IMPROVING THE CORROSION RESISTANCE OF AN ADDITIVELY MANUFACTURED TITANIUM ALLOY BY HEAT TREATMENT

SERHII LAVRYS, MARIIA-OLENA DANYLIAK, TARAS GURAL

Karpenko Physico-Mechanical Institute of NAS of Ukraine

In this work, the effect of post heat treatment (annealing) on corrosion resistance of additively manufactured (AM) Ti6Al4V titanium alloy in a 20 wt.% hydrochloric acid was studied by comparing it with a conversational manufactured one (wrought). As AM was chosen selective laser melting method which performed by 3DMetalTech company (Ukraine). It was shown that post annealing at 800°C improve anti-corrosion characteristics of AM titanium alloy. These results indicate that the selective laser melting accompanied by the post heat treatment process can be used to produce AM Ti6Al4V parts in comparison with wrought ones.

Keywords: Ti6Al4V, additive manufacturing, heat tretment, corrosion resistance

Introduction. Today, the direction of manufacturing of titanium products using additive technologies (Additive manufacturing, AM) is actively developed in scientific and industrial laboratory centres. The main advantages of AM of titanium compared to conventional technology (CT, wrought) are: 1. Higher so-called buy-to-fly ratio or yield ratio of the material. That is, during the manufacture of titanium products by TT 60...82% of the titanium becomes scrap metal. For AM this index is not higher than 5%; 2. Lower cost of titanium product as a whole (70/700 dollars per 1 kg of workpiece/product for CT and 200…110/100…210 dollars for AM). It should be noted that this indicator depends on both the feedstock (initial powder mixture) and the AM technology; 3. The ability to produce details of complex dimensional configuration with holes or internal voids; 4. The ability to produce titanium matrix composite with different types of structure and chemical composition; 5. Higher design speed and flexibile production. AM allows quickly design changes without compromising pricing and short lead times. AM is also very cost-efficient for manufacturing small details; The waste generated in the process is reused in manufacturing and does not lose any of its properties; 6. Short lead times [1–5].

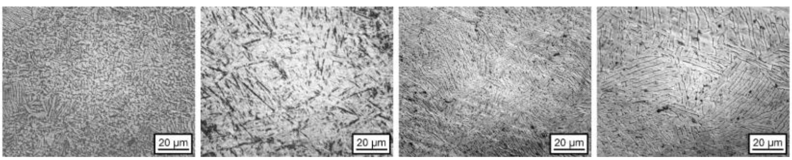
However, AM titanium alloys are characterized by low corrosion resistance compared to similar ones produced by CT. This is due to the fact that the metastable martensitic structure of titanium alloys is formed during AM as a result of rapid heating and cooling. In addition, Anisotropy, heterogeneity, residual stresses, pores, etc. inherent in AM titanium alloys can also be attributed to the disadvantages [3–5]. Therefore, the aim of the study is to improve the corrosion resistance of Ti6Al4V titanium alloy by post heat treatment (post-annealing).

Methodology. The AM Ti6Al4V titanium alloy fabricated by selective laser melting method (3D Metal Tech LLC, Kyiv, Ukraine) was investigated. For a qualitative assessment of the electrochemical and anti-corrosion characteristics of the AM titanium alloy, a wrought titanium alloy was used as a reference in the study.

The electrochemical tests were carried out by a VersaSTAT 3 potentiostat using a standard three-electrode cell with a platinum rod as the counter electrode and a saturated Ag/AgCl electrode as the reference electrode. The working electrode was consisted of wrought and porous titanium specimens with an exposed geometric area of 1 cm^2. The 20 wt.% HCl solution were used as the electrolytes. The Tafel plots were measured at a scan rate of 2 mV/s within a range of –1 V to +2 V with respect to open circuit potential (OCP). The corrosion potential and corrosion current density were determined from the polarization curves by the Tafel extrapolation method. The electrochemical impedance spectroscopy (EIS) measurements were conducted at OCP conditions. The frequency range was from 10^{-2} to 10^4 Hz with a potential perturbation of 10 mV peak to peak. The EIS spectra were analyzed by Zview software. The reproducibility of the results was checked by repeating the experiments at least three times.

Results and discussion. According to the metallographic analysis, it can be observed that the wrought titanium alloy has a typical equiaxed structure. Instead, the microstructure of AM titanium alloy is characterized by a acicular martensitic structure (Fig. 1). It is confirmed by the results of XRD, since we observe only peaks of the α-phase in the diffraction spectrum. Also, an increase of stresses in the crystal lattice of the α-phase and an increase of hardness also indicate the formation of a martensitic structure.

The post heat treatment leads to the transformation of the metastable martensitic microstructure into a two-phase lamellar structure (Fig. 1). This is confirmed by the results of the XRD analysis, where we observe the appearance of the β-phase peak, as well as a decrease of stresses and microhardness. It should also be noted that an increase of the annealing temperature also leads to an increase of grain size, approximately by 2 times.



a b c d

Fig. 1. Microstructure Ti6Al4V titanium alloy: a – wrought; b – AM; c, d – AM after heat treatment at 800°C and 850°C, respectively.

