The Low-Temperature Removal of Hydrogen Isotopes from Submicrocrystalline Ti–6Al–4V–H Alloy[1]

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Abstract – Researches of hydrogen doping effect on deformation behavior and mechanical properties of two-phase titanium alloys are lead on an example of Ti–6Al–4V titanium alloy in a submicrocrystalline state at the 773–1023 K temperatures interval. Effect of an electron irradiation modes on hydrogen yield from SMC Ti–6Al–4V alloy and stability of its SMC-structure is explored. It is shown, that a hydrogen doping in Ti–6Al–4V SMC-alloy up to 0.24 mass % and at temperatures higher than 773 K gives in growth of its ultimate strengths and flow in 2–3 times and to decrease of strain to fracture in 1.5–2 times. It set, that with increasing of current density from 3 up to 30 μA · cm^{-2} the intensity of hydrogen yield increasing super-linear up to 20 times, and at current densities 25–30 μA · cm^{-2} the warming up of a sample by beam attains temperatures more than 673 K, giving to the considerable recrystallization of a submicrocrystalline state.

1. Introduction

Formation of submicrocrystalline (SMC) structures in metals and alloys appreciably improves their operating characteristics. Homogeneous SMC structure may be received [1] by method combining a prestress by hydrogen doping and a hot flowage by a molding.

As hydrogen can influence on brittleness of received SMC materials, it necessary to remove from material and desirable to make it at temperatures below recrystallization temperature. In this connection, development of technologies for cold hydrogen removal from materials is interest. One of such technologies can be a radiation action, for example, an electrons irradiation of materials with suitable energy and current density. The purpose of present paper was examination of a hydrogen yield depending on current density of electrons for improvement of an expedient of cold hydrogen removal from Ti–6Al–4V SMC alloy.

2. Experimental technique

The SMC-structure in Ti–6Al–4V alloy has been received by a method combining the reversible doping by hydrogen and a hot flowage by a molding [1, 2]. Hydrogen doping in SMC Ti–6Al–4V alloy carried out by annealing in medium of the drained hydrogen at 923 K temperature. The hydrogen concentrations in samples are measured by coulomb metric method. The samples by the sizes 0.2×5×20 mm with hydrogen concentration of 0.005; 0.08, and 0.24 mass % was selected for examination.

Tension tests of samples were are lead on device ПВ-3012M with initial velocity of strain $6.7 \cdot 10^{-3}$ s^{-1} in the 293–1023 K interval temperatures. Before tests from a samples surface deleted a stratum thickness about 100 microns by mechanical abrasion and the subsequent electropolishing.

The electrons irradiation with energy E_{el} = 0.5–40 keV at current densities J = 3–30 μA · cm^{-2} on sample was made at pressure 10^{-4} Pa. More detailed exposition of installations see in [3, 4].

The level of the hydrogen content in samples before and after an irradiation was checked by a thermostimulate of gas release (TSGR) method (or thermodesorption method). Record of intensities hydrogen yield at an electronic irradiation and TSGR was carried out with the help of the hardware-software complex, allowing to drive scan of mass spectrometer MX-7304, done the linear heating of samples and to carry out record of values of temperature and intensities of the picked lines of a mass spectrum (from 1 up to 6 masses) with velocity from 1 up to 10 measuring in a second. Final machining of observed data was done with the help of a package applied programs OriginPro 7.0 (OriginLab Comporation). More detail about experiment in [3–5].

For definition of quantity of hydrogen removed from samples during an irradiation, the following procedure designed. TSGR temperature spectra before and after an irradiation were integrated, and the share of the removed hydrogen was defined from a relation

$$K = (I_1 - I_2)/I_1,$$

where I_1 and I_2 are the quantities, accordingly, integrals (the areas under TSGR spectra) before and after an irradiation of samples. The received K quantities at the initial stages of examinations were compared to quantities of

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$$K_m = (C_{m1} - C_{m2})/C_{m1},$$

where C_{m1} and C_{m2} are the quantities, accordingly, mass concentrations of hydrogen before and after an irradiation of samples. Appeared, that quantities K and K_m coincide to within 5%. It has allowed defining immediately quantity of hydrogen in the samples, stayed after an electrons irradiation, and to refuse from a coulomb of metric and weight methods for definition of the hydrogen quantity removed from sample during irradiation.

3. Experimental results and discussion

The typical electron-microscopic image of SMC Ti–6Al–4V–H alloy received with the help of translucent electronic microscope EM-125K presented in Fig. 1. It is visible that the alloy has the homogeneous SMC-structure.

