

INFLUENCE OF HYDROGEN ON PLASTIC FLOW OF THE TITANIUM AND ITS ALLOYS

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Abstract

In this paper the effect of hydrogen as an alloying element on the yield stress in commercial titanium and Ti-6Al and Ti-6Al-4V alloys is investigated. The connection is made between the strain resistance and phase composition in the wide range of temperatures. It has been found that the hydrogen alloying of commercial titanium in the α -field is accompanied by the yield stress decrease. The role of volume phase ratio in the alloys softening in $\alpha+\beta$ -field has been shown. The hydrogen hardening parameters in α -field are defined. The paper materials are of a usage value for researchers and technologists, developing innovative technological processes of strained semi-finished titanium products manufacturing.

Keywords: technology of titanium alloys, hydrogen technologies, influence of hydrogen, structure transformations in titanium alloys

1 Introduction

The relevance is established by the widespread titanium application in the modern machine engineering on the one hand, on the other hand – by low manufacturability. In this context, this article is aimed to exposure fundamental laws of the reversing hydrogen alloying for the titanium alloys manufacturability improvement during the plastic yield process.

Deformability of titanium alloys, formation of the structure and properties during deformation and the influence of hydrogen on these processes has been extensively studied recently [1-14].

The leading research approach is to determine stress-related characteristics by the compression-test method at the isothermal conditions and then to compare the results for three different alloys: commercial titanium, α - Ti-6Al alloy and $\alpha+\beta$ – Ti-6Al-4V alloy. Hydrogen alloying is also used as a flexible phase composition management tool for the investigated alloys

Influence of hydrogen on phase structure of the titanium and its alloys is studied well enough [15, 16]. Innovation status of hydrogen technologies is confirmed by the extensive theoretical and applied research in the field of titanium alloys carried out by Russian and foreign scientists and reported at the international conferences and published in literature (U. Zwicker, W.R. Kerr, F. H. Froes, O. Senkov, B.A. Kolachev, A.A. Ilyin, V.K. Nosov, I.S. Polkin et al) [17-26]. The research carried out by scientific group supervised by Professor Nosov V.K. has made a significant input in the development of scientific and practical basis of hydrogen technologies of titanium alloys. Extensive research of the influence of hydrogen alloying on the phase and structure transformations in titanium alloys during deformation made it possible to develop technological schemes of hydrogen plastification of titanium semi-products.

However the majority of works on research of laws of hydrogen alloyed titanium alloys deformation, have local character and are focused on the decision of technological problems of a concrete industrial alloy. Uniqueness of hydrogen as an alloying element, enables influences on phase structure of the technical titanium and the basic alloying systems, creating as mono-, and biphasic modeling alloys and excepting influence of other alloying elements. It allows to study deformation properties separately α - and β -phases of the titanium and also to analyze laws of deformation biphasic ($\alpha+\beta$) - systems.

2 Materials and methods

Samples $\varnothing 10 \times 13$ mm made from rolled rods of technically pure titanium VT1-00 (impurity Al 0,055 %, V 0,047 %, Fe 0,065 %, O 0,004 %, C 0,011 %, N 0,001 %, H 0,001 % of weights.) and alloys Ti6Al (Al 5.8 %, Ti – a basis) and Ti6Al4V (Al 5.9 %, V 4.1 %, Ti – a basis). Hydrogen alloying samples spent in Siverts equipment at temperature of single-phase β -area for alloy VT1-00 and at temperature $T_{\alpha+\beta/\beta}-50^\circ\text{C}$ for alloys Ti6Al and Ti6Al4V. The samples that are not subjected hydrogen alloying, were annealed in vacuum at hydrogen alloying temperatures for saving of identical initial structure.

The deformation properties defined by mechanical test machine FP100 at axial compression with initial strain rate $5 \cdot 10^{-3} \text{ s}^{-1}$ in conditions of isothermal deformation in a range of temperatures 300–1050°C. The samples deformable in β -areas, directly ahead of test maintained at temperature $T_{\alpha+\beta/\beta}+20^\circ\text{C}$ within 20 minutes for maintenance of really single-phase condition.

