alloys upon Reversible Hydrogenation and Plastic Deformation

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Abstract—The influence of thermohydrogen treatment combined with hot rolling on the structural formation in α- and near-α-titanium alloys has been studied. The prospects of obtaining submicron-grained sheet semi-finished products of VT5 (Ti–5.8Al–0.1Fe, wt %) and VT20 (Ti–5.9Al–1.5V–1.2Mo–1.8Zr–0.1Fe, wt %) alloys are shown. In these materials, a submicron-grained structure allows the plastic deformation to be induced by superplasticity at temperatures reduced by 100–200°C.

Keywords: titanium alloys, hydrogen technology, submicron-grained structure, superplasticity, flow stress, electron microscopy, fine structure

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INTRODUCTION

The development of innovative technologies and state-of-the-art high-tech materials is within the scope of a state program for domestic research and industry supported by the Government of the Russian Federation. Details are pointed out in the List of Critical Technologies of the Russian Federation, approved by the Decree of the President of the Russian Federation (no. 899 of July 7, 2011 [1]), and in the Strategic Directions of the Development of Materials and Technologies for Their Recycling for the Period to 2030 [2].

It is well known that creating new-generation materials or technologies is associated with the need for achieving certain properties that depend to a large extent on structural features of the material [3]. Any change in structure is likely to alter the properties, which is confirmed by theoretical and experimental metals science. There is a great variety of methods of affecting the structure of metals and alloys, such as conventional (thermal treatment and plastic strain) and innovative approaches (hydrogen treatment of materials) [4].

The most important practical results were obtained in the hydrogen technology of titanium alloys [5], which is based on thermohydrogen treatment (THT) [6]. It comprises three fundamental stages: hydrogenation of metal, thermal or mechanical exposure of hydrogenized metal, and vacuum annealing to ensure that hydrogen contents are low enough to avoid hydrogen embrittlement; i.e., there is reversible hydrogen doping. THP of alloys allows one to form structures that are unachievable in conventional ways [5–12]. So, the complementary hydrogenation may transform a coarse lamellar cast structure of near-α and α + β alloys in a fine lamellar at the nanoscale level [13] or even create a composite structure of the same classes of alloys composed of particles of the aluminum-rich α phase to the formation of ordered particles of the α_2 phase (Ti_3Al), aluminum-depleted α phase, and β phase [14]. This opens up particularly wide prospects, because the aluminum-depleted matrix leads to prerequisites for reducing flow stress in the materials and consequently for attaining a superplastic state.

One relevant problem of modern practical materials science is the creation of heterophase ultradispersed structures in industrial titanium alloys in order to obtain a superplastic molding [15, 16]. In this respect, two main conditions for superplasticity can be distinguished: the presence of extended interfaces and the micron- or submicron-grained scale of structural components [17, 18]. As shown in [19–22], both conditions are achievable through temporary (reversible) hydrogenation of titanium alloys.

The present work aims to investigate the influence of reversible hydrogenation and thermohydrogen processing combined with plastic deformation on the structure and properties of titanium α alloy VT5 and near-α alloy VT20 [23].

SAMPLES AND CHARACTERIZATION METHODS

The chemical composition of alloys VT5 (Ti–5.8Al–0.1Fe, wt %), and VT20 (Ti–5.9Al–1.5V–1.2Mo–1.8Zr–0.1Fe, wt %) met the requirements of GOST 19807-91. Samples were deformed semi-finished products (20-mm-thick slabs) of the indicated alloys, produced via the industrial technology. Hydrogenation of samples was performed in accordance with a thermodiffusive method on a Siverts laboratory setup to concentrations of 0.2–1.0 wt %, with an increment of 0.2 wt % in a temperature range of 650–900°C. Cooling to room temperature was implemented at a rate of 1 K/s. The content of embedded hydrogen was controlled by weighing samples on an analytical balance, while the residual hydrogen concentration after the vacuum annealing was measured on an ISP-51 spectrograph equipped with a MOPS-1/2048/PCI electronic analytical console.

Hydrogenated samples were exposed to pressure by hot rolling in the ($\alpha + \beta$) region. The vacuum annealing after deformation was conducted in a SVNE-1.3.1/16-I3 furnace at a temperature of 625°C for 8 h.