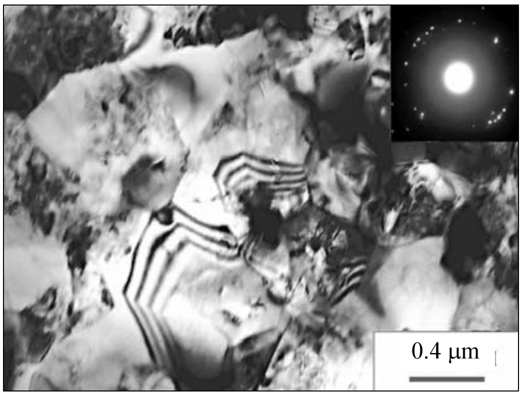

Fig. 1. Typical structure of Ti–6Al–4V submicrocrystalline alloys

On electron diffraction patterns of such structure which have been taken off from the area 1.2 μm^2, the major quantity of the reflexes located on a circle is observed. Such view of electron diffraction patterns testifies to presence more-angular des-alignments between components of structure. On boundaries of grains of separate grains, there is strip-line contrast witch characteristically for an equilibrium state of boundaries grains. The medial size of components of grains-sub grains structure makes ~ 0.3 µm.

Curves of flow at tension of Ti–6Al–4V–H alloys with the various hydrogen content at temperature 973 K obtained in approach of constant volume of a deformable material presented in Fig. 2.

It is visible, that generally on curves of flow for Ti–6Al–4V–H alloys two stages of reinforcement, a stage loss of reinforcement and stage of steady strain are observed.

On curves of flow for Ti–6Al–4V–0.24H and Ti–6Al–4V–0.08H alloys accurately deposits two stages of deformation reinforcement: the stage of an intensive reinforcement on an initial section of a curve of flow with increasing of strain is replaced by a stage with low coefficient of deformation reinforcement, further follows the stage of a sharp loss of strength. For a curve of flow for Ti–6Al–4V–0.005H alloy presence of a stage of the steady strain which follows stages of reinforcement and a feeble loss of reinforcement (Fig. 2, curve *1*) is characteristic.

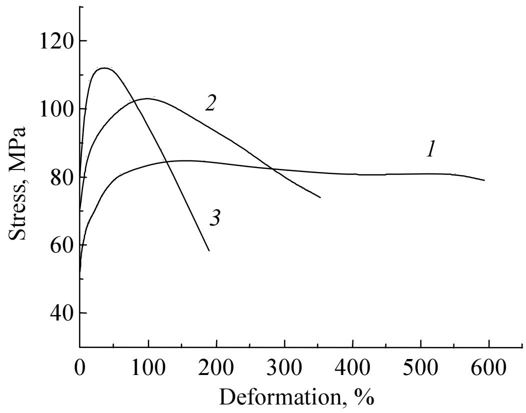

Fig. 2. Curves of flow for Ti–6Al–4V–H alloy with the various content of hydrogen at 973 K: *1* – 0.005; *2* – 0.08; *3* – 0.24 mass %

Emersion of a stage of the steady strain is accompanied by magnification of plasticity of an alloy to ~500–600%. Such a curve of flow is characteristic of micro-grained (size about 2–5 microns) Ti–6Al–4V alloy at superplastic flow at temperature 1173 K [6]. It testifies that formation of SMC-structure leads to shift of a temperature band of developing process of superplastic properties of Ti–6Al–4V alloy to field of low temperatures, at least, on 200 K. Hydrogen doping in Ti–6Al–4V alloy to concentration 1.0 mass % [7] reduces temperature $\alpha \rightarrow \beta$ transition to 973 K. Hence, the hydrogen accumulation in local sections of the sample can initiate formation enriched by hydrogen β phases in these sections and, as consequence, development of the non-uniform flowage. Strain localization at macrolevel and decrease in magnitude of strain to fracture will be effect of it.

Temperature dependences of ultimate strengths σ_B, flow $\sigma_{0.2}$ and strains before fracture δ for SMC Ti–6Al–4V–H alloys with the various hydrogen content shows, that for all explored alloys the value σ_B and $\sigma_{0.2}$ with temperature growth change on a curve with a minimum at temperatures 923–973 K. Analogous dependence of $\sigma_{0.2}$ and σ_B on temperature is observed and for the coarse-grained titanium alloys doped by hydrogen [8]. However, for titanium alloys in a coarse-grained state the minimum on graphs σ_B and $\sigma_{0.2}$ from temperature is observed at temperatures on 200–250 K higher than for SMC states.

In [8] the presence and position of minimum on the graph $\sigma_{0.2}$ from temperature in the coarse-grained titanium alloys doped by hydrogen relate to equal strength α and β phases at the given hydrogen concentration. For SMC titanium alloys the increase of $\sigma_{0.2}$ and σ_B at temperatures 973–1023 K is caused, apparently, by the beginning of growth of SMC grains.