3 Technically pure titanium

3.1 Deformation in α -area

Hydrogen alloying in single-phase α -area does not render appreciable influence on character of flow curves. Strong deformation hardening, characteristic for conditions of cold and incomplete cold deformation of the titanium, is kept within the range of all α -area (**Fig. 1a**). After achievement of a yield point the material is intensively strengthened, reaching a threshold of hardening only at the strain 0,2–0,3. With deformation temperature increase simultaneously with flow stress intensity of deformation hardening decreases also (**Fig. 1b**). It is especially

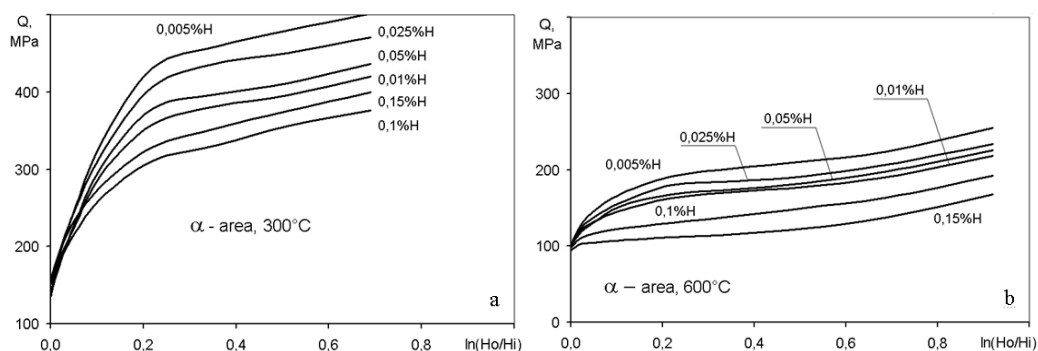


Fig. 1 Flow curves of commercially pure hydrogen alloyed titanium, deformed in α -area under 300 (a) and 600°C(b)

appreciable at the first stage of hardening before achievement of a threshold of hardening. Thus growth of the hydrogen content displaces last aside low strain. Flow stress dependence on the

hydrogen content as a whole has falling down character (**Fig. 2**). Thus with development of deformation hydrogen induced α -titanium softening increases. Such behavior of Ti-H alloy is not entered in the solution hardening theory, however can be explained by reduction of forces of elastic interaction between a dislocation and the crystal lattice deformed by an impurity of introduction – hydrogen.

Elastic predistortion of a lattice, in a combination to rather low mobility of hydrogen at temperatures 300–600°C, can provide easier sliding of dislocations. The interrelation between work hardening dislocation mechanisms indirectly proves to be true by increase in effect with development of deformation (**Fig. 2a** and **2b**). With growth of temperature, in process of increase in mobility of atoms of hydrogen, softening is replaced by hardening (800°C).

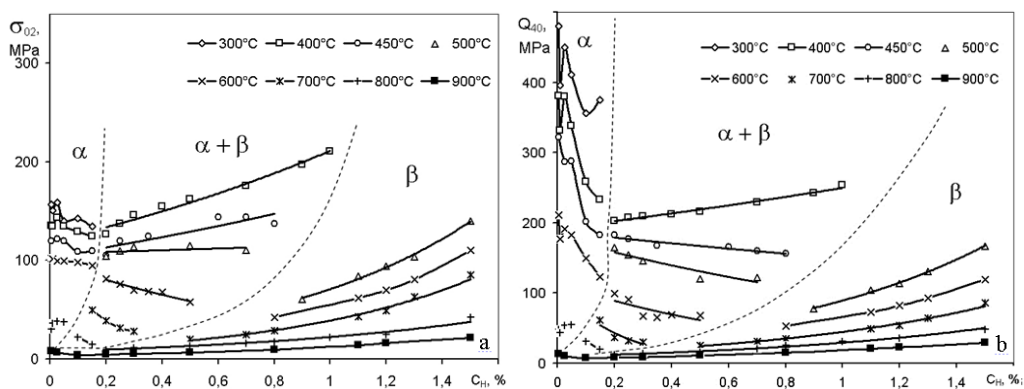


Fig. 2 The influence of hydrogen on yield point (a) and flow stress under 40% strain (b) of commercially pure titanium

3.2 Deformation in $\alpha + \beta$ -area

The deviation from the described law, consisting sharp recession of flow stress and the subsequent similar growth, is revealed at the hydrogen content of 0,01-0,025 % in an interval of temperatures 300–700°C (**Fig. 2b**). Similar results were observed by authors of work [27] at the hydrogen content of 0,1 %, temperatures 500–600°C and higher strain rate. Hydrogen alloying possessing huge diffusive mobility, within the limits of «the diluted solution» (no more than 0,1 % of weights.) can increase self-diffusion factor of the basic metal [28] and, accordingly, to raise mobility of dislocations. In process of increase in deformation temperature and growth of hydrogen atoms mobility recession of flow stress at $C_H=0,01$ % is «washed away», degenerates in insignificant step (**Fig. 2b**) or disappears at all in conditions not developed dislocation structures (**Fig. 2a**).

With $\alpha/(\alpha + \beta)$ transition appears the additional factor defining deformation behavior – a parity of volume fractions α - and β -phases.

