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EFFECT OF CARBON CONTENT ON THE MICROSTRUCTURE AND PROPERTIES OF Ti-6Al-4V ALLOY

The article shows the effect of the increased carbon content on the microstructure and properties of two-phase titanium alloy Ti-6Al-4V. Alloys with different carbon content (0.2 and 0.5 wt.%) were produced in vacuum induction furnace with cooper crucible. It was shown that the addition of carbon at the level of 0.2 wt.% increases hardness and strength properties, affects structural stability, results in grain refinement as well as improves creep and oxidation resistance. However, it has a negative effect on plastic deformation. Increasing the carbon content to the 0.5 wt.% causes the further improvement in the creep and oxidation resistance and microstructure refinement of the tested alloys, resulting also in decrease such properties as plasticity, hot deformability and in case of the susceptibility to cold plastic deformation to unacceptable level.

Keywords: titanium alloys, carbon addition, titanium carbides, microstructure, properties

1. Introduction

It is believed that the implementation of a new, less expensive and more efficient production process of titanium sponge and technologies to minimize the extremely costly mechanical working (like powder technologies, near-net-shape technologies and additive manufacturing) is the key to unlock the huge application potential of titanium or titanium alloys. For the time being, one of the methods for reducing the costs of titanium alloys is to modify their chemical compositions by introducing cheap and readily available alloying components. A small quantity of alloying components may have a large impact on the total cost of alloy. For example, 4% vanadium addition in Ti-6Al-4V alloy increases its cost by approx. 10%, but when vanadium is substituted by iron, the alloy cost is reduced by approx. 15% [1,2]. The less expensive and readily available titanium alloy components include: iron, silicon, copper, chromium and manganese [3-5]. Recently, it has been observed the increasing interest in interstitial elements, such as oxygen, carbon and nitrogen [6-11], which have been treated as impurities so far, and their contents in titanium alloys were limited and closely controlled. As they occur in all titanium alloys where they get in during the melting and casting processes, these elements may, with increased contents, effectively substitute for more expensive and hardly available molybdenum, niobium or tantalum additives or support their

substitutes. It is assumed that at low total contents these elements increase the strength of an alloy, while at high total contents they result in an unacceptable reduction in plasticity [12-14].

Oxygen in technically pure titanium has gained the status of an important component which allows for the adjustment of strength level. However, its use is strongly limited due to the negative impact on plasticity, fracture resistance or susceptibility to plastic deformation. It must also be taken in account that this adverse effect of oxygen on the properties gets intensified in the presence of nitrogen. On the other hand, carbon is a component whose strengthening impact is admittedly 1/3 of the strengthening impact of nitrogen or 2/3 of the strengthening impact of oxygen, but it does not reduce the plastic properties to unacceptable levels and creates the possibilities for additional strengthening due to the limited and variable solubility of solid carbon in titanium.

The use of graphite crucibles in production of titanium alloys, which is currently quite often proposed for the new group of TiAl intermetallic alloys [15,16], is economically justified, however it involves, particularly for pure titanium or conventional alloys, the inevitable passage of crucible components, in this case mainly carbon, into liquid metal. Therefore, this article presents the effect of increased carbon content (in the maximum amount permitted under the applicable guidelines (0.2 wt.%) and higher (0.5 wt.%)) on the microstructure and selected properties of the most popular and most often used two-phase Ti-6Al-4V alloy.

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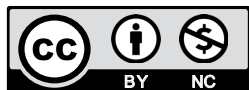
2. Materials and methods

The alloys for investigations with chemical composition as presented in Table 1 were melted in a vacuum induction furnace with a copper crucible using the homogenizing remelting. The ingots of 40 mm in diameter and 350 mm in length were homogenized in the vacuum furnace and hot rolled. The obtained bars of 12 mm in diameter were subjected to final heat treatment conducted under standard conditions for reference alloys (without additional carbon content), which consisted of annealing (750°C/2h/air) and solution heat treatment and aging (925°C/1h/water+540°C/4h/air). The analysis of the chemical composition was performed with an OES/ICP sequential spectrometer and Leco CS844 and ONH836 analyzers. The analysis of the phase composition was carried out using a JEOL JDX-7S X-ray diffractometer. The microstructure investigations were carried out with a light microscope (LM) NIKON Epiphot 200. The samples were etched with a mixture of 2 ml HF, 5 ml HNO_3 and 93 ml H_2O. Morphology of carbides was determined by using image analysis software "Met-Ilo" by using parameters: surface fraction of carbides, area fraction with area fraction variation coefficient (standard deviation / average area*100) and shape ratio. Mechanical properties were tested using a Zwick/Roell Z100 machine according to PN-EN ISO 6892-1:2010. The uniaxial compression tests at a rate of 1.0 s^{-1} up to the strain of 1.0 at room and elevated temperatures were performed with Gleeble HDS-V40 and Gleeble 3800 simulators. The short-term creep tests were carried out according to ASTM E139-11(2018). The oxidation resistance tests were conducted by the conventional isobaric-isothermal method using a GDTD16 thermobalance. Kinetic measurements were taken at 650°C in the atmosphere of technical oxygen passing at a rate of 1 l/h.

