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INFLUENCE OF REVERSIBLE HYDROGEN ALLOYING ON FORMATION OF SMC STRUCTURE IN TITANIUM ALLOYS BY SEVERE PLASTIC DEFORMATION

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A method of production of a submicrocrystalline (SMC) structure (d < 1μm) in large workpieces of the commercial pure titanium and the two-phase titanium alloys based on initiation of dynamic recrystallization (DRX) during hot working and reversible hydrogen alloying has been developed. The method involves continuous grain refinement due to DRX at decreasing temperature. Hydrogen alloying decreases deformation stresses and increases ductility at temperatures lower than in hydrogen-free alloy and promotes the formation of the finest grain structure. The grain sizes of 0 1–0.2 μm and 0.04 μm have been produced in the hydrogenated commercial pure Ti and Ti–11.4Al–1.7Mo–0.88Zr (at.%) based alloys, respectively. Specific features of phase transformations in the SMC titanium alloys after cooling from deformation temperature and after hydrogen removal by vacuum annealing were studied. Temperature dependencies of mechanical properties for SMC titanium alloys are shown.

Introduction

Materials with nano- and submicrocrystalline structure exhibit unique mechanical properties [1]. Strength of such materials is sharply increased and temperature of superplastic deformation significantly decreases [2]. That is why the development of an efficient method for obtaining SMC materials and the study of their properties is a very urgent problem. One of them is severe plastic deformation providing the intensive occurrence of DRX [2,3]. It is based on the dependence of the size (d) of recrystallized grains on the steady flow stress

$$\sigma_s = kd^{-n}, \quad (1)$$

where k is an empirical constant and the grain size exponent $n \cong 0.5$ [4]. Therefore, the size of recrystallized grains can be decreased via decreasing the temperature or increasing the strain rate since the change of these parameters leads to an increase in the flow stress. Grains produced during DR are almost the same in size as subgrains, while the subgrain size can be as less as several ten nanometers. Hence, a SMC structure is expected to be produced in materials by DRX. The SMC structure with d as low as 0.06 μm has been formed in Ti–10.30Al–1.55Mo–0.33Fe (at.%) (α+β)-titanium alloy at 570°C [5]. It should be noted that a critical strain for DRX initiation increases considerably when the deformation temperature decreases and the high strains are required to produce fully recrystallized SMC structure. Besides, high stresses and low ductility at lower temperatures lead to the crack formation in the billet [5]. However, the lower the deformation temperature, the finer the size of recrystallized grains.

Application of reversible hydrogen alloying for formation of SMC structure in titanium alloys seems to be very interesting. First, hydrogen reduces the temperature of $(\alpha+\beta) \Leftrightarrow \beta$ transformation and improves the workability of titanium alloys [6]. Second, hydrogen facilitates DRX of α-phase [7] and the formation of a finer structure in two-phase alloys during heat treatment. This leads to the increase in the fraction of recrystallized grains and the decrease in their size [6,8]. Third, one can expect for an additional effect of $\beta \rightarrow \alpha$ transformation stresses on grain refinement during vacuum annealing for hydrogen removal [6]. The present work was undertaken to answer these questions.

Experiment

The commercial pure titanium Ti with the chemical composition Ti–0.56Al–0.08Fe–0.12Si–0.20C–0.1H–0.3O and the two-phase titanium alloy VT9 with the chemical composition Ti–11.4Al–1.7Mo–0.88Zr–0.09Fe–0.45Si (both at.%) were used. The forged and then rolled materials produced by VSMPO were machined into 20 mm long by 10 mm diameter rods. Hydrogenation for these specimens was carried out in hydrogen atmosphere at 650–700°C. The commercial pure titanium was alloyed by hydrogen up to 5 and 16 at.%, the VT9 alloy up to 14 at.%. These alloys are marked as Ti–5H, Ti–16H and VT9–14H, respectively. The VT9–14H alloy after hydrogen removal is marked as VT9R. The Ti–5H alloy is an α-alloy, the Ti–16H and VT9–14H alloys are (α+β)-alloys with a close volume fraction of phases at 550–650°C. The samples of the commercial pure titanium were preannealed at the temperature of a single phase β-region, thus, after saturation with hydrogen they had a similar grain size of 270 ± 30 μm. The VT9 and VT9–14H alloy samples were quenched from the temperature of β-region, after that their grain sizes were 180 ± 20 and 30 ± 3 μm, respectively. Compression and tension mechanical tests of the samples were conducted at 20–800°C and the strain rates $5 \cdot 10^{-5}$–10^{-2} s^{-1}. The structure of the samples was studied by optical and electron microscopy. The SMC structure was obtained in billets of Ti and titanium alloy VT9, 20 mm in diameter and 40 mm in length, by a 2-stage *a*–*b*–*c*-forging at 380–420 and 530–570°C, respectively.

