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High-temperature stability and interfacial reactions of Ti and TiN thin films on Al_2O_3 and ZrO_2

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Metallic thin films are used in many applications to modify ceramic surfaces. However, during subsequent processing, chemical interactions may change the properties of the coating. In addition, differences in thermal expansion can lead to delamination of the coating. In this study, titanium and titanium nitride thin films were deposited via physical and chemical vapor deposition (PVD and CVD, respectively) on alumina- and yttria-stabilised zirconia substrates, before being heat-treated at 1200 °C or 1500 °C in static argon atmosphere and analysed via SEM, EDS and XRD to investigate the effect of temperature on the thin films. It was shown that the chemical interactions between TiN and both Al_2O_3 and ZrO_2 are weak. However, partial delamination of the TiN coating on alumina was observed after both annealing temperatures. The TiN coating on zirconia remained adherent. In contrast, the Ti coatings underwent a transformation to cubic TiO on both oxide substrates. This was due to partial reduction of the ZrO_2 to ZrO_{2-x} and dissolution of the Al_2O_3, which leads to a $Ti_3Al_{0.9}O_{1.1}$ interlayer. The TiO coating which formed remained adherent on the alumina at both annealing temperatures, but delaminated from the ZrO_2 substrate after annealing at 1500 °C.

1. Introduction

Titanium (Ti) thin films are often applied on oxide ceramics such as alumina (Al_2O_3) and zirconia (ZrO_2) as a metallisation material prior to brazing or soldering the oxides to metals. These Ti coatings improve the wettability of the filler material on the oxide ceramics during brazing and enhance the bonding strength of the joint. Ti reacts with the ceramic during the brazing process and forms a thin reaction layer which is rich in Ti [1–3]. Several oxidation states are possible for Ti, and the tolerated range of non-stoichiometry of titanium oxides is large, which enables a gradient transition of the Ti/O-ratio from the oxide ceramic to the metal. Some of the titanium oxides have a partial metallic character, which improves the wettability of the filler alloy [4]. The metallisation can either be performed mechanically or by physical or chemical vapor deposition (PVD and CVD, respectively) [1–3]. Surface metallisation is also used in the production of particle reinforced iron-based metal matrix composites (MMC) containing oxide particles. In [5], Ti was deposited by PVD on particles consisting of an eutectic mixture of Al_2O_3 and ZrO_2 (AlZrO) to increase the wettability of an iron-based ultra-high boron high carbon hardfacing alloy on the AlZrO particles during consolidation of the MMC by Induclad processing, which resulted in improved wear-resistance of the MMC.

One disadvantage of PVD is that the filling aspect ratios of PVD coatings are lower compared to CVD coatings and the films are less adherent, which makes CVD coatings more attractive for coating complex geometries or particle beds [6]. However, deposition of pure Ti via CVD is complicated. Titanium nitride (TiN) could also be an interesting material for such transfer layers. TiN thin films deposited via CVD are well known as hard coatings to increase the wear-resistance of tools [7,8]. However, the TiN phase has also a partial metallic bonding character due to a single unpaired electron, resulting in a non-zero electron density at the Fermi level [9]. In addition, its thermal expansion coefficient, α, of $9.4 \cdot 10^{-6}$ K^{-1} [10] is close to that of alumina ($8.2 \cdot 10^{-6}$ K^{-1}) and zirconia ($10.3 \cdot 10^{-6}$ K^{-1}) [11] and it has a high temperature stability. Due to these advantages, TiN was used to increase the wettability of Al_2O_3 particles in [12] and Al_2O_3-ZrO_2 particles in [13].