The microstructure was examined via the light field method on a ZEISS Axio Observer.A1m optical microscope at 1100× magnification. The digital optical micrographs were analyzed by the conventional metallographic approaches using the NEXSYS ImageExpert Pro 3 software package for image processing. The substructure was probed in a JEM-200C transmission electron microscope via the light and dark field methods, as well as electron microdiffraction. The fine structure of samples (at the atomic level) was studied via high-resolution transmission electron microscopy (TEM) on a Tecnai G2 F20 S-TWIN microscope at an accelerating voltage of 200 kV and in the scanning transmission electron microscopy mode.

Samples indented for transmission electron microscopy studies were cut off on an AQ300L electroerosion setup. Disks 3 mm in diameter were treated in two stages. At the first stage, samples on either side were thinned on a LaboPol-5 device by mechanical grinding on sanding disks to achieve a thickness of plates of 100–150 μm. As known, structural distortions caused by the coarse grinding arise at a depth of 12–75 μm, while those induced by the fine grinding are observed at a depth of 2.5–25 μm. At the second stage of the final step of thin foil production on a TenuPol-5 setup for electrolytic jet polishing (on the installation TenuPol-5 for electrolytic jet polishing using A3 electrolyte at a temperature of 248 K in a solution of 60 mL of $HClO_4$ + 600 mL of CH_3OH + 360 mL of $CH_3(CH_2)_2CH_2OCH_2CH_2OH$ at a temperature of about –30°C and a voltage of $U = 38$ V), thinning must be applied from either side to prevent the formation of artifacts in a studied foil, which can be due to the mechanical grinding at the onset of the foil preparation.

The X-ray diffraction analysis was implemented on DRON-4 and DRON-7 diffractometers using filtered CuK_α radiation ($\lambda_{av} = 0.15418$ nm). The parameters of the recording were as follows: the accelerating voltage was 40 kV; the anodic current was 30 mA; the scan increment was 0.05°; the exposure time at a point was 2 s.

Samples for metallographic and X-ray diffraction studies were prepared in accordance with conventional techniques. Samples to be tested for superplasticity were cut off from sheet semifinished products of the studied alloys pursuant to the experimental drawing.

RESULTS AND DISCUSSION

For α and near-α alloys of titanium (VT5 and VT20 respectively), it becomes difficult to manage the structure via conventional thermal treatment because of a lack (or a very small amount) of the second thermodynamically stable phase. In this respect, a unique way to impact the structure of these alloys is using pressure, which allows one to increase their hardness at avoiding a gain in plasticity [24].

Various studies reveal that uniformity in the arrangement and size of particles of the α phase can be improved by combining THP and plastic deformation. The embedded hydrogen reduces the amount of α phase in the alloy and consequently makes it aluminum-rich. At the same time, the aluminum concentration enriches enough for the formation of ordered α_2 phase based on Ti_3Al intermetallic. A superstructure α_2 emerges in the individual microvolumes of the aluminum-rich α phase in accordance with second-order phase transitions and possesses the ordered HCP structure of type $D0_{19}$ [10, 11, 15, 19–21]. On the other hand, hydrogen stabilizes the α phase, and the increase in the volume fraction of the latter causes a noticeable improvement of plastic characteristics of alloys [25–27].

The higher the amount of the β phase, the lower is the degree of its doping with β stabilizers and aluminum because of its accommodation in the α phase. Further plastic deformation leads to the emergence of a large number of new crystalline defects in the hydrogenated β phase, which are predominately linear (dislocations) and play the role of nucleation centers of the particles of the α phase upon degassing. The processes of nucleation of particles prevail over their growth owing to the low diffusion mobility of atoms of the main alloying elements during vacuum annealing, because nucleation obeys the shear mechanism and remains independent of diffusion [28].