Results

In the initial condition the alloys had microstructure of two types: coarse-grained single-phase – in Ti and its alloy Ti–5H, coarse lamellar two-phase – in alloy Ti–16H, and martensite α″-structure in VT9 and VT9–14H. During compression tests at 400–700°C and $\dot{\varepsilon} = 10^{-4}$–$10^{-3}$ s^{-1} the occurrence of DRX and the refinement of the initial microstructure were observed in all alloys. A decrease in the deformation temperature leads to decrease in the size of recrystallized grains (Fig. 1). The mean grain sizes in Ti, Ti–5H and Ti–16H alloys at final testing temperatures were 0.30 ± ± 0.05, 0.20 ± 0.03 and 0.10 ± 0.02 μm, respectively, and in the VT9 and VT9–14H alloys – 0.1 ± 0.02 and 0.04 ± 0.01 μm, respectively. The dependence of recrystallized grain size on flow stress at $\varepsilon = 50\%$ is given in Fig. 2 and obeys to Eq. 1. For the two-phase alloys (Ti–16H, VT9, VT9–14H) the experimental data in

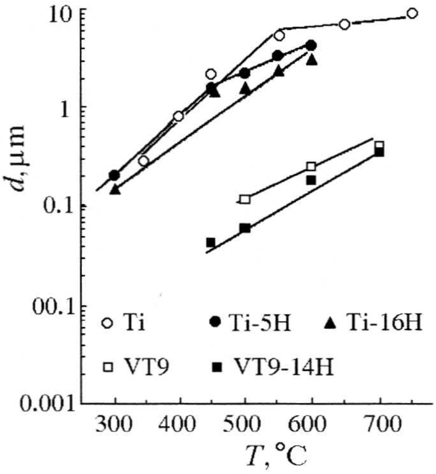

Fig. 1. Dependence of deformation temperature on size of recrystallized grains d in titanium alloys

this figure can be approximated by straight lines. The curves for the single phase Ti and Ti–5H alloys have two parts with significantly different slopes with the inflexion points at 650 and 550°C, respectively. The presence of inflexion points on the curves evidently shows a change in the recrystallization mechanism of these alloys with a decrease in the deformation temperature. Such a decrease leads to a significant increase in flow stress. Hydrogen alloying reduces a value of flow stress required for formation of the same grain size, but doesn't change the recrystallization mechanism of titanium alloys.

A decrease in the testing temperature reduces ductility. For example, the VT9 alloy samples failed already after compression by 20% at 580°C and $\dot{\varepsilon} = 1\cdot10^{-3}$ s^{-1}. At lower deformation temperatures the ductility can increase due to a decrease in the initial grain size. Hydrogen alloying provides the retarding of grain growth [7]. The size of β-grains in the VT9–14H alloy after β-region quenching is three times less as compared to the basic VT9 alloy. Hydrogen alloying provides the increase in dispersity of metastable phase decomposition (for instance, martensite) that contributes to formation of the finest grain size during DRX. In particular, after holding of β-quenched samples at 600°C for 20 min a mean thickness of precipitates in the VT9–14H alloy was 0.05 μm and 0.15 μm in the VT9 alloy. The occurrence of phase transformation along with DRX should contribute to formation of a SMC structure [2].

