Mechanism of formation of macrodefects in titanium alloys

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Abstract. The mechanism of formation of carbon- and gas-containing metallurgical macrodefects in titanium alloys and the mechanism of modification of these defects in the processes of smelting and heat treatment are established. As the main investigation method, the nuclear microanalysis was used, which allowed measurements of concentration distributions for oxygen, nitrogen, and carbon atoms in the zone of macrodefects. It is found that the source of carbon-containing macrodefects was fragments of a cutting tool. As a source of gas-containing macrodefects, the Ti-O-N particles served, which possess the liquidus temperature exceeding the temperature of smelting.

1. Introduction

Metallurgical macrodefects with high content of O, N, and C atoms exert a strong negative effect on the mechanical properties of titanium alloys [1]. At the same time, no reliable information on the mechanism of formation of such defects is available. One of the possible approaches to solving such problem may be investigation of distributions of light-element atoms in the zone of a defect and distributions of the number of defects over oxygen, nitrogen, and carbon concentrations for defects which were found under industrial conditions. In this work it was made using the nuclear microanalysis technique of increased locality. Earlier [2], we used the same approach to investigate the mechanism of macrodefect modification upon smelting and heat treatment of titanium alloys. In particular, it was established that in the course of smelting and high-temperature treatment of alloys in solid state the content of light-element atoms in defects decreases in accordance with the diffusion regularities. The rate constants of these processes turned out close to the diffusion coefficients for the light-element atoms in solids that have approximately the same chemical composition as the defect material.

2. Experimental

In total, more than 70 macrodefects of metallurgical origin with linear dimensions from 0.2 to 2 mm were investigated, titanium being the basic element of the defect material in majority of cases. More than 40 defects studied were revealed upon smelting the alloy Ti6Al4V which contained 6% aluminum and 4% vanadium (here from mass percent is given unless another is specified). The rest
defects were discovered in titanium alloys of other ten grades. Besides, there were some metallurgical
defects that consisted of tungsten and carbon atoms. The macrodefect location in an ingot or semi
product was determined using an ultra-sound technique. The samples under study were metallographic
sections containing in-plane macrodefects. The investigations were performed using a 2MB Van-de-
Graaf accelerator. The parameter under measurements was the average concentration of light elements
in the defect bulk. The diameter of the analyzing beam was chosen equal to the defect diameter. The
precision of the beam incidence onto the object under study was 0.01 mm. Concentration profiles for
oxygen, nitrogen, and carbon atoms were measured using reactions $^{16}\text{O}(d, p)^{17}\text{O}$, $^{14}\text{N}(d, \alpha)^{12}\text{C}$ and
$^{12}\text{C}(d, p)^{13}\text{C}$, respectively. In the cases of oxygen and nitrogen the energy of incident beam was 0.9
MeV, whereas for carbon, 0.85 MeV. The measurement conditions and method of treating the data of
nuclear-physical experiments were described in detail in [3,4]. Using electron probe microanalysis,
concentrations of the main alloying metal atoms (vanadium and aluminum) were determined in the
core of defects in the Ti6Al4V samples.

3. Results and discussion
The origin and initial composition (WC) of the W – C macrodefects are quite obvious. The source of
such defects is fragments of hard-metal cutters that are applied for mechanical treatment of ingots.
According to the binary diagram for W – C system, it is obvious that the modification cannot lead to
dissolution of such defects. The product of modification, depending on the conditions under which the
process occurs, may be a solid solution of carbon in tungsten or a solid solution with carbide
inclusions. In our case the range of carbon concentration was 6 – 30 at. %.

For the Ti – O (N, C) defects, concentrations of oxygen and nitrogen were found to increase (from
several up to hundreds times in comparison with titanium matrix) in all cases, while that of carbon,
only in three cases. In figure 1, distribution of the number of defects over the ratio of nitrogen and
oxygen concentrations is shown in the form of histogram. You can see that for the majority of defects
the concentration ratio for oxygen and nitrogen $C_N/C_O$ was less than 1 and only in four cases the
nitrogen concentration was higher than that of oxygen. In the range of $C_N/C_O$ from 0 to 1 the higher
the ratio was, the lower the number of defects N, and the N dependence on $C_N/C_O$ was approximately
linear in this range. No correlations between the linear defect dimension and concentration of oxygen
and nitrogen in them were detected.