It is found that reversible hydrogenation combined with plastic deformation in a hydrogenated state allows one to achieve a submicron-grained heterophase structure in semifinished products, composed of particles with sizes of 300–500 nm. For alloy VT5, there is a two-phase ($\alpha + \alpha_2$) structure (Figs. 1a–1c), while the structure of VT20 is multiphase ($\alpha + \alpha_2 + \beta$) (Figs. 1d–1f). The presence of the ordered α_2 phase is highlighted by

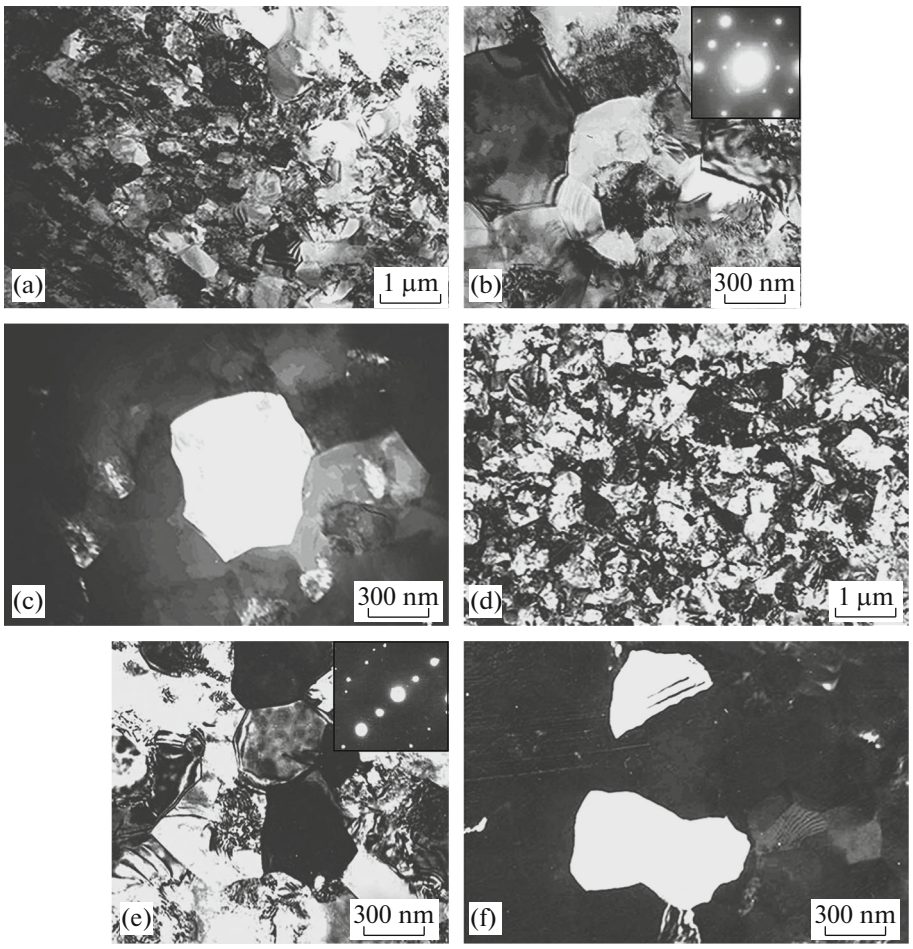

Fig. 1. Structure of alloys VT5 (a–c) and VT20 (d–f) exposed to THP in combination with plastic deformation: (a, b, d, e) light-field images; (c, f) dark-field image in (c) [00.1] and (f) [02.1] superstructure reflexes used to acquire TEM electron diffraction patterns (b, e).

electron microdiffraction data (Figs. 1b, 1e), as well as by (10.1) and (11.0) superstructure reflexes on the X-ray diffraction patterns.

A structure with the α_2 phase based on the Ti_3Al intermetallic compound is metastable and is atypical of alloys VT5 and VT20 under equilibrium conditions. In connection with this, heating to processing and/or operating temperatures may cause diffusion processes leading to the transformation of the metastable structure to the equilibrium one.

To determine the temperature and temporal stability parameters of $(\alpha + \alpha_2)$ and $(\alpha + \alpha_2 + \beta)$ structures, alloys VT5 and VT20 were exposed to isothermal heating in furnaces with air atmosphere at temperatures corresponding to anticipated temperatures of superplastic molding (725–750°C). The total exposure time τ_e ranged from 1 to 100 h. The changes in the structure-phase state of samples undergoing diffusion processes were monitored at room temperature via XRD in the form of dependences of the interplane distances (Fig. 2) for lines $(22.0)_{\alpha 2}$ and $(11.0)_\alpha$ with consideration of the reflection order d/n, as well as using the diffraction line area ratio $I_{\alpha 2}/I_\alpha$ of the α_2 and α phases.