From the analysis of hydrogen influence on performances of strength of SMC Ti–6Al–4V–H alloys follows that at temperature 773 K the hydrogen doping within explored concentrations practically does not influence on quantities of σ_B and $\sigma_{0.2}$ (observable increase or decrease of values σ_B and $\sigma_{0.2}$ no more than 10–20%). In the interval of 923–1023 K temperatures increase of hydrogen concentration in SMC alloy from 0.005 to 0.24 mass % lead to growth of values σ_B and $\sigma_{0.2}$ in 2–3 times. For example at temperature 923 K value $\sigma_{0.2}$ for Ti–6Al–4V–0.005H, Ti–6Al–4V–0.08H and Ti–6Al–4V–0.24H alloys makes accordingly 38, 71, and 111 MPa. The increase of σ_B and $\sigma_{0.2}$ values with increasing of hydrogen concentration in an alloy can be related to increase of β-phases strength because of dissolution of hydrogen in it [8].

Temperature dependence of strain before fracture δ explored SMC Ti–6Al–4V–H alloys, as well as dependence σ_B and $\sigma_{0.2}$ from temperature, has nonmonotonic character. At an increase of temperature of trial from 773 to 1023 K in the beginning sharp increment of magnitude δ and then – decrease is observed. Thus magnitude of δ in 773–1023 K interval temperatures those above, than more low the hydrogen concentration in alloy.

X-ray diffraction studies after a tempering of Ti–6Al–4V–0.24H alloy from 973 K temperature have shown that at the specified temperature in an alloy the volume fraction β-phases is increase as evidence increasing of reflexes intensity in diffractogram.

About of deformation level it is possible to judge from magnitude of η coefficient of strain localization which is calculated by the formula [9]

$$\eta = 1/[(1-\psi)(1+\delta)],$$

where ψ is the narrowing in the neck (a place of the subsequent rupture); δ is the strain before fracture.

From comparison of η for explored alloys it is visible (see table), that hydrogen doping reduces stability of SMC Ti–6Al–4V alloy to strain localization at macrolevel at increased temperatures.

Table. Coefficient of strain localization for Ti–6Al–4V–H SMC alloys at the various hydrogen content

T, K	H_2 concentration, mass %		
	0.005	0.08	0.24
773	8.4	7.2	8.1
923	6.8	9.6	13
973	5.1	10.4	21

Electron-microscopic examinations of thin foils have shown, that medial grain size of Ti–6Al–4V alloy with the hydrogen content of 0.24 mass % in initial SMC-state is 0.085 microns (Fig. 3).

Figure 4 shows a structural change of samples depending on temperature of the sample Fig. 3 directly depending on current density of a primary electron beam.

Electrons irradiation by a beam during 1 h at 523 K led to decreasing of hydrogen concentration to 0.17 mass %. The SMC-structure is maintained, but medial grain size is increase from 0.085 to 0.17 microns (Fig. 4).

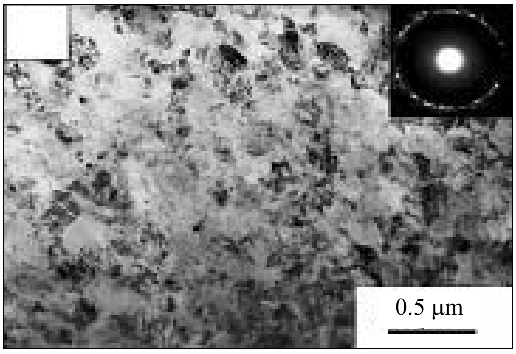

Fig. 3. Structure of Ti–6Al–4V submicrocrystalline alloys before irradiation

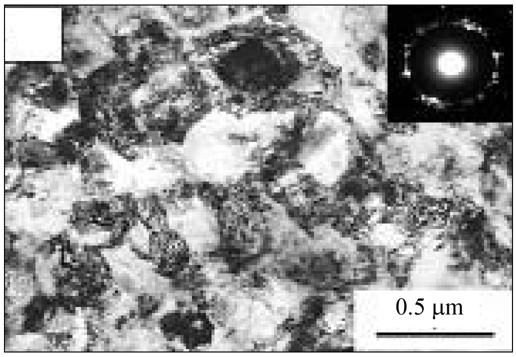

Fig. 4. Structure of Ti–6Al–4V submicrocrystalline alloys after electron irradiation at *T* = 523 K

At an increase of temperature to 573 K after 1 h of irradiation (Fig. 5) a hydrogen concentration in alloy decreases to 0.13 mass %. Medial grains size of SMC-structure is increased to 0.21 microns.

