ARTICLE PRODUCTION FROM TITANIUM ALLOYS BY THE METHOD OF HOT ISOSTATIC PRESSING IN GLASSY-CERAMIC SHELLS WITH TITANIUM AND NIIOBIUM BARRIER COATINGS

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ANNOTATION

By using reactions of disproportionation in molten salts coherent titanium and niobium coatings on glassy ceramic shells have been obtained. The glassy ceramic shells with barrier coatings were used to obtain articles from a titanium alloy powder by the method of hot isostatic pressing. It was shown that compacting titanium alloys in a gasostate at a temperature of 1173 K, pressure 2000 atm and the time of pressing 4 hours allows to obtain articles easily removable from the glassy ceramic shells. The thickness of coatings after hot isostatic pressing was shown to decrease by 25-30% without the disruption of the coherence coating. In glassy ceramic shells with titanium and niobium coatings articles with a density close to the theoretical one, without any visible defects and pores were obtained and the character of the microstructure allows to refer them to the type 3-4 titanium α-alloys.

Key words: hot isostatic pressing, glassy-ceramic shell, titanium and niobium coatings, titanium alloy.

1. INTRODUCTION

In the powder metallurgy technologies the responsible parts are obtained by hot isostatic pressing (HIP). The shape of an article is determined by the shape of the shell used. The most extensively employed nowadays are metal capsules obtained by an expensive and labour-intensive method which is not always applicable for manufacture of intricately shaped parts. Good results are achieved by using shells from quartz glass, but intricately shaped parts cannot be made from it either. Capsules from ceramics and glass-ceramics obtained by the method of rejection mask model are the widest spread. The shell is produced by multiple immersion of the model (predominantly a wax one) into a refractory material suspension to form a coating. The model is smelt, the shell is burned obtaining the ready shape. The ceramic shell thus obtained is porous. The shell’s porosity is sometimes up to 60% [2], which renders it inapplicable for HIP as in the compaction temperature range of the ceramic shell must be hermetic and press the powder into a compact blank without disrupting the hermeticity. In order to provide hermeticity, a powder with glass particles not smaller than 50 µm is introduced to the suspension composition. The suspension is applied onto wax models and fixed with a powder of the same glass with the particle size from 100 to 500 µm. During the process of thermal treatment sintering occurs and the powder vitrifies. However, even with this technology of glassy ceramic shell production they appear to be unhermetic.

Leaking is only one of the drawbacks of the ceramic and glassy-ceramic shells, the most important one being high adhesion and depth of interaction with the titanium alloy during. Interaction of the metal powder with the shell at 1273 K and the pressure of 2000 atm is so vigorous that the article is impossible to separate from the shell. The cause for the article intensive interaction with the shell are the chemical processes occurring on the shell-article interface. The thermodynamic calculations performed by the Temkin-Shwartzman method in the temperature range of 873-1473 K have shown that the titanium alloy components may enter into chemical reactions with oxides incorporated into ceramic and glassy-ceramic shells.

The aforementioned disadvantages can either be eliminated by applying new gas-tight materials incorporating no oxides which interact with the metals compacted, or by depositing onto the shell an inert as regards the alloy coating that may simultaneously act as a gas-tight and barrier layer precluding the metal contact with the glassy ceramics. The metals to be used as coatings should be sufficiently refractory, i.e. have the melting point not lower than the temperature of the alloy pressing, namely 1273-1473 K. The metals satisfying these requirements are titanium, niobium, iron, nickel, chromium, etc.

The methods of the metallic layer deposition should be various, i.e. atomization, deposition from the vapour phase in vacuum, precipitation from suspensions, chemical and electrolytical deposition. Thus, in work [3] where
a protective layer of silver was deposited from a suspension, which was followed by burning it in the surface of shell; and then during 50 hours at the current density 0.03 A/cm² a nickel coating was electrologically deposited onto silver. It should be noted that the methods of atomization, deposition from a vapour phase in vacuum and electrolytical deposition do not provide the formation of a coating on intricately shaped shells. So narrow grooves, channels, holes turn out to be uncoated and the capsule comes into an immediate contact with the article being compacted.

Chemical nickel-plating of nonmetallic materials is widely used [4-5]. This method permits to plate complex articles. The principal drawback to the method of chemical nickel-plating is the presence of phosphorus in nickel, which decreases the melting temperature drastically until it becomes only 1163 K [6]. This makes these coatings inapplicable for compacting articles at a temperature higher than that of chemical nickel melting, whereas the commonly used temperature of compacting is 1273-1473 K. Besides, the testing of isostatic compacting of granulated titanium alloy PT3V with a Ni-P barrier layer showed the depth of the compact changed layer (the microhardness measurements) to be 400 to 600 µm.

2. RESULTS AND DISCUSSION

In this study on formation of barrier layers from titanium and niobium on glassy ceramic shells the reactions of disproportionation (DPP) in molten salts [6] were employed. Without dwelling on how the reactions of disproportionation are carried out we will note that the DPP reactions with the formation of titanium and niobium coatings are self-controlled as they occur until on the surface remain spots unplated with the metal in the form of a coating. The mechanism of these reactions by itself permits to obtain uniform, coherent coatings on glassy-ceramic shells of any shape including those having narrow, channels, openings.

Outward appearance of glassy ceramic shells prior and after the niobium coating deposition is shown in Fig. 1. The shape of the shell is determined by that of the article compacted and may be diverse.

To determine the composition of the coatings formed on glassy-ceramic shells the method of X-ray photoelectron spectroscopy (XPS) was used. The measurements were performed at Escalab MK-II unit, the X-ray source anode was Mg (MgKα, 1253.6 eV) Since the samples analyzed evolved gas vigorously, they were exposed in a preliminarily evacuated chamber during 48 hours.