The results indicate that $(\alpha + \alpha_2)$ and $(\alpha + \alpha_2 + \beta)$ structures are stable at a temperature of 750°C for at least 12–14 h, which is enough for plastic deformation upon superplasticity.

The atomic lattice images were acquired via high-resolution transmission microscopy on the axis of the $[10.0]_{\alpha 2}$ and $[10.0]_\alpha$ zones. The direct and inverse Fourier transformation enabled one to determine the characteristic interplane distances and the position of atoms for the ordered HCP α_2 structure with a symmetry $D0_{19}$ (Figs. 3a and 3b). A schematic of the package of atoms in the lattice of the α_2 and β phases on the axis of the $[10.0]_{\alpha 2}$ and $[10.0]_\alpha$ zones is shown in Fig. 3c.

It is worth mentioning that a two-phase composite structure was successfully obtained for single-phase alloys (VT5) through the THP, which cannot be achieved by the conventional treatment. The creation of a submicron-grained structure causes an increase in the relative elongation, and the depletion of the α and

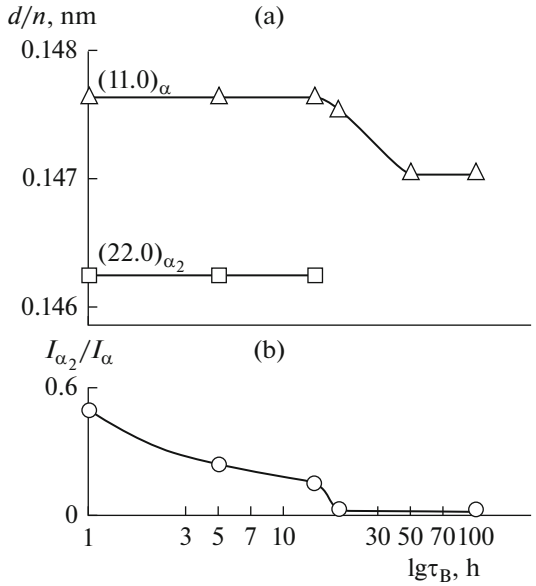

Fig. 2. (a) Interplane distances of $(22.0)_{\alpha 2}$ and $(11.0)_{\alpha}$ planes and (b) their intensity area ratios as functions of isothermal exposure duration at a temperature of 750°C for samples of alloys VT5 and VT20 after THP.

β phases in aluminum makes the flow stress less pronounced.

In the context of the regularities highlighted, an experimental technology combining thermohydrogen and thermomechanical processing was developed, allowing a submicron-grained structure to be formed in sheet semifinished products of alloys VT5 and VT20. It includes the hydrogen saturation of semifinished products, rolling in the upper temperature range of (α + β) area exposed to hydrogen plasticization [25, 29], and low-temperature vacuum annealing (at temperatures of 600–700°C). The latter ensures the refinement of the structure, because the processes of nucleation of new particles of the α phase prevail over the processes of their growth owing to the low diffusion mobility of the main alloying elements upon the (β→α) transition during annealing.

The final stage of the work was to test superplasticity of flat samples of alloys VT5 and VT20 at temperatures 725 and 750°C respectively. The temperatures of tests were chosen to account for the expected decrease in flow stresses in samples after THP and deformation, being 100–200°C below temperatures responsible for the maximum relative elongation in agreement with conventional concepts about the conditions favorable for superplastic deformation mechanisms (these temperatures for titanium alloys range from 825 to 950°C when the structure is composed of elements with sizes not larger than 5–7 μm).

Samples were cut off from 2-mm-thick sheet semifinished products with micron-grained and submicron-grained structures in accordance with the experimental design. The obtained values of relative elongation and flow stress are listed in Table 1. The appearance of samples before and after tests is shown in Fig. 4.

