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Characterization of hydrogen barrier coatings for titanium-base alloys

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Abstract

The purpose of this study was to investigate the barrier efficiency of a thick thermal spray deposit on the α-titanium alloy, Ti–5Al–2.4Sn against hydrogen penetration. Therefore, a duplex coating has been applied by plasma spraying using a Sulzer Metco F4 gun. The selected duplex coating system consisted of a 0.1–0.2 mm thick tantalum bond layer and a chromium oxide top layer doped with 3 wt% titanium oxide. The achieved thickness of the top layer was about 0.6 mm. The coated specimens have been characterized with regard to bond strength, hardness and microstructure. Hydrogen charging experiments were performed in a Sievert's apparatus.

1. Introduction

Titanium alloys exhibit a number of properties that make them attractive candidates as structural materials for fusion reactors. High strength-to-weight ratio, plasticity, good fatigue and creep rupture properties, high electrical resistivity, heat capacity, low coefficient of thermal expansion, low long-term (>10 years after shutdown) residual radioactivity (after V and Cr, Ti exhibits the fastest decay rate), compatibility with coolants such as helium and water, and corrosion resistance are some of the favorable properties, see e.g. [1–4], together with good resistance to void swelling under a wide variety of irradiation conditions. Commercial availability is assessed by established mine and mill capacity, and from processing point of view high workability and good weldability are beneficial.

However, titanium and its alloys have a high chemical affinity with hydrogen which, in fusion environment, leads to hydrogen embrittlement and tritium inventory [3,5–7]. For first wall applications in fusion reactors, titanium alloys require hydrogen barrier coatings in order to prevent hydrogen intake and subsequent hydrogen isotope induced deterioration. Moreover, the applicability of such coatings will depend on their ability to protect the structure against excessive thermal fatigue resulting from disruptions, as well as on their intrinsic resistance to thermal shock. In addition, they should also resist rapid degradation due to plasma erosion. As a consequence, the deposited coatings should be thick enough (≃1 mm). Among the different technologies capable of processing thick coatings, plasma spraying is a promising option; it allows high deposition rates and in situ repair operations, and both metals and ceramics can be deposited using the same technology. In order to accommodate the mismatch between the coating and the substrate, and then to improve the mechanical and thermal stability of the whole, a graded coating is preferred. Plasma sprayed thick coatings with an adaptive bond layer, i.e. a duplex coating design, may satisfy all these requirements.

Titanium alloys can be divided into three major classes determined by phase constitution [8], that are referred to as the alpha (α), beta (β) and alpha/beta

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(α/β), where the α phase is hcp and the β phase is bcc. The alloying elements used in the titanium system can be divided into two classes upon the basis of which phase the element stabilizes. The α stabilizers are Al, Zr and Sn, while the β stabilizers are V, Cr, Mn, Fe, Co, Ni and Mo. Tensile and low-cycle fatigue mechanical tests have shown recently [9] that, for two well-known commercial alloys, the resistance to radiation damage is superior for Ti–5Al–2.5Sn, an α-titanium alloy, as compared to the more complex Ti–6Al–4V, an α/β titanium alloy. As a consequence, the α-titanium alloy Ti–5Al–2.5Sn has been chosen as base material and a duplex coating has been applied by plasma spraying on a series of specimens of Ti–5Al–2.5Sn. The coated specimens have been subsequently evaluated with regard to structural integrity, microstructure, and hydrogen penetration using a Sievert's apparatus. The results are described in the present paper.

2. Experimental procedures

2.1. Preparation of substrates

Two sets of specimens have been prepared from a rod of the α alloy, Ti–5Al–2.5Sn, by using spark machining: (i) disk-shaped specimens (25 mm in diameter, 8mm in height) destined to be one-face coated for bond strength tests, microhardness measurements and microstructure observations, (ii) disk-shaped specimens (14 mm in diameter, 4 mm in height) destined to be fully coated for hydrogen charging tests.

A special technique had to be used to prepare the disk-shaped, entirely coated specimens for hydrogen charging tests. A rod was prepared which exhibited equidistant, circular grooves on the surface (see Fig. 1). At first, the surface was coated. Then, the rod was cut into disks along the pre-machined grooves. Subsequently, i.e. after machining, the disk faces were coated.