3. Results and discussion

The microstructure of alloys in the as-received condition, after homogenization and hot rolling, was characterized by
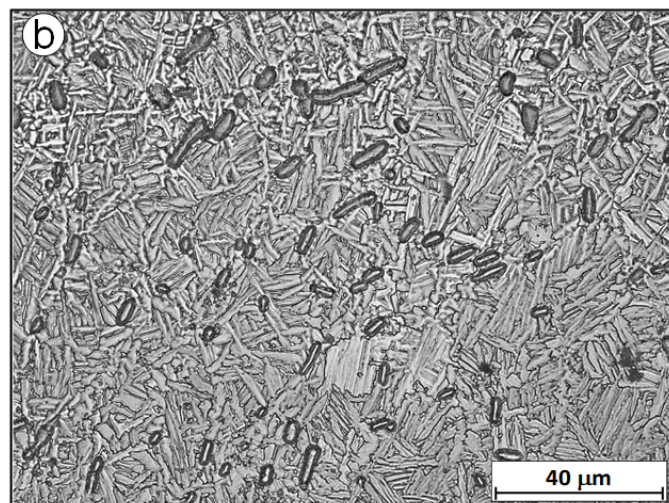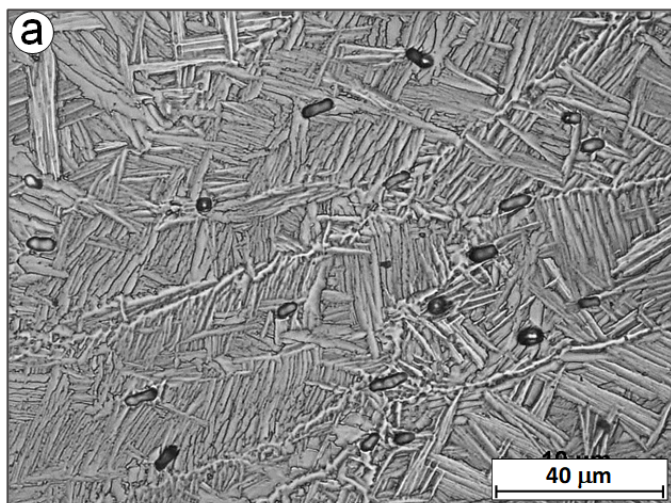
TABLE 1

Chemical composition of investigated alloys

Alloy	Elements content, wt. %				
	Al	V	C	O	Ti
Ti-6Al-4V	5.99	3.89	0.03	0.15	
Ti-6Al-4V-0.2C	5.91	3.84	0.27	0.14	Rest
Ti-6Al-4V-0.5C	5.98	3.85	0.55	0.14	

the matrix made of alternately arranged lamellar alpha- and beta-phase crystals with varying orientation and quite evenly arranged carbides (Fig. 1). This matrix is a typical microstructure characteristic of two-phase alloys in which deformation starts in the range of β phase stability and ends in the range of β → α + β phase transition temperature.

The primary carbides that occupy 1.13 and 3.21% of the area fraction for alloys containing 0.2 and 0.5 wt.% C, respectively, were identified as TiC (Fig. 2). The amount of carbides is the result of impact of aluminum, which increases carbon solubility in titanium, and vanadium contained in the alloy, which is in turn responsible for the presence of the β phase characterized by a very low carbon solubility [17]. With the increase in the amount of carbon, which translates into the increase in the area fraction occupied by carbides, a distinct refinement of lamellar microstructure can be observed (Fig. 1a, b).

The annealing of Ti-6Al-4V-0.2C and Ti-6Al-4V-0.5C alloys does not change their nature as compared to the microstructure after hot rolling (Fig. 3). It only affects the increase in uniformity of carbide size distribution. For example, the area fraction variation coefficient for carbides in Ti-6Al-4V-0.5C alloy decreases from 66 to 49% compared to that in the as hot-rolled condition. Carbides in the test alloys after annealing are characterized by the shape ratio of around 0.92-0.93. At this stage, the addition of carbon also creates favorable conditions for the refinement of lamellar microstructure of alloy (Fig. 3a, b).

The effect of the hardening heat treatment consisting of solution treatment and aging of α + β alloys is the processes responsible for the formation of the final microstructure and properties of

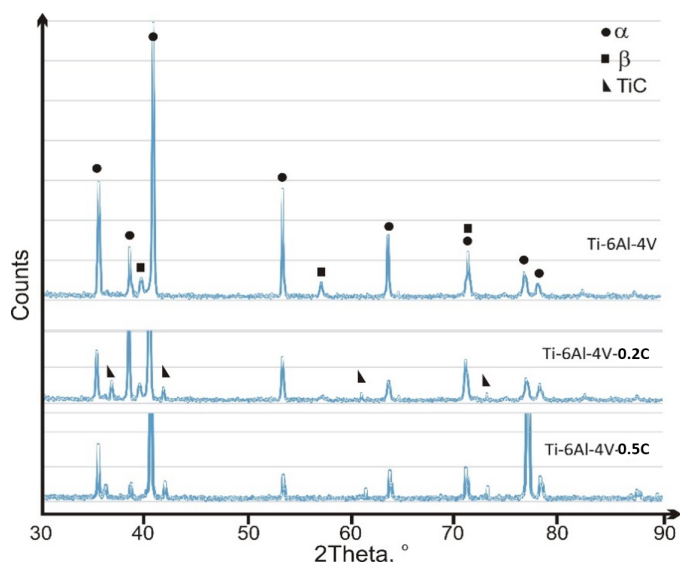Fig. 1. Microstructure of Ti-6Al-4V-0.2C (a) and Ti-6Al-4V-0.5C (b) alloys after hot rolling