It is reflected in strong dependence of the flow curves form on the hydrogen content (**Fig. 3a**, **3b**). At the moderate temperatures (450°C, **Fig. 3a**) deformation of an alloy in the beginning ($\alpha + \beta$)-area (0,2% H , 3 % of β -phase) are accompanied by strong work hardening, though a yield point is minimal as deformation of the alloy is supervised by α -phase having smaller than β -phase durability at these temperatures [29]. With hydrogen content increase yield point increases with simultaneous transition from work hardening to softening at strain 0,2–0,25. This process comes to the end to the ($\alpha + \beta$)-areas middle (0,5÷0,6 % H and 45–60 % of β -phase) with the

maximal intensity deformation softening at the hydrogen content of 0,6 %. Further hydrogen concentration growth and increase in β -phase fraction up to a maximum conduct to insignificant decrease softening degrees and flow stress, it is obvious due to decrease in a degree of heterogeneity of phase structure. In more high-temperature part ($\alpha+\beta$)-area (600°C, **Fig. 3b**) the described tendency is kept, but in the transformed kind.

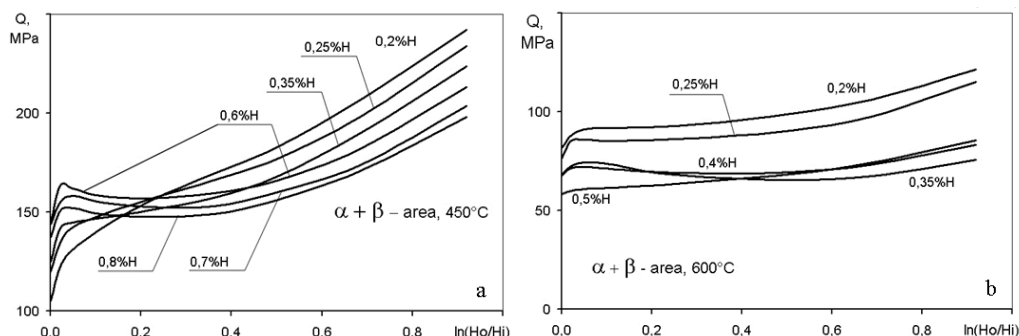


Fig. 3 Flow curves of commercially pure hydrogen alloyed titanium, deformed in $\alpha+\beta$ -area under 450 (a) and 600°C(b)

Intensity of work hardening is essential below, and the softening maximum is observed already at the 0,35 % H, but nevertheless in the middle of the given isothermal section ($\alpha+\beta$)-areas (50% of β -phase).

Dependence of a flow stress on the hydrogen content and deformation temperature in biphasic area grows out interaction of three processes: increase in a volume fraction of β -phase, change of a parity of durability α - and β -phases depending on temperature and deformation softening presence. It is obvious, that in the beginning of plastic deformation, when softening is completely absent (**Fig. 2a**), more stronger at temperatures below 500°C β -phase growth due to hydrogen alloying conducts to increase in flow stress of an alloy as a whole. With increase in deformation temperature α -phase becomes stronger and hardening in ($\alpha+\beta$)-area with hydrogen content growth is replaced by softening. With development of deformation and passage in the alloy dynamic softening processes, presumably dynamic return and partial dynamic α -phases recrystallisation, the temperature border of transition from hardening by hydrogen alloying to softening decreases (**Fig. 2b**).

3.3 Deformation in β -area

Deformation of Ti-H alloys in single-phase- β area is accompanied by rather short first stage of hardening which are coming to the end after achievement of the strain 0,03–0,05, and fast transition after that or to the steady state of flow, or to monotonous work hardening (**Fig. 4**). Research of area of small hydrogen concentration has allowed to reveal the unusual phenomenon – small β -phase hydrogen induced softening at temperature 900°C and above in an interval of 0,01-0,1 % H (**Fig. 2**). The most probable explanation of the found out effect is the mentioned above mechanism of increase in self-diffusion factor of the basic metal with addition to it of the "fast" dissolved element within the limits of low concentration [28]. However, unlike α -phases, β -phases softening in conditions of the "diluted" solution and mobility of atoms of the hydrogen, a dislocation exceeding mobility, is observed in essential wider interval of

concentration and it is expressed not in so sharp form. On flow curves in these conditions with growth of hydrogen content up to 0,1 % the increase in duration of a steady state of flow (**Fig. 4b**) is observed, that can testify to easier dynamic polygonisation development.