Two series of the experiment were conducted, i.e. immediate recording of XPS spectra from the shell surface after preliminary degassing) and recording of the spectra after the shell working surface was etched with a bunch of ionic rays (Ar+, E0=10KeV) to the depth of 100 nm. Analysis of the spectra has shown the presence of predominantly niobium oxides on the shell surface, which agrees with the data of work [7] where the causes of their formation on the metal surface were considered. The spectra obtained after ionic etching (Fig. 2) show that the coatings incorporate the niobium metal, niobium oxides in a minor concentration as well as inclusions of the molten salt used.

The resulting titanium coatings had titanium dioxide at the depth of ~ 1µm (Fig.3) and the presence of the titanium metal is also possible. Moreover, the coatings contain traces of the molten salt used for the coating deposition.

Thus, washing in distilled water does not provide complete separation of the electrolyte from the coating. The washing process is rather lengthy and results in hydrolysis of the electrolyte with possible subsequent interaction of the hydrolysis products with the coating. Therefore the electrolyte was hereafter removed from the shell by vacuum distillation which was conducted at a temperature of 1123 K and in vacuum 0.26 Pa. The vacuum distillation provided a practically complete removal of the electrolyte from the glassy ceramic shells and prevented the gaseous substance liberation.

The glassy ceramic shells with titanium and niobium-bearing coatings were used for compacting by the HIP method of a granulated PT3V alloy. The chemical composition of the granules used for the production of compact blanks is given in the Table.

<table>
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<th>Chemical composition of granulated PT3V alloy</th>
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<tr>
<td>Ti</td>
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<td>base</td>
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The granulated powder was charged into the shells that acquired plasticity on heating and placed in a static gas medium. The medium was imparted pressure, and the pressure imparted to a static gas is transferred by it equally in all the directions and affects the surface it comes into contact with a force directly proportional of the values of these surfaces. The pressure through the intermediate medium (Al₂O₃, filling up) affects the shell's surface and compacts the granulated powder. The heated powder undergoes all-round pressing. As a result an article is
Fig. 1. Outward appearance of glassy-ceramic shells; a- prior to coating deposition; b-after the coating deposition.
Fig. 2. X-ray photoelectronic spectrum of the niobium-containing shell surface after ionic etching (a layer 100 nm thick was removed);
a - a section of the spectrum corresponding to binding energies 1250-620 eV;
b - a spectrum section corresponding to binding energies 620-10 eV).

Fig 3. X-ray photoelectron spectra of the titanium-containing surface: a,b - after preliminary degassing; c,d - after ionic etching.
formed with a shape corresponding to the initial shape of the inner shell surface, but with the sizes diminished in the proportion depending on the material shrinkage and the value of pressure applied. Pressing of the titanium alloy was carried out in a gasostate at 1273 K, pressure 2000 atm and the time of compaction 4 hours. As a result, articles easily removable from the glass ceramic cells were produced. The microstructural analysis of both the compact and surface layers of the shells prior and following the pressing was performed. The studies were carried out using optical microscopes «Reichert» and Polyvav-Met». It was found that the starting metal-bearing glassy ceramic shells have a coherent layer of the coating on the surface. The titanium layer thickness was 50 µm and that of the niobium-bearing one was 100 µm. During the HIP process, under high temperatures and pressures the coatings become compressed and their thickness diminishes by 25-30%, but the coherence of the shell’s interior surface is not damaged. The microstructure of the PT3V alloy after pressing is presented in Fig. 4.

![Fig.4. Microstructure of the samples after the PT3V granule pressing in glassy-ceramic shells coated with: a - niobium; b - titanium.](image)

Fig.4. Microstructure of the samples after the PT3V granule pressing in glassy-ceramic shells coated with: a - niobium; b - titanium.

The obtained article samples have a density close to the theoretical one without any visible structural defects and pores. The character of the microstructure allows to refer them to the 3-4 type of titanium α-alloys. Microhardness of the compact has been determined. The measurements were conducted by the standard methods at «Metallux» hardness gage at the load of 50 g. The results are shown in Fig. 5, presenting the microhardness dependence on the depth of the surface layer of a compact obtained in shells with barrier metal-bearing coatings.

![Fig.5. Microhardness change depending on the depth of the surface layer of the compact obtained in shells coated with: a - niobium; b - titanium.](image)

Fig.5. Microhardness change depending on the depth of the surface layer of the compact obtained in shells coated with: a - niobium; b - titanium.

As follows from Fig.5, in the case of titanium and niobium coatings the microhardness of the compact’s surface layer changes. The reasons for the microhardness increase are unknown yet and call for a more detailed study. With the use of a titanium-bearing coating the depth of the layer is approximately 100 µm; the microhardness change does not exceed 100-150 kg/mm² in comparison with the microhardness of PT3V alloy (Hv=300-350 kg/mm²). The use of a niobium-containing coating results in a greater depth of the modified layer. The depth of increased microhardness attains 300 µm, however, the microhardness excess is about 50 kg/mm². It should be noted that the depth of the changed layer on compacting a titanium alloy in glassy ceramic shells without any barrier coatings is 700 µm and after the HIP the articles cannot be separated from the shell without damaging its shape.
3. CONCLUSION

By using reactions of disproportionation in molten salts coherent titanium and niobium coatings have been obtained on glassy-ceramic shells. In glassy-ceramic shells with titanium and niobium barrier coatings articles from PT3V titanium alloy with a density close to theoretical and no visible defects and pores have been produced. The character of their microstructure allows to refer them to titanium alloys of the 3-4 type.

4. REFERENCES