Fig. 2. X-ray diffraction pattern of Ti-6Al-4V alloy with different content of carbon

the modification of chemical composition by carbon, solution processes (Fig. 4) and reprecipitation of carbide phase. Fig. 4a shows the microstructure of Ti-6Al-4V-0.2C alloy after solution heat treatment at 925°C for 1 h. Taking into account the carbon content at a level not exceeding its limit solubility in alpha phase and the transition sequence of $\alpha + \beta + TiC \rightarrow \alpha + \beta \rightarrow \alpha' + TiC$ which takes place with increase in temperature, it is possible to obtain a two-phase solution heat-treated microstructure made of lamellar $\alpha + \beta$ phase precipitates only (Fig. 4a). After aging (Fig. 5a, b), the lamellar α-precipitates in the microstructure of the test alloys are separated by transformed β phase which occurred as a result of decomposition of the metastable β_m phase. After this state, the surface fraction of carbides was determined at 1.03 and 3.07% for alloys containing 0.2 and 0.5 wt.% C, respectively.

The main and most important effect of carbon presence in titanium and titanium alloys is the significant increase in strength properties and hardness [17]. The tensile strength of alloy containing 0.5 wt.% C in the as-annealed condition is by approx. 100 MPa higher than that of the reference alloy (Fig. 6), and a disproportionately lower gain in tensile strength and yield strength is observed after the addition of 0.5 wt.% C to Ti-6Al-4V alloy compared to that after the addition of 0.2 wt.% C. For

carbon-containing alloys. Among them, the most important role is played by the processes related to the formation and decomposition of metastable β_m phase as well as those resulting from
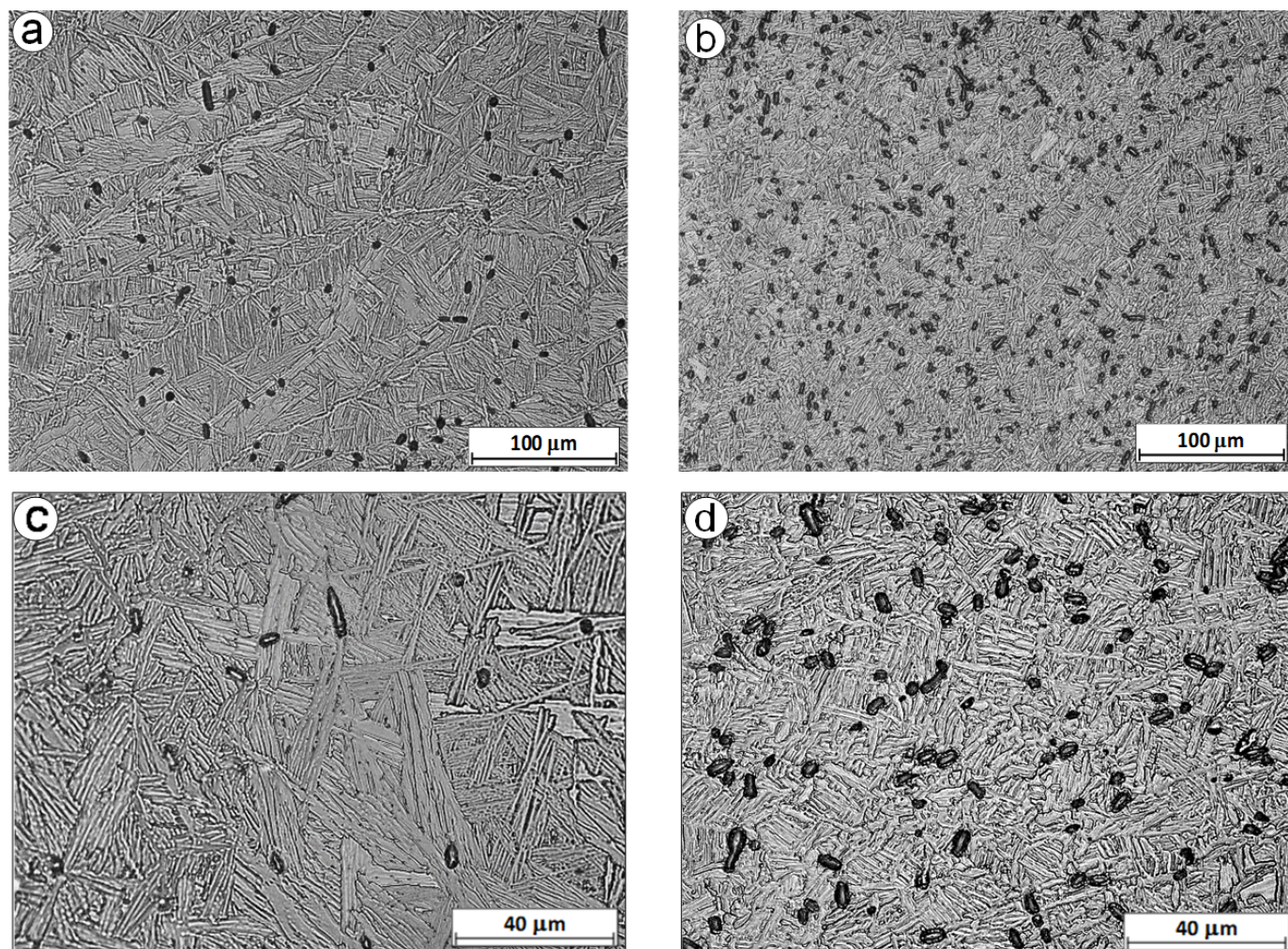