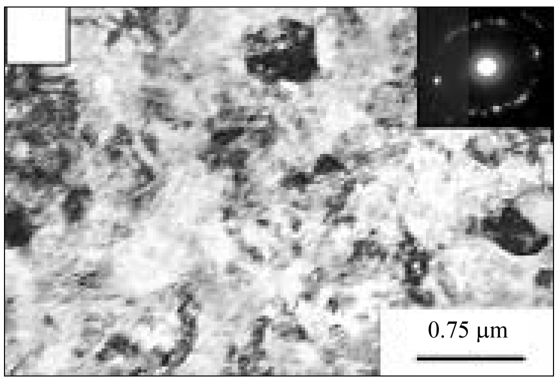

Fig. 5. Structure of Ti–6Al–4V submicrocrystalline alloys after electron irradiation at *T* = 573 K

In Fig. 6, the temperature spectra of H_2 hydrogen release from SMC Ti–6Al–4V samples after their irradiation by electrons beam in different regimes are shown.

The curve *1* on Fig. 6 corresponds to initial (not irradiated) sample which structure is shown on Fig. 3. The curves *2* and *3* in Fig. 6 correspond to irradiation regimes after which the structure of the sample changes accordingly Figs. 4 and 5.

The regime of irradiation corresponding to curve *4* (Fig. 6) leads to increases of grains to 0.8–1 microns, i.e., the structure thus becomes not SMC. The hydrogen concentration in the sample after that regime decreases to 0.1 mass% only.

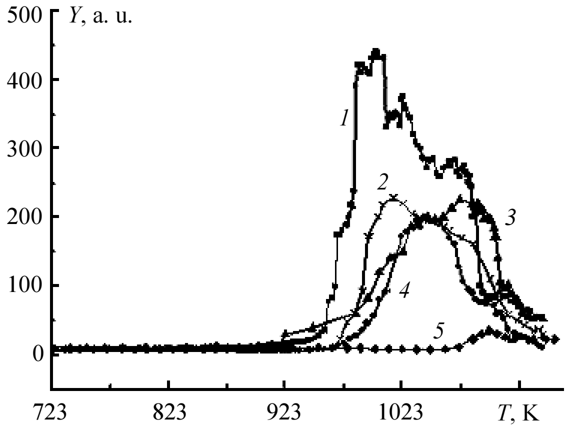

Fig. 6. Temperature spectra of hydrogen release from samples Ti–6Al–4V before and after electrons irradiation with 40 keV energy during 1 h at different current densities: *1* – the initial sample; *2* – $J = 10\ \mu A \cdot cm^{-2}$, $T_{max} \sim 523$ K; *3* – $J = 15\ \mu A \cdot cm^{-2}$, $T_{max} = 573$ K; *4* – $J = 20\ \mu A \cdot cm^{-2}$, $T_{max} = 653$ K; *5* – $J = 30\ \mu A \cdot cm^{-2}$, $T_{max} > 800$ K

The regime of irradiation corresponding to curve *5* (Fig. 6), leads to the full recrystallization (to increases of grains to tens micron) and to significant (to 90%) to a bakeout of the sample (hydrogen concentration in the sample after irradiation ~0.002 mass%). Thus, optimum parameters of electrons irradiation at which is possible maximally effective bakeout of Ti–6Al–4V alloy with conservation of SMC-structure are: pressure in vacuum chamber at irradiation of samples – 10^{-2} Pa and more low; optimum electrons current density of an beam (not demanding standards for cooling of the sample) – $20\ \mu A \cdot cm^{-2}$.

At the same time, the used energies of irradiation (from 0.5 to 40 keV) are insufficient for an effective bakeout of alloy. At the specified regimes irradiation without its recrystallization during 1 h manage leave from the sample of alloy no more than 50% of hydrogen, whereas from samples of palladium foils (not SMC) leaves to 90% of hydrogen at more feeble current densities [10].

4. Conclusion

1. Hydrogen doping in SMC Ti–6Al–4V alloy to 0.24 mass % at temperatures above 773 K leads to growth of limits of its strength and flow in 2–3 times and to decrease in magnitude of strain to fracture in 1.5–2 times it is installed by methods of physical tests and X-ray crystal analysis. It is most probably caused by formation in the course of strain in the most intense sections of the sample hardened by hydrogen β phases and, as consequence, development of the non-uniform flowage.

2. Examinations of influence of electrons beam current density at irradiation of the sample on an hydrogen yield and structure of Ti–6Al–4V alloy have shown, that with increases of current density from 3 to $30\ \mu A \cdot cm^{-2}$ intensity of hydrogen yield increases to 20 times (over-linearly). At the same time, at 25–$30\ \mu A \cdot cm^{-2}$ current densities the warming up of the sample by beam attains temperatures (more than 673 K) leading to significant recrystallizations of a SMC-state.

3. For an effective hydrogen remove from SMC Ti–6Al–4V alloy is necessary to increases the energy of an electrons beam up to 100 keV or more.

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