According to the electrochemical investigations (Table 1), it was determined that the AM titanium alloy has worse anti-corrosion characteristics than the wrought one. This is confirmed by higher corrosion currents and lower polarization resistance. The corrosion resistance of heat treated AM alloy depends on the annealing temperature. Heat treatment at lower temperature (800°C) improves the anti-corrosion characteristics of AM titanium alloy and approaches them to the level of wrought one. On the other hand, heat treatment at higher temperature worsens them.

Table 1. Electrochemical characteristics of the AM Ti6Al4V titanium alloy after heat treatment

Samples	i_{corr} [$A \cdot cm^{-2}$]	i_{pass} [$A \cdot cm^{-2}$]	E_{corr} [V]	R_f [$\Omega \cdot cm^2$].	R_{ct} [$\Omega \cdot cm^2$].	R_p [$\Omega \cdot cm^2$].	K, [mm/y]
Wrought	$8.13 \cdot 10^{-5}$	$6.16 \cdot 10^{-5}$	-0.63	247.4	180.4	427.8	1.16
AM	$9.07 \cdot 10^{-5}$	$8.71 \cdot 10^{-5}$	-0.62	198.3	168.0	366.4	2.43
AM+HT1	$8.47 \cdot 10^{-5}$	$6.53 \cdot 10^{-5}$	-0.61	215.4	175.3	390.8	1.62
AM+HT2	$9.52 \cdot 10^{-5}$	$6.03 \cdot 10^{-5}$	-0.61	138.0	151.0	289.1	2.31
Remark	E_{corr} is corrosion potential; i_{corr} and i_{pass} are corrosion and passivation current density; R_f, R_{ct} and R_p are oxide native film, the electric double layer and polarization resistance, respectively; K is corrosion rate.						

The immersion tests (holding 522 hours) correlate well with the electrochemical tests (Table 1). The AM titanium alloy has higher corrosion rate than the wrought on. And heat treatment at lower temperature provides a decrease of the corrosion rate of the AM titanium alloy.

So, base on the corrosion tests it can be assumed that during corrosion tests the surface passive film of titanium is exposed to the aggressive action of chlorine anions, which leads to the formation of crevices in the passive film, the release of titanium ions and their subsequent interaction with chlorine. That is, when the passivity is locally broken, and the oxygen that can repassivate the system is depleted, titanium dissolution occurs inside the crevices in passive film.

However, despite the similar corrosion mechanism, the AM titanium alloy has worse electrochemical parameters than conventional produced alloy (wrought). This can be explained as follows:

- α′ martensitic phase formation. The α′ martensitic phase, is in “higher energy state” and metastable, and has less corrosion resistance compared to the α or β phases.
- Lack of a more stable β phase. β phase, in comparison with the α or α′ martensitic phase, has higher corrosion resistance, and, as a consequence, the better electrochemical parameters.

- Residual stresses. Residual stresses in titanium alloy, which can intensify the corrosion dissolution of titanium.

Heat treatment at lower temperature allows to improve the corrosion resistance of AM titanium: formation of (α+β)-structute instead of martensitic phase and decrease of residual stresses. Instead, heat treatment at higher temperature, although it provides a reduction of the martensitic phase in AM titanium alloy, leads to a significant increase of a grain size, which effect negatively on the corrosion resistance.

Conclusions. Therefore, in this work, the regularities between the phase-structural state and the corrosion resistance of AM titanium alloy were determined and the post-heat treatment for improving its anti-corrosion characteristics was proposed.

The main conclusions are the following:

- The AM titanium alloy provides lower corrosion resistance than the conventional wrought one that is caused by the presence of metastable martensite and residual stresses in the structure.
- Carrying out the post-heat treatment allows to improve the corrosion resistance of AM titanium alloy and to approach it to the level of the wrought one. This improvement is mainly explained by the softening of the structure, namely the reduction of the metastable martensitic phase and the release of the corrosion-resistant β-phase.
- The optimal regime of post-heat treatment should not exceed a temperature of 800°C, because at higher temperatures the intensive growth of α-phase grains occurs, which leads to the deterioration of the corrosion resistance of the alloy.

1. *Dutta B. and Froes F. H.* The additive manufacturing (AM) of titanium alloys // Met. Powder Rep. – 2017. – 72. – P. 96–106.
2. *Zhemanyuk P.D., Basov Yu.F., Ovchinnikov A.V., Dzhugan A.A. and Mykhailitenko A.V.* Application of new generation titanium powders (HDH2) in additive technologies // Aviatsiyno-kosmichna tehnika i tehnologiya. – 2016. – 135. – P. 139–144. (in Ukrainian)
3. *Dong-Il Seo and Jae-Bong Lee*. Effects of competitive anion adsorption (Br^- or Cl^-) and semiconducting properties of the passive films on the corrosion behavior of the additively manufactured Ti–6Al–4V alloys // Corros. Sci. – 2020. – 173. – No. 108789.
4. *Meng K., Guo K., Yu Q., Miao D., Yao C., Wanga Q. and Wang T.* Effect of annealing temperature on the microstructure and corrosion behavior of Ti–6Al–3Nb– 2Zr–1Mo alloy in hydrochloric acid solution // Corr. Sci. – 2021. – 183. – No. 109320.
5. *Lavrys S., Pohrelyuk I., Veselivska H., Skrebtsov A., Kononenko J. and Marchenko J.* Corrosion behavior of near-alpha titanium alloy fabricated by additive manufacturing // Mater. Corros. – 2022. – 73. – P. 2063-2070.