2.2. Thermal spraying

The selected duplex coating system consisted of a tantalum bond coat and a chromium oxide top layer. Low activation of the components was one of the main requirements for the selection of the coating system. Thermal and mechanical properties were also factors of importance. Plasma spraying has been selected, as it is the standard deposition technique for high melting materials such as ceramics and refractory metals.

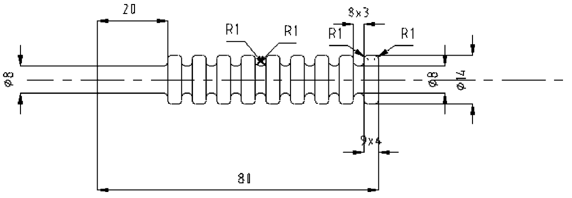

Fig. 1. Preparation of fully coated specimens.

Tantalum exhibits a high melting temperature ($T_m = 3287$ K) and is highly reactive in presence of oxygen. A relatively fine particle size distribution in the range 5–22 μm is required to fully melt the powder in a plasma spray process. The tantalum powder was sprayed under inert conditions in order to avoid oxidation during the deposition process. The process is typically performed under reduced pressure, which leads to an increased interaction time with plasma plume and contributes to a more efficient heating of the particles. This method is commonly called vacuum plasma spraying (VPS). The tantalum bond coat was deposited by the VPS process in an argon gas atmosphere at a pressure of 100 mbar. A layer thickness of about 20–25 μm was deposited in each pass. At least four passes were necessary to achieve a tantalum bond coat of about 100 μm.

Chromium oxide melts at 2570 K. The melt already forms at lower temperature in presence of silica or titania. In general, Cr_2O_3 is processed by plasma spraying under atmospheric conditions (atmospheric plasma spraying, APS) to avoid oxide reduction which could lead to pure chromium formation. This process has been also applied in the present work. The layer thickness of the APS deposited chromia top coat was about 15 μm in each pass. So, 32–34 passes were necessary to obtain a coating thickness of about 500 μm.

The spray trials were carried out at Sulzer Metco, Switzerland. The Sulzer Metco F4 gun was used for APS as well as for VPS. The tantalum bond coat and the Cr_2O_3 overlay have been sprayed with hydrogen addition in the plasma gas in order to reach the required high enthalpy for particle melting inside the plasma. Thus, the as-deposited duplex coating already contains a certain amount of hydrogen, which had to be taken into account for the hydrogen charging tests. Reference specimens were prepared for calibration purpose.

2.3. Spraying materials

The spraying materials were supplied by Sulzer Metco, Switzerland. As a standard, commercial tantalum powder was not available in the desirable particle size distribution between 5 and 22 μm, a fine fraction (<32 μm) was prepared by sieving a 63 μm powder. The purity of this experimental tantalum plasma spray feedstock was 99.5%.

The chromium oxide powder, Metco 106 F, has been chosen for the preparation of the ceramic top coat. This material contains 3 wt% TiO_2, which acts beneficially on the coating ductility.

3. Results and discussion

3.1. Thermal spraying

The thickness of the tantalum bond coat was of the order of 100 μm, as required. However, it was not possible to obtain a thickness greater than 600 μm for the chromia overlay without severe macrocracking or spallation. Further development of the deposition procedure and/or the coating design is clearly required to reach deposits in the millimeter range. Cracking of thick, thermally sprayed ceramic overlays is frequently observed. In the present case, residual stresses in combination with moderate mechanical anchoring to the bond coat may be considered as the reason for coating failure at a thickness above 600 μm.

3.2. Characterization

The coated specimens were characterized with regard to bond strength, hardness, microstructure and hydrogen penetration.

3.2.1. Determination of bond strength

The bond strength of the duplex coating system Ta/Cr_2O_3 on Ti–5Al–2.5Sn as substrate material has been determined for a set of five specimens, according to DIN EN 582. The mean bond strength was found equal to 14.1 MPa. Around 50 MPa is a typical value for a dense, 300 μm thick chromia coating. Optical inspection of the fracture surface revealed that the ceramic top coating failed at the interface to the bond coat. The poor adhesion of the ceramic overlay is certainly due to the relatively low roughness of the tantalum deposit. The roughness of the tantalum bond coat is low as it was necessary to use a fine powder for thermal spraying. The use of a coarser powder would have naturally allowed to achieve a higher roughness.