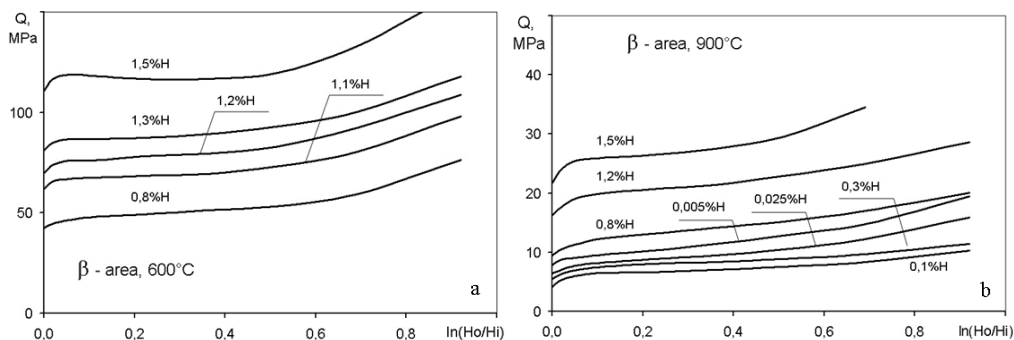


Fig. 4 Flow curves of commercially pure hydrogen alloyed titanium, deformed in β -area under 600 (a) and 900°C (b)

Hydrogen alloying of β -phase more than 0,1 % lead to its hardening. It is shown both in high-temperature, and in low-temperature parts of β -area. In the latter case work hardening of an alloy with the greater hydrogen content is low (**fig. 4a**), that corresponds to the отрыва dislocations break off mechanism from hydrogen impurity atoms atmospheres in conditions of diffusive mobility decrease of the hydrogen. β -phase flow stress at all investigated temperatures with growth of hydrogen content more than 0,1 % monotonously increase according to the solution hardening theory.

4 Ti6Al alloy

Hydrogen alloying of Ti6Al α -alloy, as however and the technical titanium, promotes to formation on the phase diagram extensive biphasic $\alpha+\beta$ -area.

4.1 Ti6Al deformation in α -area

Work hardening of the alloy at an initial flow stage essentially exceeds the technical titanium hardening (**Fig. 5a**). It is consequence of strong aluminum solution α -phase hardening. With growth of deformation temperature hardening is replaced by softening (**Fig. 5b**). Hydrogen alloying in single-phase α -area does not render appreciable influence on character of flow curves neither at the first stage of hardening nor on the subsequent. Most likely it is connected with masking action of aluminum α -phase solution hardening.

Hydrogen alloying of Ti6Al α -phases within the limits of solubility leads to its hardening (**Fig. 6**). Intensity of hardening accrues with decrease in deformation temperature and, accordingly, with decrease of hydrogen diffusive mobility in the titanium.

4.2 Ti6Al deformation in $\alpha+\beta$ -area

Occurrence in structure β -phases are little reduced with the general level of flow stress and, in process of hydrogen content increase, in an alloy develops deformation softening (**Fig. 7**) This tendency is kept down to high-temperature border $\alpha+\beta$ -area (700°C, 0.7%H). At more heat of

deformation (800°C) the deformation softening maximum is displaced to the $\alpha+\beta$ -area middle (0.1%H). Dependence of a flow stress on the hydrogen content and deformation temperature in biphasic $\alpha+\beta$ -area (Fig. 6) grows out interaction of two processes: increase in a volume fraction of β -phase, and its solution hardening by hydrogen. Up to the hydrogen content 0.3÷0.4 %

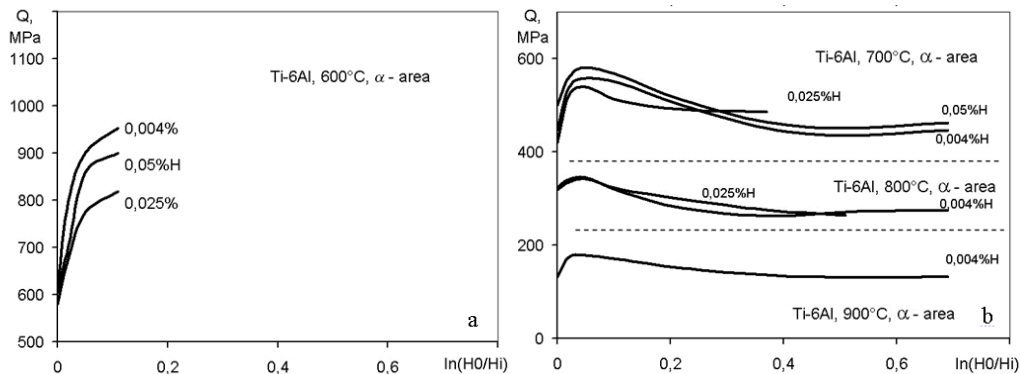


Fig. 5 Flow curves of Ti6Al alloy, deformed in α -area under 600 (a) and 700÷900°C (b)