Fig. 3. Microstructure of Ti-6Al-4V-0.2C (a, c) and Ti-6Al-4V-0.5C (b, d) alloys after hot rolling and recrystallization annealing
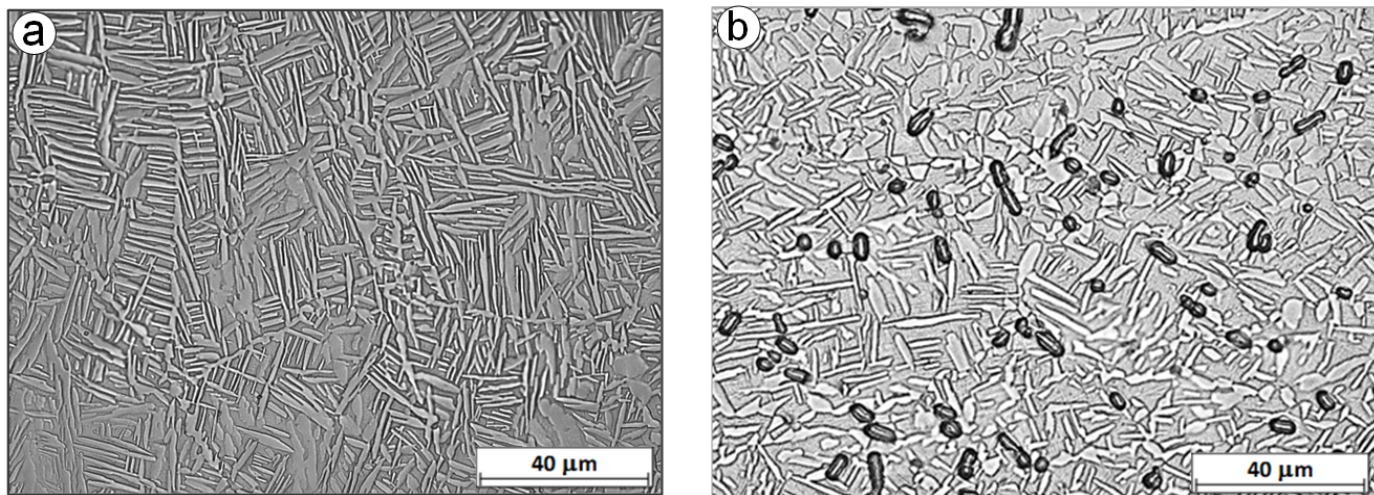
Fig. 4. Microstructure of Ti-6Al-4V-0.2C (a) and Ti-6Al-4V-0.5C (b) alloys after solution treatment at 925°C for 1 h
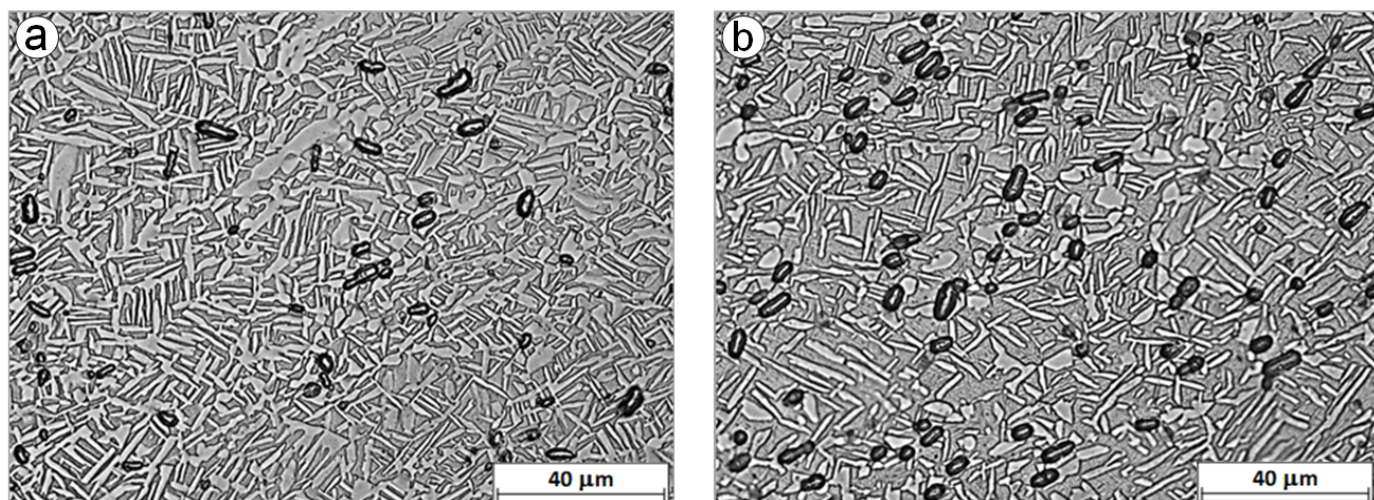

Fig. 5. Microstructure of Ti-6Al-4V-0.2C (a) and Ti-6Al-4V-0.5C (b) alloys after hot rolling and further solution treatment and aging

precipitation-hardened alloys, the role of carbon is not so unambiguous. In this case, hardening is also related to the presence of carbon, but it results mainly from quench annealing of α + β alloys after holding at a temperature in the α + β → β phase transition range, which allows the $β_m$ phase to be partially or completely retained in the microstructure.