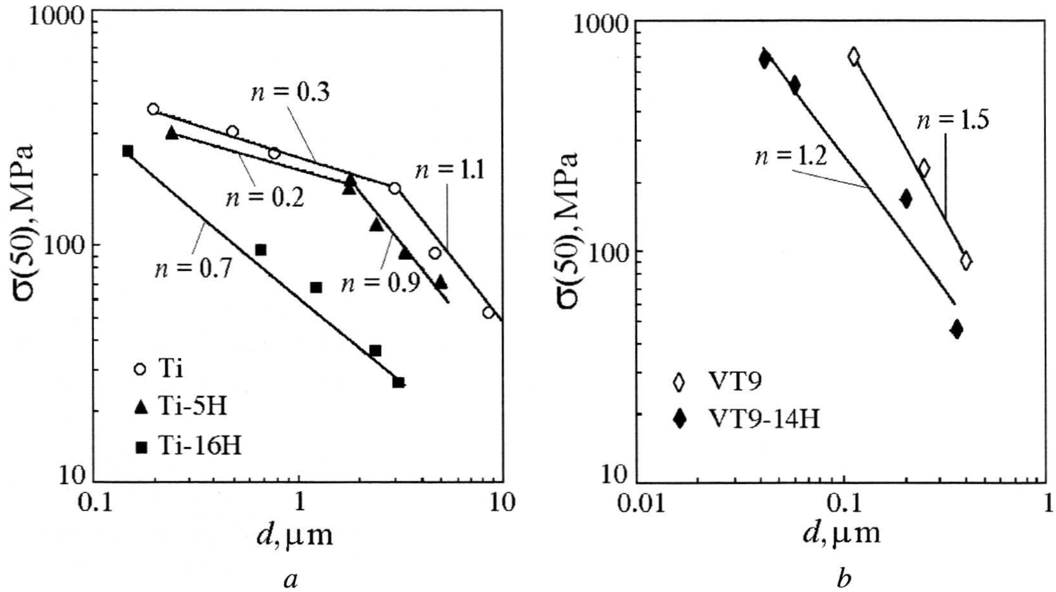

Fig. 2. Size of recrystallized grains d versus steady-state stress σ_{50} in titanium alloys: *a* – Ti, Ti–5H, Ti–16H; *b* – VT9, VT9–14H

In this condition the samples were deformed by 80% at 525°C without crack formation. As a result, after deformation of the VT9–14H alloy at 530°C a microstructure with a grain size of 0.04 μm was formed.

The billets with dimensions of 30×20×10 mm with SMC structure were produced by using multiple forging. Depending on alloy composition, the grain sizes corresponding to the smallest ones in Fig. 1, 2 were formed in the billets. The microstructure in the SMC condition is typical of alloys produced by severe plastic deformation: the presence of internal elastic stresses caused by high density of dislocations at grain boundaries was observed (Fig. 3). In the SMC titanium alloys Ti–5H and Ti–16H fine hydrides of a globular shape are mainly formed. As known [6], in hydrogenated titanium alloys hydride in the form of plates to several micrometers in size precipitate during cooling from the temperature higher than eutectoid (328°C). The estimation of grain growth has shown that the grain size doesn't become coarser in Ti, Ti–5H and Ti–16H alloys at $T < 400$°C and in VT9 and VT9–14H alloys at $T < 550$°C.

a *b*

Fig. 3. Microstructure of titanium alloys obtained by *a–b–c*-forging: *a* – Ti–16H; *b* – VT9R after hydrogen removal

One of the important aspects of applying hydrogen alloying for refinement of microstructure is retaining of the SMC condition after hydrogen removal. The presence of an oxidized layer in titanium does not allow to remove hydrogen at temperatures up to 500°C at which retaining of SMC structure is possible. At the same time the structure of VT9 alloy is more stable. A vacuum annealing at 550°C of VT9-14 alloy specimens decreases hydrogen concentration until safety level, like in basic alloy, and retains SMC structure (Fig. 3,*b*).

The initial microstructure affects its evolution during the hydrogen removal. First, degassing rate of the SMC specimens (d = 0.04 μm) is higher than that of the specimens with grain size of 5 μm. Second, hydrogen removal out of hydrogenated VT9 alloy is accompanied by $\beta \rightarrow \alpha$ transformation and α-phase particles appearance. It was shown, that after vacuum annealing the shape of these α-particles is of a globular type in the samples with SMC structure, whereas in samples with the grain size more than 1 μm these α-particles are of a lamellar shape. Third, the study of structure evolution after vacuum annealing performed on hydrogenated SMC alloy VT9 with grain size of 0.2 μm shows that the grain size decreases after vacuum annealing when its temperature is less than the deformation temperature. The increased hydrogen content in the initial condition of SMC VT9 alloy promotes formation of a finer globular structure after hydrogen removal.

The tensile properties of Ti, Ti–5H, Ti–16H alloys were determined at 20–400°C (Fig. 4,*a*). At room temperature the SMC titanium both in basic and hydrogen-alloyed conditions displays high values of yield strength. The larger the hydrogen content, the higher these values. The latter is connected with strengthening of titanium by fine hydrides, whose volume fraction increases with increasing hydrogen concentration. It seems to be interesting that a significant elongation (17–20%) was obtained in hydrogen-alloyed alloys. In the coarse-grained condition the hydrogen-alloyed titanium is brittle. An increase in temperature up to 400°C leads to a sharp drop of yield strength, while relative elongation changes slightly. However, the ductility of hydrogenated samples in the temperature interval 20–400°C is higher than in Ti due to finer and more stable structure in the former alloys.