![Figure 1. Histogram of distribution of metallurgical defects over the ratio of nitrogen and oxygen concentrations](image)

Figure 2 shows a histogram of the defect distribution over aluminum concentration in the
Ti6Al4V alloy after smelting. The distribution is seen to have a maximum. For vanadium, the result
was analogous. For aluminum, the maximum is pronounced more distinctly and corresponds to the
concentration close to that for the Ti6Al4V alloy. The average concentration of vanadium in the alloy was 2 times as high as in the distribution maximum. Besides, the following regularities should be noted: (i) in defects with the lowest aluminum concentration the amount of vanadium was low as well; (ii) all the defects that are presented in the distribution peak in figure 2 manifest themselves in the distribution peak for vanadium. For the defects that correspond to the distribution peaks, the aluminum and vanadium concentrations were virtually independent of the inclusion size (figure 3).

**Figure 2.** Histogram of distribution of metallurgical defects over aluminum concentration.

**Figure 3.** Dependence of aluminum concentration on linear dimension of defect.

Based on the results of measurements performed on the chemical composition of the defect material and literature data on the binary phase diagrams for titanium alloys [5], the liquidus temperatures $T_L$ of the defect materials were calculated. In doing so, each element A was assumed to change the liquidus temperature of the alloy by the same value as in the system Ti—A. Actually, the data shown in figure 1 do not fully correspond to the defect state gained by the time of completion of the smelting process. This is related to the fact that upon cooling ingots after crystallization and several production steps (e.g., heating slabs for rolling) a decrease in the concentration of light-element atoms in the defects would take place. As was noted in Introduction, in [2] it was established that the modification of defects upon heat treatment proceeds via the diffusion mechanism. Taking this into account, the average concentrations $C_0$ of oxygen and nitrogen atoms in each defect after the completion of smelting were estimated with the use of diffusion equations. The estimations were performed using, for example, equation that describes diffusion of atoms from a limited-size body into an infinite space. In case of a spherical particle it has the form [6]

$$
C_0 = C_S + (C - C_S) \left( \frac{6}{\pi^2} \sum_{s=1}^{s} \frac{1}{s^2} \exp \left( -\left( \frac{s \pi}{r} \right)^2 D t \right) \right)^{-1},
$$

where $D$ is the diffusion coefficient for impurity atoms; $t$ is the time of cooling an ingot; $r$ is the particle radius; $C_S$ is the concentration of impurity atoms in the titanium matrix; $C$ is the measured concentration of an impurity atom (oxygen or nitrogen). Using the results of these estimations, the $T_L$ values were calculated and it was obtained that in all the defects investigated, the concentration of light-element atoms was enough to provide their occurrence in solid state upon smelting. The decisive contribution into the formation of refractory inclusions was made by the saturation of the defect material by nitrogen atoms.
Data shown in figure 2 were discussed in the frame of a model suggesting the diffusion mechanism of modification of the subsystem of metal atoms in the macrodefects in the course of smelting. For simplicity, the changes in the defect size are omitted in figure 4. It is seen that, according to this mechanism, the dopant concentration in the defect core must be intermediate between $q_1$ and $q_2$.

In accordance with this model, the source of about 70% defects is particles of the return production wastes. These defects are represented by the distribution peak in figure 2. In this case, the role of diffusion processes in the aluminum subsystem in the course of smelting was neglected, which manifest itself in the absence of the dependence of Al concentration on the inclusion size (see figure 3). According to the model the source of the rest 30% defects could be particles of titanium sponge, smelting products, and ligatures.

Conclusions
According to the results of the study presented, upon smelting titanium alloys the metallurgical macrodefects originate from the particles which have the melting temperature higher than that of smelting. The formation of refractory particles is caused by their saturation with light-element atoms, primarily, nitrogen. In the course of smelting these particles change their size and chemical composition, yet remaining solid by the time of smelting completion.

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