This phase decomposes into the mixture of α + β phases during the later aging process [18-20]. The presence in the mi-
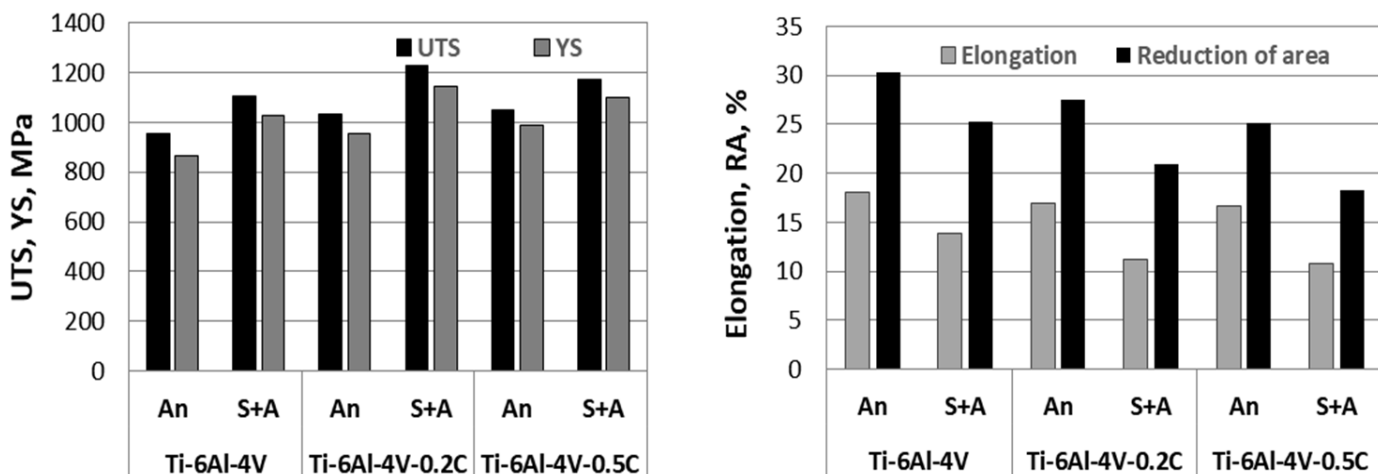

Fig. 6. Effect of carbon on the mechanical properties of Ti-6Al-4V alloy(An-annealing, S+A-solution treatment + aging)

crostructure of two-phase alloys of the β phase, characterized by low carbon solubility forces the occurrence of carbon as carbides, which reduces the effectiveness of titanium and titanium alloy hardening by carbon [21]. It is assumed to be higher when carbon is present in interstitial solid solutions and lower when it is in titanium carbides. Lower strength properties of hardened Ti-6Al-4V-0.5C alloy compared to those of hardened Ti-6Al-4V-0.2C alloy (Fig. 6) indicate that carbon content in multi-component alloys should be limited so that carbon can completely dissolve in the α phase and/or in the β phase, or in the presence of increased carbon content, the content of other interstitial elements, such as nitrogen [22] and/or oxygen [23], should be minimized. The hardening obtained for carbon-containing alloys, both in the as-annealed condition and in the as-solution heat-treated and aged condition, reduces the plastic properties (Fig. 6), but even at a higher carbon content (0.5 wt.%), these values are higher compared to the minimum ones as specified in the standards for conventional two-phase alloys [24-26]. Hardness of the test alloy containing carbon in the as-annealed and as-hardened conditions is higher than hardness of the reference alloy (Fig. 7) by approx. 40-50 HV, depending on the carbon content and state.
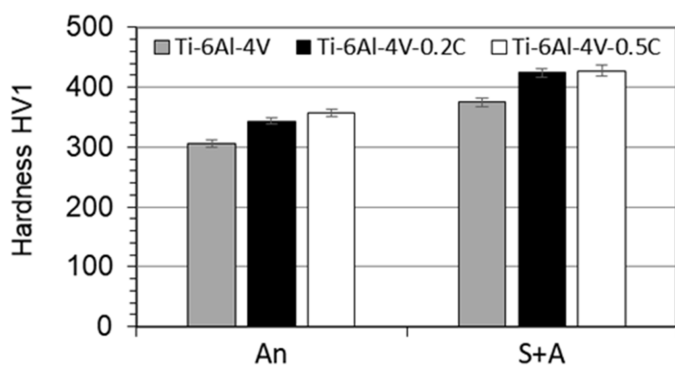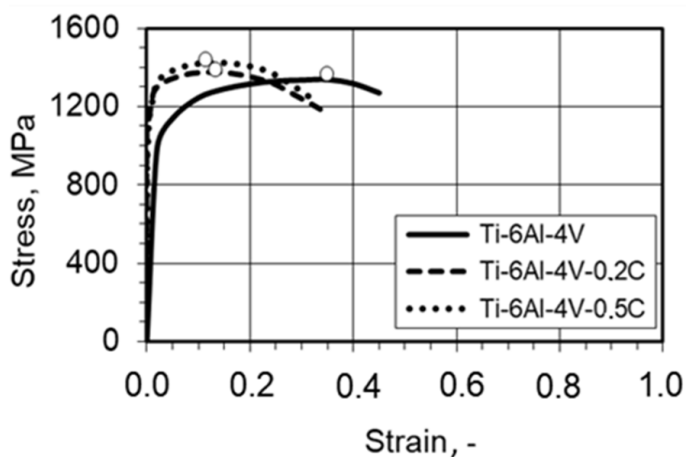