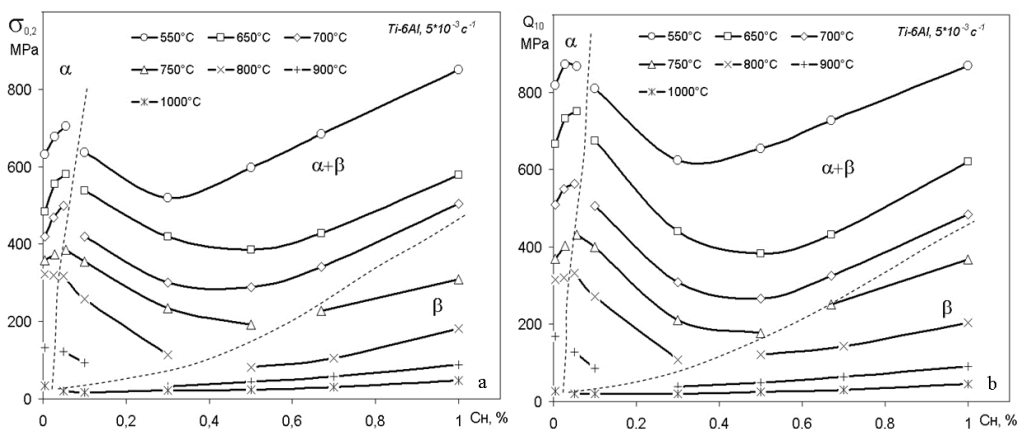


Fig. 6 The influence of hydrogen on yield point (a) and flow stress under 10% strain (b) of Ti6Al alloy

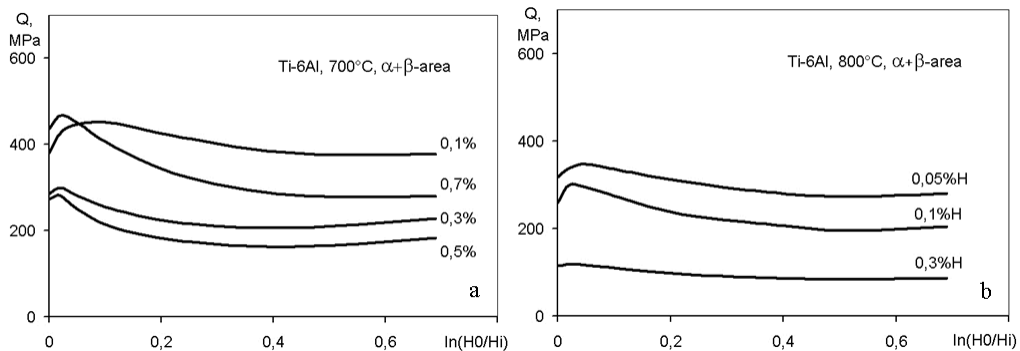


Fig. 7 Flow curves of Ti6Al alloy, deformed in $\alpha+\beta$ -area under 700 (a) and 800°C (b)

prevail the first mechanism according to which flow stress of an alloy decreases, because β -phase in these conditions is less strong. Solution hardening prevails at the hydrogen content above 0.4÷0.5 % also are obviously expressed at temperatures 550 ÷ 700°C, because temperature growth strengthens process of β -phases volume fraction increase, that weakens its hardening by the fixed concentration of hydrogen. Besides at more heats α + β -border is displaced aside smaller concentration of hydrogen.

It is necessary to note, that action of two opposite processes supervising Ti6Al plastic deformation in α + β -area, leads to formation of a minimum of flow stress. Position of this minimum on C_H axis to the greatest degree depends on temperature and in a little bit smaller from the strain.

4.3 Ti6Al deformation in β -area

Deformation of alloy hydrogen alloyed Ti6Al, in single-phase-area is accompanied by rather short first stage of work hardening which are coming to the end after achievement of strain 0,08–0,1, and fast transition after that or to insignificant softening in low temperature part of β -area (**Fig. 8a**), or to monotonous hardening at more heats (**Fig. 8b**). Thus, the more hydrogen in an alloy, the above flow stress. Flow stress of β -phase at all investigated temperatures with growth of hydrogen content more than 0,1 % monotonously increase according to the solution hardening theory (**Fig. 6**). Thus intensity of hardening increases with reduction of deformation temperature that corresponds to decrease in hydrogen mobility.