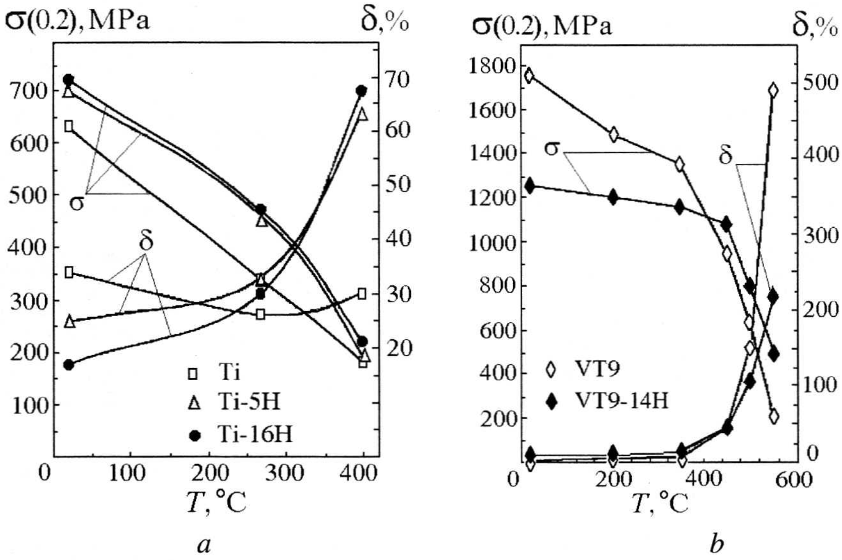

Fig. 4. Dependence of yield stress σ_{02} and elongation δ on deformation temperature at $\dot{\varepsilon}$ = $= 5\cdot10^{-4}$ s^{-1} in SMC titanium alloys: *a* – Ti, Ti–5H, Ti–16H; *b* – VT9R and VT9–14H

The influence of hydrogen on deformation behavior of the complex alloyed SMC alloys VT9R, VT9–14H is ambiguous too. The temperature dependence of strength and ductility is shown in Fig. 4,*b*. In the temperature interval 20–350°C the both alloys are characterized by low ductility and high strength. In the temperature interval 500–550°C the ductility of SMC alloys is increased and their strength is decreased. The presence of hydrogen suppresses the low-temperature superplasticity: $m = 0.24$ and maximum elongation is 240% (T = 550°C, $\dot{\varepsilon} = 4.2\cdot10^{-4}$ s^{-1}). At the same time dehydrogenated VT9R alloy is superplastic at 550°C and at $\dot{\varepsilon} = 2\cdot10^{-4}$ s^{-1}: $m = 0.52$, relative elongation achieves 550%.

Discussion

The results of the present study testify to the favourable influence of hydrogen alloying on formation of SMC structure in titanium and two-phase titanium alloy. Actually hydrogen alloying decreases flow stress during processing for an ultrafine grain size and increases maximum acceptable strain values. A number of features contribute to formation of microstructure with fine grain size. First, in the hydrogen-containing alloys the rate of grain growth is decreased. In single-phase state it may be connected with increasing concentration of impurities (O, C, N, Fe) at grain boundaries, which are replaced by hydrogen from intergranular defects [6]. In case of two-phase structure formation the grain growth is retarded by second-phase particles. Another feature that can be applied for refining microstructure is the formation of finer precipitates of phases in the hydrogenated alloys as compared to the basic alloy. That occurs due to quenching and subsequent decomposition of metastable phase. However, the potentialities of hydrogen application along with the retention of the SMC structure during vacuum annealing are determined by the final temperature of treatment. The necessity of hydrogen removal at the temperature higher than dissolution of an oxidized layer (500°C) does not allow to retain it from titanium, but it becomes possible in complex alloyed titanium alloys with a more thermal stable structure. No grain growth was observed after vacuum annealing of the VT9 alloy with initial hydrogen content of 14 at.% that is possibly due to transformation stresses and recrystallization at dehydrogenation.

Conclusions

A new method of obtaining a submicrocrystalline structure in workpieces made of titanium and two-phase titanium alloy by employing dynamic recrystallization and reversible hydrogen alloying was developed. At the same deformation temperature and strain rate hydrogen alloying decreases flow stress during processing for an ultrafine grain size and increases maximum acceptable strains. Grain sizes of 0.1–0.2 μm and 0.04 μm were produced in hydrogenated Ti and two-phase Ti–11.4Al–1.7Mo–0.88Zr (at.%) based alloys, respectively. Retention of SMC structure during hydrogen removal can be employed only in two-phase alloy because of an oxidized layer, which does not allow to remove hydrogen at temperatures lower than 500°C.

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