Fig. 7. Effect of carbon on the hardness of Ti-6Al-4V alloy (An-annealing, S+A-solution treatment + aging)

The effect of increase in strength properties and hardness of titanium alloys containing carbon is their higher resistance to forming. The flow curves for Ti-6Al-4V alloy (Fig. 8a) re-corded during the plastometric compression test conducted at room temperature show that the cohesion-loss processes of the cold deformed Ti-6Al-4V alloy containing 0.2 and 0.5 wt.% C begin at small strains of 0.13 and 0.12, respectively. Cracking is preceded by hardening up to 1374 and 1426 MPa, respectively. Deformed under the same conditions, the Ti-6Al-4V alloy with no carbon content is hardened up to the stress of 1338 MPa before its cohesion-loss process begins at a strain of 0.35. The investigations performed revealed that cold deformation of the test alloy with addition of carbon was virtually impossible (Fig. 8a).

The flow curves for the test alloy with and without the addition of carbon and deformed under a temperature slightly below the α → β allotropic transformation temperature (Fig. 8b) show that with the increase in carbon content the increase in maximum yield stress and strain at which this stress occurs is observed. The decrease in stress upon reaching the maximum value is the evidence of dynamic recrystallization in alloys being deformed. In Ti-6Al-4V alloy deformed at 890°C, the yield stress reaches its maximum value of 106 MPa at a strain of 0.05. The introduction of 0.2 wt.% C to the Ti-6Al-4V alloy resulted in approx. 40% increase in the maximum yield stress up to 149 MPa, obtained at a strain of 0.075. The increase in carbon content to 0.5 wt.% in the Ti-6Al-4V alloy caused further, though disproportionately lower, increase in the maximum yield stress up to 165 MPa, obtained at a strain of 0.084. It has been found that carbon has a very strong impact on the reduction in susceptibility to hot plastic deformation of the test alloy. However, this does not constitute a limitation in the contemporary deformation processes, and a solution to this problem can be, for example, the increase in deformation temperature. The authors of [27] even maintain that the addition of carbon well beyond the analyzed range (up to 1.2%) has only a slight impact on the susceptibility to deformation during the titanium rolling process, provided the appropriate process parameters are applied.

Solid solution strengthening and precipitation hardening are the most important mechanisms for hardening titanium and titanium alloys by the addition of carbon [28-29], therefore carbon can also be a component that enhances the suitability of titanium and titanium alloys for operation under elevated temperature
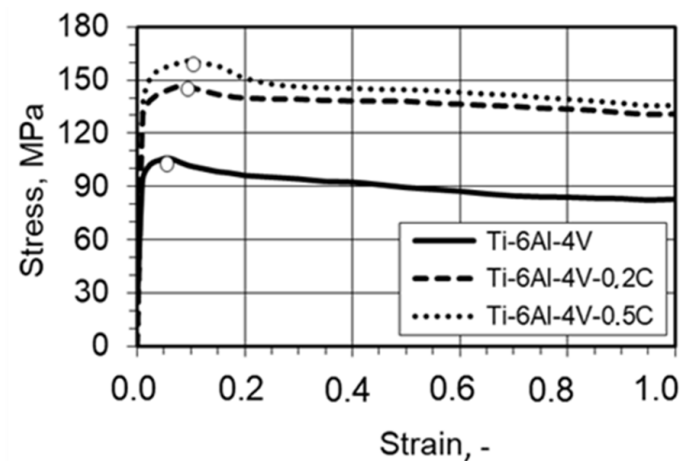

Fig. 8. Effect of carbon on the flow curves of Ti-6Al-4V alloy at room temperature (a) and at elevated temperature (890°C) (b)
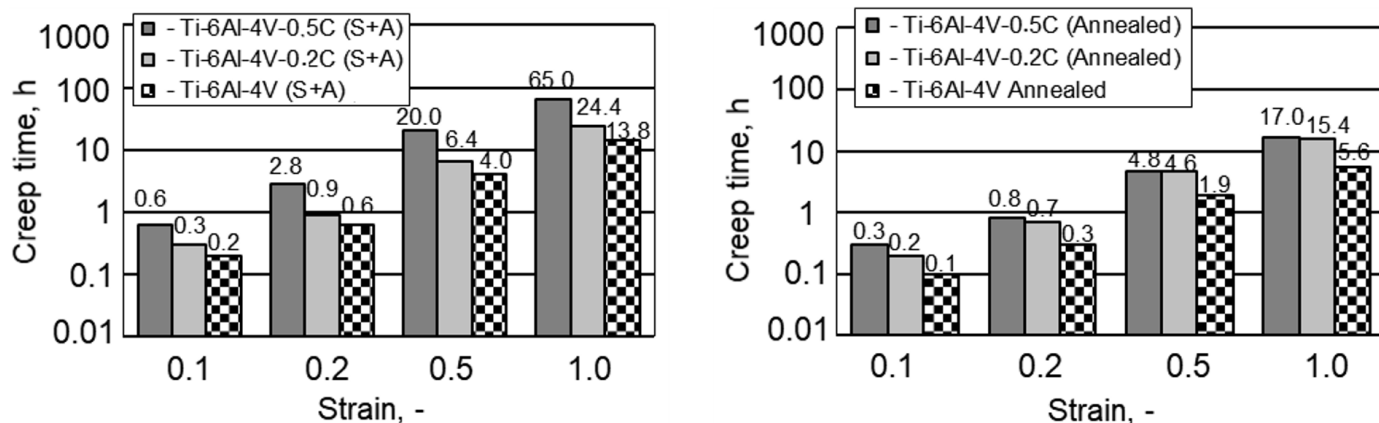
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Fig. 9. Effect of carbon content on the creep resistance (500°C, 300 MPa) of Ti-6Al-4V alloy (S+A-solution and aging)

and stress conditions. The addition of carbon improves creep resistance of titanium alloys in the as-annealed condition and, to even a higher extent, in the as-hardened condition (Fig. 9). This takes place by reduction in the rate and extension of the time of secondary creep stage, delay in transition to primary creep stage or extension of the time corresponding to determined values of strain that accompanies creep.