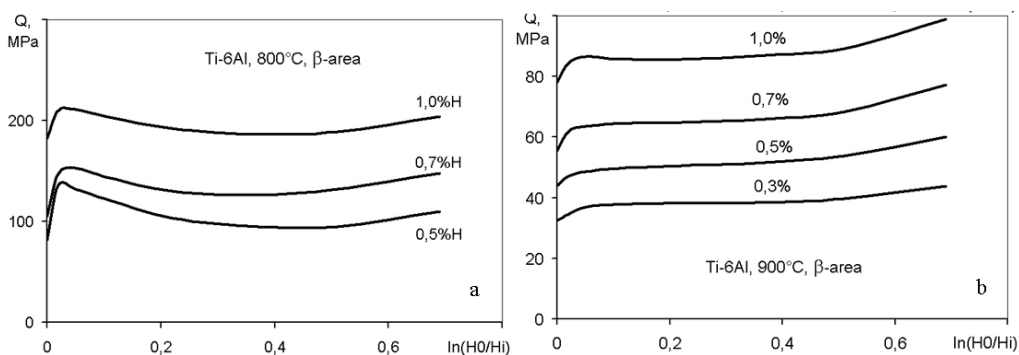


Fig. 8 Flow curves of Ti6Al alloy, deformed in β -area under 800 (a) and 900°C (b)

5 Ti6Al4V alloy

Ti6Al4V alloy in normal conditions contains in the structure about 15 % β -phases. Results of the phase x-ray analysis show, that its hydrogen alloying up to 0.1, 0.2, 0.3 and 0.5%H leads to growth of a β -phase volume fraction up to 18, 40, 50 and 60 %.

5.1 Hydrogen Influence on the flow curves form

Presence β -phases in structure leads to that even at rather low deformation temperatures 400 and 600°C (**fig. 9**) the increase in the hydrogen content essentially influences the form of flow curves. Deformation in low temperature zone of α + β -area (**fig. 9a**) is characterized by strong hardening at an initial stage of flow and fast, unlike α -alloys at this temperature, achievement of a hardening threshold at strain 0.05 ÷ 0.1.

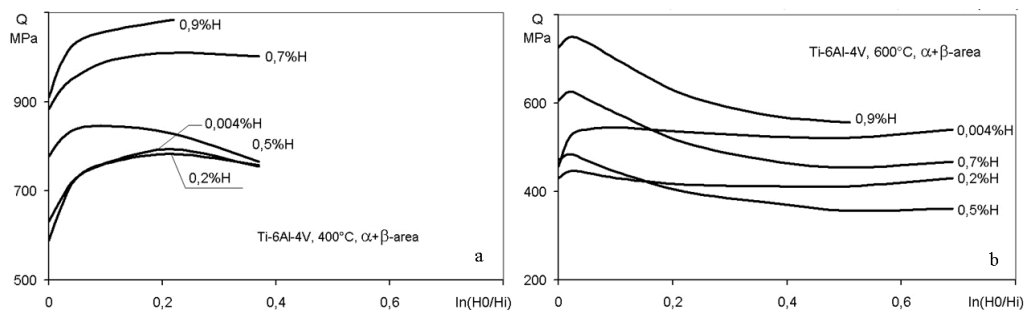


Fig. 9 Flow curves of Ti6Al4V alloy, deformed in $\alpha+\beta$ -area under 400 (a) and 600°C (b)

Character of the further flow is defined by the hydrogen content in an alloy and corresponding phase structure. The hydrogen content increase more than 0.2 % conducts to insignificant softening (0.5%H) which at greater content is replaced by so insignificant hardening (0.7-0.9%H). The increase in deformation temperature up to 600°C (**Fig. 9b**) practically does not render influence on a parity of hardening and softening processes in an alloy with the initial hydrogen content of 0.004 %. Hydrogen alloying unequivocally leads to deformation softening intensification. And this tendency is kept in parallel growth of the general level of alloy flow stress. It is consequence of action of several, described above, processes. Alloying up to 0.2%H sharply increases a β -phases fraction because of what its alloying degree quickly decreases and flow stress falls. However the further growth of the hydrogen content does not cause strong increase in a β -phase fraction and prevailing influence starts to play hydrogen solution hardening of β -phase. Biphasic $\alpha+\beta$ -structures deformation is accompanied deformation softening presumably by dynamic recrystallisation which greatest intensity is observed near to a parity of volume fractions of phases 1:1.

Preferable dynamic softening processes passing in biphasic area proves to be true the data presented on **Fig. 10**. Deformation of the alloy containing less 0.3%H, occurs in $\alpha+\beta$ -areas also it is accompanied deformation softening. Here the more hydrogen content, the softening is less, since the phase parity leaves from optimum 1:1 and prevalence β -phase amplifies. With transition in β -area character of current essentially changes: softening is absent.