During preheating and processing, the metallising thin film can be influenced by interaction with the substrate or residual oxygen in the furnace atmosphere, which in turn may result in a change to the properties of the coating. The interaction between titanium and both alumina and zirconia has been extensively investigated over recent decades [14–25], but not specifically for Ti and TiN thin films at high temperatures. Therefore, the aim of this paper is to analyse the interactions of PVD titanium and CVD titanium nitride coatings on alumina and zirconia after high-temperature annealing in a technical static argon atmosphere. To achieve this, the thin-films were analysed via X-ray diffraction (XRD) for overall phase analysis in as-coated and annealed conditions. The temperatures 1200 °C and 1500 °C were chosen for annealing since these are typical temperatures the coating/oxide system

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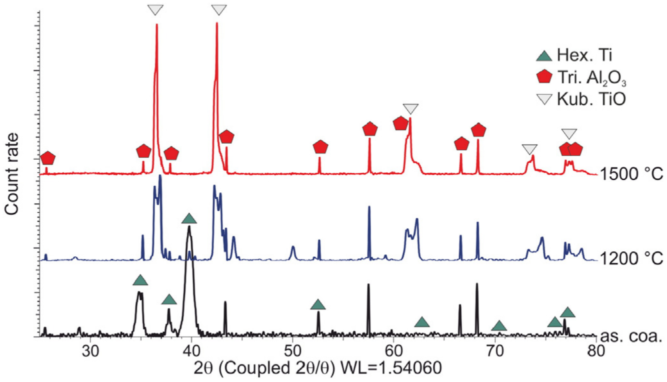

Fig. 1. Phase identification of Ti coating on Al_2O_3 in as-deposited state and after heat treatment at 1200 °C and 1500 °C by means of X-ray diffraction.

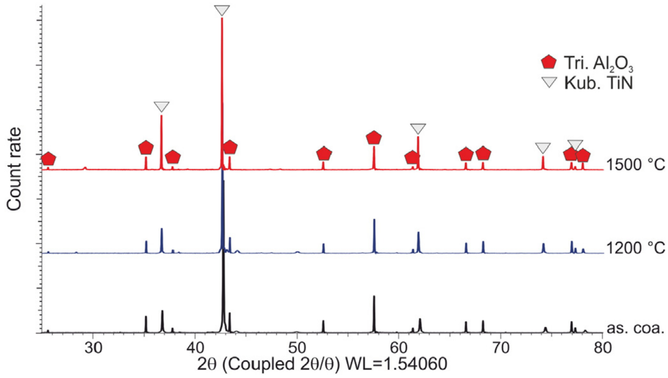

Fig. 3. Phase identification of TiN coating on Al_2O_3 in as-deposited state and after heat treatment at 1200 °C and 1500 °C by means of X-ray diffraction.

must withstand during production of MMCs, e.g., under supersolidus liquid-phase sintering (1200 °C) or pressureless infiltration (1500 °C). Subsequently, scanning electron microscopy (SEM) was used for microstructural analysis with energy dispersive spectroscopy (EDS) for analysis of the local chemistry and electron backscatter diffraction (EBSD) for local phase analyses.

2. Materials and experimental methods

Alumina 998 (99.8 mass% alumina) and 5.4 mass% yttria stabilised zirconia (YTZP) (94.2 mass%) purchased from CoorsTek Inc. USA were used as substrate materials. The substrates were cut to a size of 10 × 10 × 5 mm and polished with diamond paste down to 1 μm. Ti thin films were then deposited via arc-PVD in $3 \cdot 10^{-4}$ mbar with a constant flow of argon gas. The bias voltage was around 30 V, the current 90 A and the total electric charge 30 Ah. The substrates were heated to 290 °C during the process. TiN coatings were deposited in a self-built CVD device [13] at 700 °C with a constant gas mixture of 50 sccm N_2, 50 sccm NH_3 and 36.2 sccm $TiCl_4$ on alumina and 32.6 sccm $TiCl_4$ on zirconia for 60 min. The annealing was performed at 1200 °C and 1500 °C for 2 h in a graphite furnace in 1 bar static argon atmosphere.