After 0.3 h of testing and reaching the strain of 0.2%, the annealed Ti-6Al-4V alloy subjected to creep test at 500°C and 300 MPa enters the secondary creep stage at the rate of $13.51 \cdot 10^{-4}$ s^{-1}. Under such conditions, the Ti-6Al-4V alloy reaches the strain of 0.5 and 1.0 % after 1.9 and 5.6 h, respectively. The introduction of carbon into the test alloy resulted in a slight change in the course of the creep process. The secondary creep rate of annealed Ti-6Al-4V-0.2C alloy is four times lower and amounts to $3.35 \cdot 10^{-4}$ s^{-1}. The time required to reach the strain of 0.5 and 1.0 % is 2.5 and 3 times longer, respectively. Alloy hardening during the solution heat treatment and aging processes cause further positive changes in the course of creep for this alloy. Hardened Ti-6Al-4V-0.2C alloy enters the secondary creep stage at a rate 7 times lower than that of the alloy annealed at the rate of $1.9 \cdot 10^{-4}$ s^1, and the time required

to reach the strain 0.5 and 1.0 % is 6.4 and 24.2 h, respectively. At the higher carbon content, the secondary creep rate is 2.69 and $1.10 \cdot 10^{-4}$ s^{-1} for Ti-6Al-4V-0.5C alloy in the as-annealed condition and in the as-hardened condition, respectively. The creep time required to reach the strain of 0.5 % for hardened Ti-6Al-4V-0.5C alloy is five times longer compared to that of the alloy without carbon in the same condition and amounts to 20 h. The obtained results confirm the positive impact of carbon on creep resistance presented for other groups of conventional titanium alloys [30], and recently also for the new group of TiAl intermetallic alloys [31]. Responsible for the improvement in creep resistance are carbides, including large and quite plastic primary carbides. They are usually arranged at the grain boundaries where they effectively hinder their slipping, which translates into the increase in creep resistance – the greater the higher the carbon content in the alloy.

Carbides present in the analyzed alloys have also a positive impact on the microstructural stability at elevated temperature under long-term annealing conditions. The selection of annealing temperature depended on aging temperature of the test alloys and was assumed to exceed the operating temperature of commercial equivalents of the test alloys [24-26]. Fig. 10 shows the
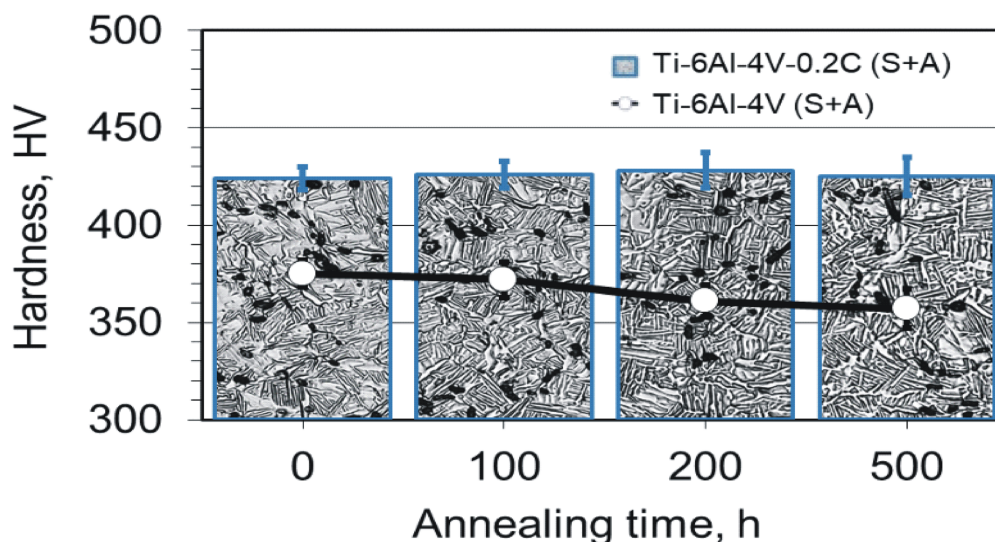

Fig. 10. Effect of carbon and annealing time at 475°C on the hardness and microstructure of Ti-6Al-4V alloy after solution treatment and aging (S+A)

effect of annealing time on the microstructure and hardness of the test alloy in the as-hardened condition after 500 h heat treatment at 475°C. No morphological changes in the carbide phase or changes implying a degradation of its matrix were observed in the microstructure of the alloy, which was confirmed by the results of hardness measurements. However, a drop in hardness was observed after 200 h annealing of alloy without carbon content (Fig. 10).