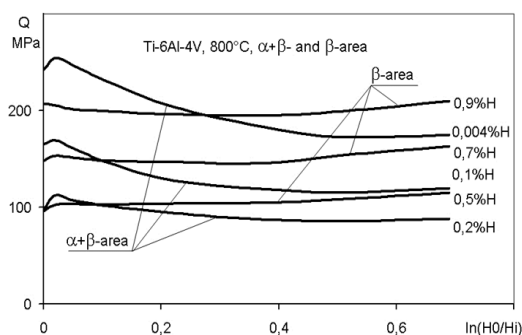


Fig. 10 Flow curves of Ti6Al4V alloy, deformed in $\alpha+\beta$ - and β -area under 800°C

5.2 Influence of hydrogen on flow stress

The beginning of plastic deformation (**Fig. 11a**) at temperatures below 500°C and low is characterized by hydrogen induced hardening.

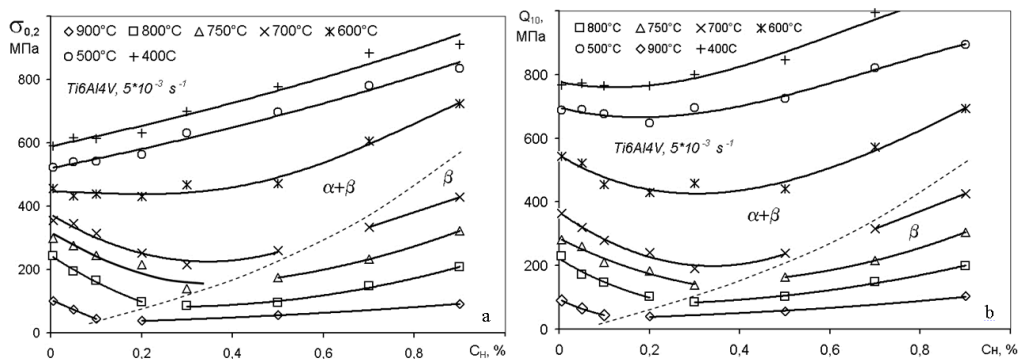


Fig. 11 The influence of hydrogen on yield point (a) and flow stress under 10% strain (b) of Ti6Al4V alloy

It corresponds to growth of a volume fraction β -phase provided that its durability in this temperature area above, than at α -phase. At temperature 600°C and above β -phase becomes less strong and flow stress becomes the result of two opposite processes: growth of a β -phase fraction (reduces flow stress) and β -phase hydrogen solution hardening (raises flow stress). It is obvious, that as approaching $\alpha+\beta/\beta$ -border last process prevails. However at temperatures above 700°C flow stress with the hydrogen content growth decreases down to $\alpha+\beta/\beta$ -border that speaks by displacement of temperature $\alpha+\beta/\beta$ -transition in area of the small hydrogen concentration which was not leading strong solution β -phase hardening. In process of plastic deformation development (**Fig. 11b**) and dislocations density increases flow stress decrease from hydrogen alloying is observed and at the moderate temperatures 400÷500°C. It speaks easier dynamic softening processes passing, including low temperature processes, in hydrogen alloyed Ti6Al4V.

Deformation in β -area of hydrogen alloyed Ti6Al4V, differs from considered above only quantitatively higher flow stress in conformity with higher alloying degree of β -phase.

6 Discussion

6.1 Deformation hydrogen alloyed α -titanium

The α -titan softening by its hydrogen alloying is observed only on technically pure titan. At the minimal degree of crystal lattice distortion by impurity atoms Al, V, Fe, etc. hydrogen atoms distributed in regular intervals on octahedral pores provide elastic predistortion of a lattice that can provide easier sliding of dislocations. In work [30] similar softening is explained by hydrogen ability to reduce intensity of the dynamic deformation ageing caused by coupling of mobile dislocations with atoms of impurity (Fe, C, O). However in that case strain rate growth and deformation temperature reduction should reduce the described effect due to reduction of relative and absolute hydrogen mobility in the titanium. There are no data confirming it. Moreover, on our data, temperature decrease strengthens softening effect in α -area that corresponds to the stress growth necessary for the beginning and continuation of dislocations movement. Alloying α -titan of 6 % Al (Ti6Al alloy) strongly deforms a crystal lattice, completely excepting softening effect, caused by hydrogen.

6.2 Deformation of titanium alloys in $\alpha+\beta$ - area

The character of hydrogen influence on flow stress in $\alpha+\beta$ -area essentially depends on alloying system. For not alloyed titanium decrease in flow stress, caused by growth of a volume fraction

of less strong β -phase is characteristic (**fig. 12a**). Aluminum alloying (Ti6Al) raises the general level of flow stress and on dependences there is a minimum. Its presence is caused by change of the phase parity aside β -phase, and position corresponds to the hydrogen content $0.5 \div 0.6 \%$.