3.2.2. Hardness measurements

The hardness of the tantalum bond layer (530 HV0.1) is relatively high as compared to that of the as-wrought bulk material (about 200 HV0.1). Oxygen contamination of the spraying powder may explain this discrepancy. The hardness of the chromia (Cr_2O_3) overlay was found equal to 1230 HV0.3 and 1480 HV0.1. These values are typical for chromia in the as-plasma sprayed condition.

3.2.3. Microstructure observations

The microstructure of the duplex coating is shown in Fig. 2 (optical microscopy). Fig. 2(a) shows a general view of a cross-section specimen, while Fig. 2(b) shows a detailed view of the duplex coating and its interface to the substrate. The tantalum bond coat is dense (its porosity was estimated to be around 3%) and its surface appears smooth. Local debonding between the tantalum layer and the Cr_2O_3 overlay could be observed (see Fig. 2(b)). The chromia coating is also dense, as can be seen in Fig. 2(c) that shows a back-scattered electron micrograph of a chromia coating which has been sprayed directly onto the substrate material by using the same

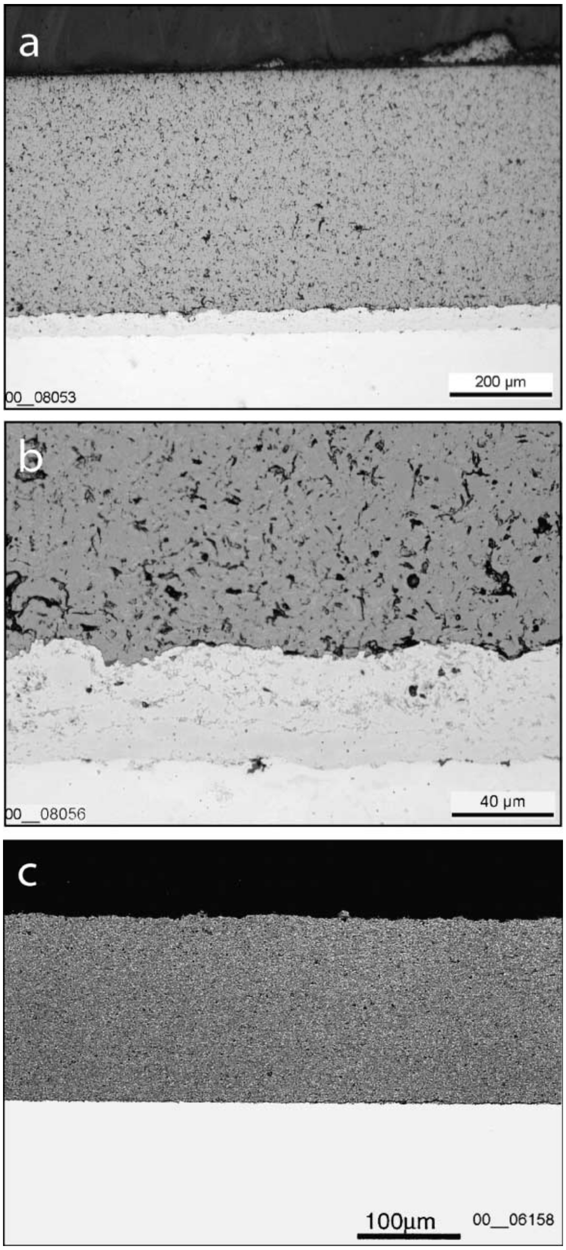

Fig. 2. Optical micrographs of a cross-section specimen: (a) general view of the duplex coating plasma sprayed on a substrate of Ti–5Al–2.5Sn, (b) detail of (a) and (c) back-scattered electron micrograph of a chromia overlay on a substrate of Ti–5Al–2.5Sn.

parameter set. Its porosity was estimated to fall in the range 3–5%. However, interconnected cracks as inherent defects facilitating hydrogen penetration cannot be excluded in plasma sprayed ceramic overlays. In a latter stage, sealing of the plasma sprayed ceramic coatings may be required to close the open crack paths.

