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Fatigue and surface structure of titanium after oxygen diffusion hardening

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ABSTRACT

The characterization of oxygen diffusion zone in titanium and the effect of this zone on macroscopic properties are still of high interest for a base to predict and to enhance life time of titanium and titanium alloy components. The aim of this study was to contribute to the understanding of the impact of oxygen on fatigue properties of oxygen diffusion hardened Ti and Ti alloys. Oxygen diffusion hardening implies two process steps, first the oxidation of the surface and secondly the diffusion of oxygen into metal matrix. Due to the one-step treatment used in this study the oxidation step could take place easily avoiding scaling and grain boundary diffusion. In spite of this precaution, the fatigue properties in the present study were found to be decreased after the performed oxygen diffusion hardening. The reason for the reduction of mechanical properties were claimed to be oxide clusters on the surface acting as crack initiation sites. Comparison and discussion with literature revealed varying partially contradictory fatigue results. Therefore precise analysis of the fatigue failure is necessary as a base for further development of the oxygen diffusion hardening.

1. Introduction

1.1. *Avoiding α-case*

Titanium alloys are susceptible to surface degradation from oxygen ingress during elevated temperature use in ambient air. Beside the formation of an oxidized surface layer, the oxygen is diffusing into the metal matrix, which may concern 10 μm, 100 μm or more penetration depth depending on time and temperature of the heat impact and oxygen atmospheric content. During oxygen diffusion (OD) the ductility of the titanium α phase is decreasing with increasing oxygen content, which may result in a deterioration of fatigue properties and reduction of life time. That is the reason that titanium materials are limited for use in the cold parts of engines, cp-titanium up to about 500 °C and titanium alloys up to about 600 °C. In the particular case of titanium alloys containing α and β phases, the dissolved oxygen stabilizes α phase, resulting in a surface layer that is rich in α phase, sometimes referred to as the α case. The term α case is also known by casting titanium alloys and implies the reactions on the surface of titanium components with environment and embedding materials during casting. Casting technologies are aiming to reduce all reactions on the surface of titanium components, because the residual reaction layers have to be extensively removed after casting [1]. Finally, every oxidation will induce an OD zone, not only during casting, also during high temperature application, thermal treatment, anodisation and glow discharge plasma oxidation [2]. Even thermal treatment in vacuum will cause an OD zone as the native oxide layer will then diffuse inside the substrate [3].

1.2. *Using oxygen diffusion zone*

Due to the oxygen diffusion, one expects an increase in hardness with increasing oxygen content. The principle OD process is not new, various studies of diffusion hardening of Ti and Ti alloys were performed, most of them included measured hardness profiles of the diffusion layers, which showed high values of 200 HV and more [4–10] or of 3–5 GPa [11,12]. The increased hardness of the OD zone is raising the wear resistance [4,5,12,13]. It is known that the wear resistance of the surface of Ti and Ti alloys without any treatment is relatively low therefore these materials as implant materials are no longer recommended for the use as a bearing surface [14]. However, the increase of wear is still of interest when the material is used for tribological pairing of metal–metal contact as it cannot be avoided for example for temporary endoprosthetic screws in plates. Controlled OD treatment has been commercially implemented for biomedical application (for example by Listemann AG), and for application of scratch resistant watch casing and bracelets [15]. Beside the increase of wear resistance, the diffusion of oxygen into titanium matrix is also a possibility to prevent hydrogen embrittlement as it reduces the hydrogen content [3]. However, the changes of mechanical properties,

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especially fatigue, are not evident, various studies revealed partially contradictory results.

1.3. *Aim*

Studies of OD zone, its properties and its effect on macroscopic properties, are still of high interest as a base to predict and to enhance life time of Ti and Ti alloy components. This concerns surfaces of components, which were OD treated to enhance tribology properties as well components, which were run through production or application processes like casting, anodisation or any thermal treatment and received in this way an OD zone as a negative side effect. The greatest issue for technical application is the possible decrease in fatigue properties caused by the OD zone. The topic of the present study was to use OD as a surface hardening technique, which is easily available, inexpensive and biocompatible, and to evaluate the important characteristics of OD zone. The aim thereby was to contribute to the understanding of the impact of oxygen on fatigue properties of OD hardened Ti and Ti alloys.

2. Materials and methods

2.1. *Preparation*

The rolled sheet of titanium (AAP) used for experiments has the typical composition of Ti grade 2. The sheets were grinded using water and several silicon carbide papers: SiC 500, 800, 1200 and 2400 grit. Out of those sheets the samples for mechanical testing were milled, see Fig. 1. The polishing of the surfaces was finished with 6, 3 and 1 µm diamond paste. Before microscopy, etching was performed on the titanium surface. The etching medium composed of 95 ml distilled water, 3 ml nitric acid and 2 ml hydrofluoric acid [16] was applied for 45 s.

