SURFACE HARDENING OF TITANIUM DURING THERMOCYCLING IN NITROGEN

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Interaction of titanium with molecular nitrogen under the thermocycling conditions has been studied. It has been shown that cyclic variation of the temperature affects on the saturation intensity, inhibiting (low-temperature nitriding) or intensifying (nitriding at high temperatures or in the region of $\alpha \leftrightarrow \beta$-transition) the process. The temperature range of cycling determines the character of near-surface hardening. Deviation from the stoichiometry to the side of nitrogen shortage is typical for nitride films.

Surface hardening, in particular, nitriding of titanium alloys, is broadly used in machine building for increasing anticorrosive and antifriction properties of products. To harden satisfactorily the surface layers during thermodiffusive saturation of titanium in nitrogen under atmospheric pressure, high temperatures and long soakings are necessary. This negatively affects the metal phase-structural state, quality of the surface, etc., and, therefore, the operational properties of products. Thermocycling makes it possible to shorten the residence of the material in the high-temperature zone. It is impossible to estimate the intensity of titanium saturation because of the absence of appropriate investigations. However, it is known that the diffusive processes in steels, aluminium and nickel alloys during cyclic variation of the temperature, pressure, and gas composition (carbon, nitrogen) become more active [1-3]. The objective of this work consists of establishing the laws of titanium interaction with molecular nitrogen under thermocycling conditions.

Procedure and Materials

We studied technically pure VT1-0 titanium with content of admixtures at most 0.5 wt. %. We polished the specimens (10 x 15 x 1 mm) to $R_a = 0.02 \mu m$ in order to eliminate the surface defective layer. The specimens were saturated in technically pure nitrogen (\leq 0.4 mol \% of oxygen, and \leq 0.07 g/m$^3$ of water vapor) under atmospheric pressure. The heating rate was 250°C/h, and the cooling rate was 100°C/h. Since titanium can exist in the form of the low-temperature $\alpha$-phase and high-temperature $\beta$-phase, which differ from one another both by the type of crystal lattice and by nitrogen diffusion rate [4], we performed tests in various temperature ranges. The cycle with the amplitude $A = 100^\circ C$ was realized in the regions of $\alpha$-titanium ($800 \pm A/2^\circ C$), $\alpha \leftrightarrow \beta$ transition ($900 \pm A/2^\circ C$), and $\beta$-phase ($1000 \pm A/2^\circ C$). The results were compared with data of isothermal soaking at maximum, minimum, and mean temperatures of every thermocyclic treatment.

We studied the influence of the thermocycle amplitude, saturating the specimens in the regions of $\alpha \leftrightarrow \beta$ transition and $\alpha$-phase of titanium, and of the thermocycling frequency (number of cycles $m = 10$ and $16$ at 6-hour base) in the range of $900 \pm 50^\circ C$. We chose these parameters, proceeding from the possibilities of laboratorial and industrial vacuum thermal equipment.

The specimens were tested for low-cycle pure bending on a UMDU-01 machine [5] with the assigned amplitude of deformation ($\varepsilon_a$) and frequency of 0.5 Hz at room temperature.

Results and Discussion

Saturation of titanium by nitrogen depends on the temperature region of cycling. In the temperature range of $\alpha \leftrightarrow \beta$-transition and $\beta$-region, the growth of the specimen mass is more (by 1.3 and 1.5 times, respectively) than after isothermal soaking at the mean temperature, but it does not exceed the growth at the thermocycle maximum.
temperature. Therefore, nitriding is intensified. The depth and degree of hardening of modified layers exceed not only the mean values, but the maximum ones as well. For example, during cycling in the region of polymorphic conversion, the growth of the specimen's surface microhardness is not higher than after isothermal nitriding at the mean temperature, but the curve of microhardness distribution across the depth of hardened layers lies in the region of greater hardenesses, providing evidence of more efficient near-surface hardening. The nitrided layer is deeper after cycling than the layer formed by isothermal nitriding at the maximum temperature.

![Diagram](image_url)

Fig. 1. Parameters of the crystal lattice of α-solid solution of nitrogen in titanium after isothermal and thermocyclic nitriding in the α-region.

Owing to cyclic nitriding in the β-region, the nitrided layer depth is commensurable with the depths after isothermal saturation at the maximum, mean, and minimum temperatures, the growth of the surface microhardness exceeds the value after isothermal soaking at the thermocycle maximum temperature by 3.5 GPa, and the curve of microhardness distribution across the hardened zone section lies in the region of high values, especially in near-surface layers up to 30 μm. Therefore, cycling provides more efficient near-surface hardening than isothermal saturation, but it differs qualitatively from cycling in the region of polymorphic conversion.

The growth of the specimen mass during cycling in the α-region is the same as after isothermal soaking at the thermocycle minimum temperature, and it is 2.0 and 3.3 times less than at the mean and maximum temperatures, respectively, i.e., the saturation rate decreases.

With nitrogen introduction into the octahedral interstices, the hexagonal closely-packed lattice of α-titanium is deformed: its parameters \(a\) and \(c\) increase proportionally to the nitrogen quantity [4]. Therefore, lower values of \(a\) and \(c\) after cyclic nitriding as compared with isothermal (the difference between values of the parameter \(a\) is more, Fig. 1) are evidence of weaker saturation of α-solid solution with nitrogen and prove the inhibition of nitriding under the thermocycling conditions in the α-region. The qualitative effect of surface hardening (albeit much weaker) is related to cycling in the β-region: the hardened zone depth is less than after isothermal soaking at the mean temperature of the thermocycle, and the growth of the surface microhardness is more, but lower than after soaking at the maximum temperature. This is connected with an increase in the energy of the crystal lattice of α-solid solution caused by the presence of defects in it after cyclic chemical and heat treatment, which is corroborated by higher values of the ratio \(c/a\) as compared with isothermal nitriding (Fig. 1).