Thus, the technology developed to fabricate sheet semifinished products is found to favor the reduction of flow stresses by 3–4 times and a gain in relative elongation upon deformation by 5 times. It is also

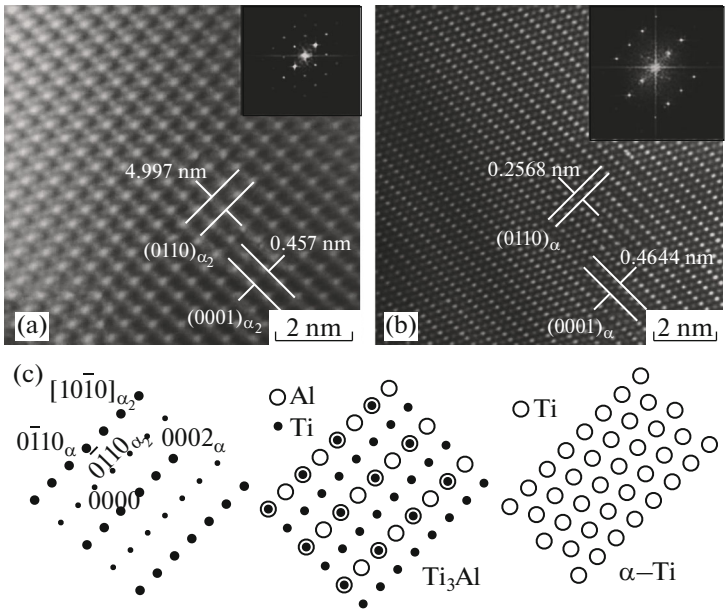

Fig. 3. High-resolution transmission electron microscopy patterns with Fourier transformation for titanium alloy VT5 after THP: (a) axis of $[10.0]_{\alpha 2}$ zone; (b) axis of $[10.0]_{\alpha}$ zone; (c) packing of atoms in α_2 phase with $D0_{19}$ lattice of the axis of $[10.0]_{\alpha 2}$ zone.

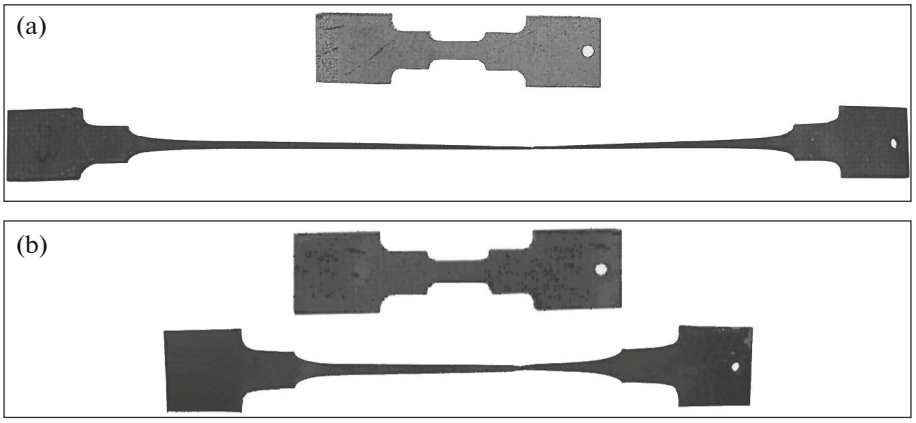

Fig. 4. Appearance of samples of alloys (a) VT5 and (b) VT20 before and after plastic deformation upon superplasticity.

worth mentioning that samples were tested in a furnace with air atmosphere, and deformation led to their intense oxidation. The use of a protective medium allows not only the relative elongation to be increased but also the flow stress to be noticeably reduced.

CONCLUSIONS

(1) The combination of THP and plastic deformation in the hydrogenated state ensures the formation of a submicron-grained structure in sheet semifinished products of titanium alloys VT5 and VT20, the elements of which have sizes of 300–500 nm.

(2) The creation of a submicron-grained structure in sheet semifinished products with the α phase depleted in aluminum allows one to reduce the maximum flow stress. Plastic deformation temperatures are also decreased by 100–200°C in comparison with those of 825–950°C corresponding to the activation of superplastic deformation in samples with micron-grained structure.

(3) The tests reveal that sheet semifinished products obtained via the developed method are suitable for superplastic molding.

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Table 1. Plastic deformation characteristics for samples of alloys VT5 and VT20 with different structures (the initial deformation rate is 3×10^{-4} s^{-1})

Alloy	Temperature of tests, °C	Structure	Relative elongation, %	Flow stress, MPa
VT5	725	MS	280	93
		SMS	1190	29
VT20	750	MS	310	140
		SMS	630	36

MK—micron-grained structure composed of elements with sizes of 1–5 μm (industrial technology); SMC—submicron-grained structure with size of structural components of 300–500 nm (technology developed in this work).

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