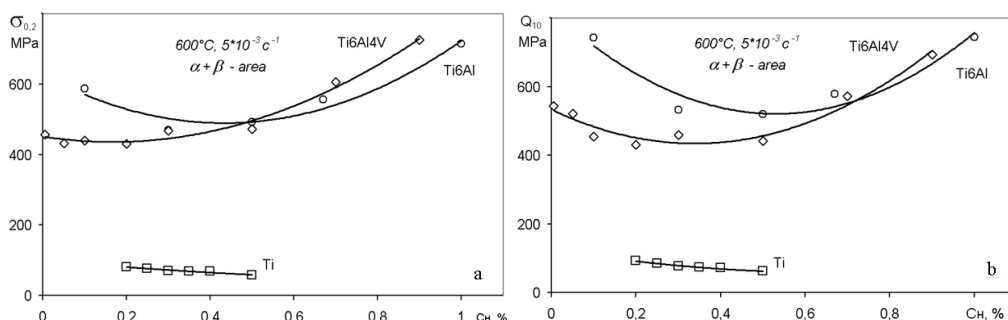


Fig. 12 The influence of hydrogen on yield point (a) and flow stress under 10% strain (b) of Ti-based alloys

It is obvious, that position of a minimum is defined by the moment, when decrease in flow stress due to increase in a β -phase fraction is replaced by growth due to its solution hardening by hydrogen. The further vanadium alloying (Ti6Al4V) displaces position of a minimum in area of smaller hydrogen concentration that confirms defining role of the β -phase hydrogen solution hardening at the hydrogen content more than $0.5 \div 0.6 \%$. Really, Ti6Al4V β -phase, in comparison with Ti6Al, is alloyed by vanadium and its solution hardening by hydrogen will prevail, since smaller concentration. Besides at the greater hydrogen content close to $\alpha + \beta / \beta$ -border, Ti6Al4V possesses greater durability, than Ti6Al, that will well be coordinated with higher β -phase alloying degree. With strain growth the described scheme undergoes only quantitative changes (**fig. 12b**). Minimums on dependences are displaced aside greater concentration of hydrogen, and softening intensity caused by hydrogen increases because of development in alloys dynamic softening processes.

6.3 Deformation of titanium alloys in β - area

In single - phase β - area (**Fig. 13**) the hardening degree caused by hydrogen will be well

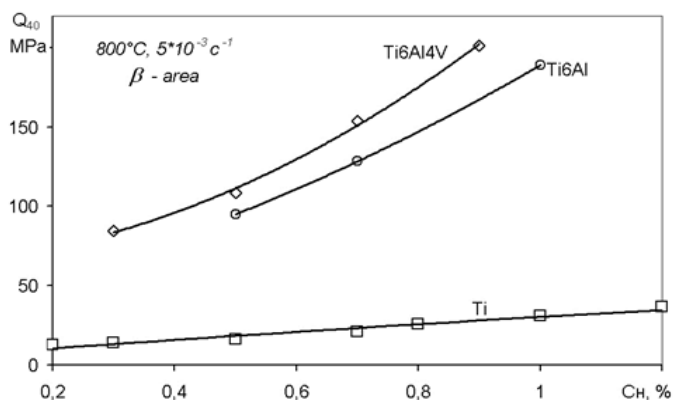


Fig. 13 The influence of hydrogen on flow stress under 40% strain of Ti-based alloys

coordinated with the general alloying level. Weak hardening not alloyed β -titan is replaced by appreciable hardening at alloying it of 6 % Al. Maximal solution hardening degree in single-phase β -area shows Ti6Al4V.

7 Conclusion

It has been established that deformation behavior of the only hydrogen-containing α -phase conceptually depends on the aluminium content. Yield stress of the commercial titanium α -phase decreases with the hydrogen content increase, whereas the solution hardening is specific for the Ti-6Al alloy α -phase.

Deformation behavior of the investigated alloys in the $\alpha+\beta$ -field is subjected to the consistent pattern: softening, replaced with hardening due to the hydrogen content growth. Quantity differences between the investigated alloys are determined by the alloying system. It has been established that the minimum yield stress of the more alloyed Ti-6Al-4V $\alpha+\beta$ -field is observed with the lower hydrogen content than of Ti-6Al. Thus, it should be expected that the desired hydrogen content to allow maximum stress decrease would be lower for the $\alpha+\beta$ -alloys than for the α -alloys.

To conclude, it should be noted that in the design of strain semi-finished titanium alloys products manufacture technological process the main process quantity (the desired hydrogen content) would be defined by the alloy α - of $\alpha+\beta$ -class.

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