The addition of carbon also has a positive impact on oxidation resistance of titanium alloys. The results of investigations of isothermal oxidation kinetics of annealed titanium alloys containing carbon and their carbon-free equivalents are presented as oxidation curves (Fig. 11).
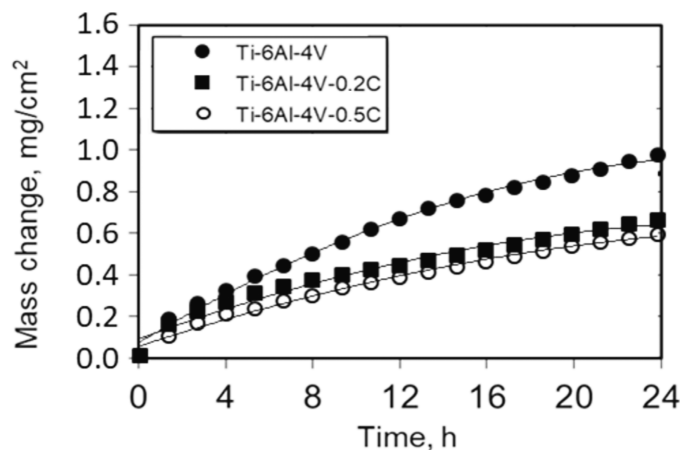

Fig. 11. Effect of carbon on the oxidation kinetics of Ti-6Al-4V alloy

The oxidation curves for carbon-containing alloys and their carbon-free equivalents are consistent with the parabolic oxidation law as evidenced by high values of correlation coefficients R^2, which indicate the compliance of obtained experimental results with those described by the Pilling-Bedworth equation [18,32]. For alloys containing 0.2 and 0.5 wt.% C, they are 0.9944 and 0.9911, respectively. The addition of 0.2 wt.% C to Ti-6Al-4V two-phase alloy results in a significant improvement of oxidation resistance. The oxidation rate constant of the Ti-6Al-4V-0.2C alloy is $4.65 \cdot 10^{-12}$ and is by approx. 50% lower than the oxidation rate constant of the carbon-free alloy. At a twice higher carbon content (0.5 wt.%), a further slight improvement of oxidation resistance takes place.

The reasons for the impact of carbon on the improvement of oxidation resistance of titanium alloys are sought in reduced oxygen diffusion activity [1-5, 21]. Atoms of interstitial oxygen and carbon take up the same octaedric gaps in α-Ti and tetraedric gaps in β-Ti. Thus, carbon in interstitial solid solutions will reduce the solubility and diffusive activity of oxygen. In turn, carbon in non-stoichiometric TiC_x carbides will reduce the diffusive activity of oxygen by reducing its content in the matrix due to taking over the oxygen atoms from the matrix and locating them in unsettled nodes in the carbon sublattice of carbides.

4. Summary

Carbon is present in all grades of technically pure titanium and all commercial titanium alloys as an impurity. Its content does not exceed 0.1 wt.%, and very often it is at a much lower level. By increasing the carbon content in Ti-6Al-4V alloy to the maximum permitted, under the applicable guidelines, level of 0.2 wt.% and higher (0.5 wt.%), it was found that the most important and expected effect of increased carbon content in the test alloy was a significant increase in tensile strength and yield strength.

The improvement of titanium alloys' strength is determined by their phase composition. The efficiency of hardening of titanium and titanium alloys by carbon is higher when carbon is present in the interstitial solid solutions and lower when it is present as titanium carbides. It was found that the addition of 0.5 wt.% C to Ti-6Al-4V alloy resulted in a disproportionately lower gain in strength than that obtained after the addition of 0.2 wt.% C. In addition, the lower strength properties of hardened Ti-6Al-4V-0.5C alloy compared to the properties of hardened Ti-6Al-4V-0.2C alloy indicate the need to limit the carbon content in multi-component alloys or, at the increased carbon content, minimize the content of other interstitial elements.

It can be concluded that the gain in strength properties of annealed titanium alloys containing carbon is only the result of the presence of carbon (content and form), whereas the gain in strength properties of hardened titanium alloys containing carbon is the result of the presence of carbon and decomposition products of metastable phases formed during the solution treatment and aging. The improvement of strength properties of the produced titanium alloys containing carbon takes place while maintaining high plastic properties.

The positive effect of carbon on the increase in hardness is another argument for the gradual and controlled introduction of carbon to titanium alloys, which are characterized by a relatively high strength at a relatively low hardness, and thus low wear resistance, which is still one of the reasons that limit the wider use of titanium alloys. However, it should be taken into account that the obtained increase in hardness of the produced alloys due to both the presence of carbon and the performed heat treatment may result in a reduction in workability of the test alloys.

Carbon has a strong impact on the reduction in susceptibility to hot plastic deformation of titanium and titanium alloys, which however now is not a technological problem. The negative impact of carbon on their susceptibility to plastic deformation at room temperature was revealed too.

Carbon improves the creep resistance of the test alloy, which is more visible in hardened alloys than in annealed alloys. This effect becomes stronger as the strain increases due to the progress of the creep process.

The addition of carbon (0.2-0.5 wt.%) improves the oxidation resistance of Ti-6Al-4V alloy, which is expressed by the decreasing mass growth on the oxidation curves and lowering oxidation rate constant – k_p.

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The results of the investigations confirmed the positive effect of carbon addition on the microstructural stability of Ti-6Al-4V alloy under long-term annealing (500 h) at elevated temperature (475°C) conditions.

The effect of the presence of primary carbides in the microstructure of the test alloy is also the refinement of microstructure, which is visible at individual stages of production and processing of Ti-6Al-4V alloy containing carbon – the greater the higher the carbon content in the alloy.

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