2.2. *Oxygen diffusion procedure*

In preliminary tests, the diffusion behavior of oxygen into titanium as a function of time and oxygen partial pressure was determined in a two-step process. The first step is the thermal oxidation cycle, and afterwards the sample is cooled down. The second step comprises heating up again in vacuum respectively low pressure. After air cooling of the sealed samples and breaking of the quartz glass container the latter showed an opaque metallic surface on the inside of the cylinder, which was detected as TiO_2 layer. This sublimation was an indication that not the entire TiO_2 from the sample surface dissociated and diffused into the bulk material. In order to avoid this loss, the intermediate cooling step during the process was eliminated, and a process was performed to do evacuation of the sample container in situ after the thermal oxidation, that means, oxidation followed by oxygen diffusion was carried out in one thermal cycle. That was performed by putting the polished titanium samples and a defined amount of potassium permanganate $KMnO_7$ as an oxidizer into a silica glass recipient. After purging with argon and evacuation process, which achieved a low pressure of about 8 mbar, the recipient was closed and heated up, see Fig. 2. Temperature and annealing time were adjusted to produce a thickness of OD zone of about 50 µm. The first 30 min are used to heat the furnace slowly up to 860 °C, during this time the potassium permanganate decomposes at 240 °C and releases oxygen. After reaching the temperature of 860 °C, the samples were annealed for further 150 min.

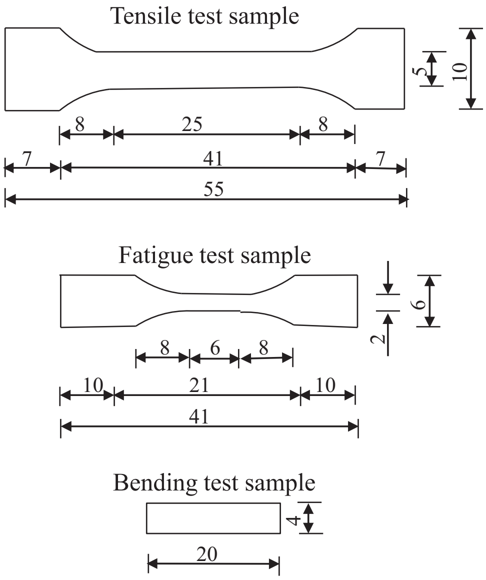

Fig. 1. Samples for mechanical testing, the sample thickness was 1.1 mm.

2.3. *Microstructure*

The microstructure was studied by optical microscopy (OM) scanning electron microscopy (SEM) including energy dispersive X-ray analysis (EDX) using the device CamScan 2CS24. The apparent grain sizes were determined by making linear intercept of grain boundaries on the base of ISO 643. For the determination of an apparent mean grain size at least 30 intercept lines were randomly drawn into OM images, i.e. 10 lines at 3 various positions. At the end the entire length is divided by the intercept points. The oxygen content of the titanium was measured at sample cross-sections by wave-length dispersive X-Ray analysis (WDX) as a function of the distance to the surface. The measured counts were calculated in % oxygen concentration by using the oxygen content of 0.18% of the Ti grade 2. The surface of titanium samples was additionally studied by electron back scatter diffraction (EBSD) of the SEM Hitachi S-2700 using a HKL Nordlys II detector, and the phases of titanium and oxide were identified.

2.4. *Mechanical testing*

Vickers hardness was evaluated using micro-hardness Zeiss MHT-4 Tester for HV0.05, HV0.1 and HV0.3. Tensile fatigue tension experiments were performed in axial stress-controlled mode using a constant minimum tension of 10 MPa and 5 Hz. Thereby the servo-hydraulic testing machine Schenck Hydropuls PSA 100 and a load cell of 2 kN were applied. The ultimate number of cycles was 2×10^6, thereby 8 OD-treated samples and 4 not treated samples were tested.

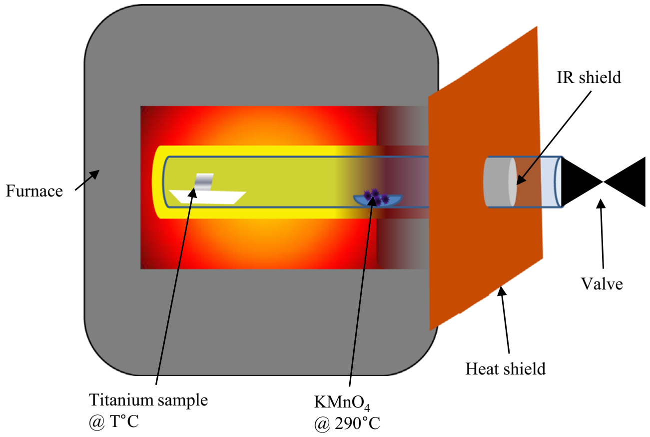

Fig. 2. Titanium samples were oxidized and diffusion heated at the same time with a defined mass of potassium permanganate.