Phase analyses of the coatings were conducted via X-ray diffraction (XRD) with a Bruker D8-Advanced in a Bragg-Brentano configuration and Cu-Kα radiation. Diffractograms were generated in a 2-θ configuration of 25 to 80° with an acceleration voltage of 40 kV and a heating current of 40 mA. Diffractograms were collected with a step size of 0.01° 2Θ and a dwell of 5 s per increment. During testing, the specimens were rotated to prevent texture influence. The diffractograms were subsequently evaluated using Diffrac.EVA 3.0 software and the JCPDS-PDF-2 database.

For microstructural and chemical analysis, all samples were cut and prepared in accordance with standard metallographic procedure and investigated under a Teskan MIRA 3 scanning electron microscope (SEM) in backscattered electron (BE) mode. Electron dispersive X-ray spectroscopy (EDS) measurements were performed by using an attached Oxford Instruments X-Max^N system. The acceleration voltage was set to 5 keV and the working distance to 15 mm. The measurement was calibrated using pure silicon standard material. EBSD measurements were taken using an attached Oxford Instruments NordlysNano system with 15 keV, a working distance of 17 mm and at a sample tilt of 70°.

3. Results

3.1. Overall phase analysis via X-ray diffraction of as-deposited and heat treated thin films

In its as-deposited state, the Ti coating has a hexagonal crystal structure on both alumina and zirconia substrates (Figs. 1 and 2). On both substrates, heat treatment at 1200 °C led to the formation of the cubic TiO phase. However, the TiO phase was indicated by several peaks in each orientation, corresponding to different lattice parameters ranging from 0.420 to 0.427 nm on alumina and 0.419 to 0.427 nm on zirconia. On both substrates, peaks at 44.1° and 50.0° were observed after annealing at 1200 °C but could not be identified. After the heat treatment of the Ti coated alumina at 1500 °C, the identified phase was still cubic TiO, but the observed effect of several peaks for each orientation was less pronounced. The Ti coating on zirconia delaminated after heat treatment at 1500 °C. Thus, only the tetragonal zirconia phase was observed via XRD.

The TiN coatings on both alumina and zirconia substrates had a preferred (200)-orientation in the as-deposited state (Figs. 3 and 4). This

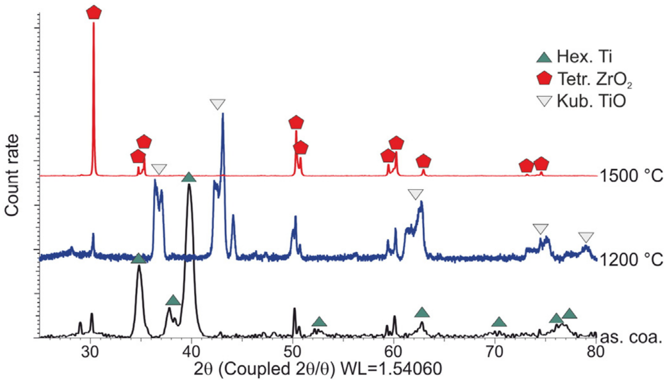

Fig. 2. Phase identification of Ti coating on ZrO_2 in as-deposited state and after heat treatment at 1200 °C and 1500 °C by means of X-ray diffraction.

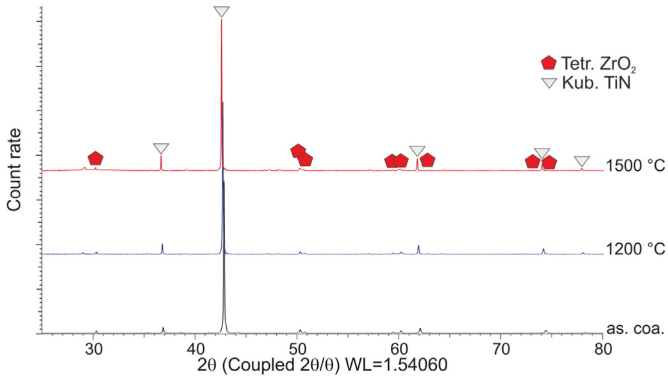

Fig. 4. Phase identification of TiN coating on ZrO_2 in as-deposited state and after heat treatment at 1200 °C and 1500 °C by means of X-ray diffraction.