3.2.4. Hydrogen charging tests

Hydrogen charging tests were realized in a Sievert's apparatus (see Fig. 3). It consists of a vacuum chamber that can be filled with a controlled amount of hydrogen (or other gases like Ar, He or N_2) through a flowmeter controller. It has attached a furnace that can reach temperatures up to 1000 °C. Three different pressure gauges are installed, as well as three thermocouples and a number of hydrogen leak detectors for safety reasons.

Different tests were realized. First, an uncoated specimen was annealed at 750 °C in a vacuum of 1.2×10^{-7} mbar to remove the oxide layer from its surface. After one hour the furnace was pulled out and the specimen was cooled down to room temperature. Then, the chamber was isolated from the vacuum system. A certain amount of hydrogen was introduced into the chamber through the flowmeter until the desired pressure was obtained. The pressure was calculated in order to obtain a pre-selected amount of absorbed hydrogen. The selected amount for the trials was 400 ppm. Then, the furnace was pushed again around the specimen and maintained at 750 °C for three hours to allow diffusion of the hydrogen inside the material.

Another specimen was hydrogen charged without any vacuum heat treatment, so that an oxide layer remained at its surface. Finally, the same procedure was also applied to a fully coated specimen. The chamber pressure that is inversely related to the amount of absorbed hydrogen, is reported in Fig. 4 as a function of time in case of the three different specimens described just above. It can be observed that there was no drop of pressure for the coated sample, which indicates that no hydrogen penetrated the specimen. On the contrary, a large amount of hydrogen penetrated the uncoated specimen with no oxide layer. An intermediate amount of hydrogen penetrated the uncoated specimen with an oxide layer that acts as a protection layer against hydrogen intake. So, these first results appear highly satisfactory in terms of effectiveness of the duplex coating as a hydrogen barrier.

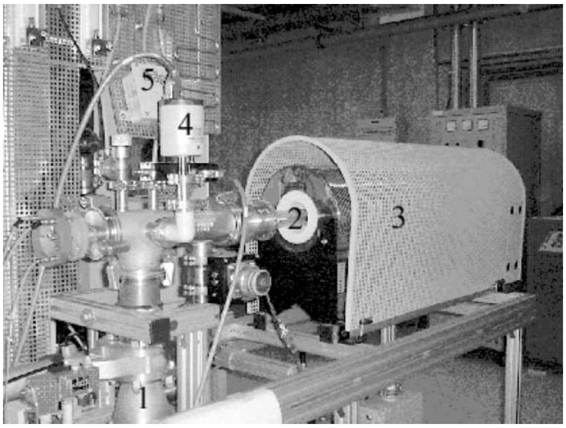

Fig. 3. Sievert's apparatus built for the hydrogen charging tests. (1) Vacuum system, (2) quartz tube, (3) furnace, (4) flowmeter and (5) gas inlet.

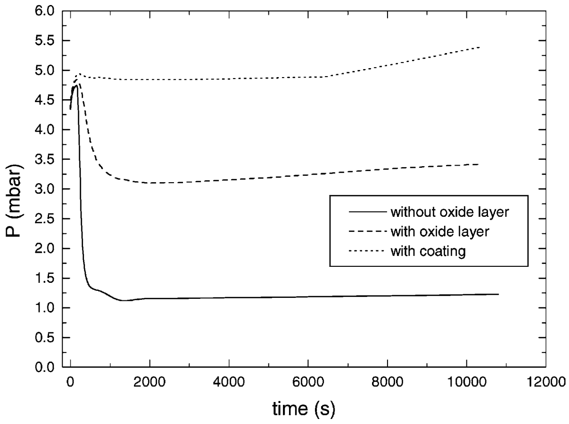

Fig. 4. Chamber pressure versus time for three different specimens.

4. Conclusion

A Ta/Cr_2O_3 duplex coating system has been plasma sprayed on a Ti–5Al–2.5Sn substrate. Results of hydrogen charging tests appear encouraging with regard to barrier efficiency of the plasma sprayed deposits against hydrogen intake. However, bond strength measurements revealed a poor adhesion of the ceramic overly to the tantalum bond coat, certainly due to the low roughness exhibited by the latter. Bond strength will be further improved by acting upon the roughness of the interfaces.

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