



Influence of grain size and microstructure on oxidation rate and mechanism in sintered titanium carbide under high temperature and low oxygen partial pressure



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ARTICLE INFO

Article history:

Received 8 February 2016

Received in revised form 15 April 2016

Accepted 18 April 2016

Available online 28 April 2016

Keywords:

TiC
Oxidation
Surface marker
Microstructures
Grain size

ABSTRACT

Titanium carbide (TiC) pellets were prepared by Spark Plasma Sintering (SPS). Three different microstructures were synthesized with average grain sizes of 340 nm, 1.34 μm and 25 μm, respectively. Prior to oxidation treatment, TiC samples were implanted with xenon ions. This noble gas is used as a marker of the initial surface. Oxidation behavior was studied by Rutherford Backscattering Spectroscopy (RBS) and electronic microscopy through thermal treatment at 1000 °C for 10 h and under different low oxygen partial pressure (OPP). No detectable oxidation was observed after thermal treatment at $OPP \leq 2.10^{-7}$ mbar whereas an oxide layer is formed at $OPP = 2.10^{-6}$ mbar. Thickness, composition and morphology of the oxide layer depend on the initial microstructure of the material. Numerous grain boundaries and the porosity ($\approx 10\%$) of the nano-grained material were responsible for the enhanced penetration of oxygen which resulted in the formation of a thick oxide layer. This layer is composed of external oxide and interfacial band sublayers. Ti_4O_7 was identified by XRD (X-Ray Diffraction) as being the main phase in the oxide layer concerning the nano-grained material whereas a relatively thick layer of TiO_2 (rutile) is formed for larger grain microstructures. We proved the presence of carbon in the interfacial band as well as possible evacuation paths for CO/CO₂ gas. There is less release of xenon from nano-grained material than larger grained materials during oxidation at $OPP = 2.10^{-6}$ mbar for 20 h attesting to the superior gas-tightness of the oxide layer in this case. A schematic model is then proposed to explain growth mechanisms and properties of the oxide layer.

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1. Introduction

Transition metal carbides and nitrides have a real potential for use in many aggressive environments as they have both some physicochemical characteristics of ceramics and electronic properties of metals. Ceramic long term oxidation resistance is a key parameter for a large number of industrial applications and must be evaluated carefully under high temperature and in the presence of various oxygen partial pressures (OPPs). For example, the following ceramics have been studied as they may be used in future nuclear power reactors (fusion [1–3] or fission concepts [3–6]): titanium carbide (TiC), silicon carbide (SiC), zirconium carbide (ZrC),

zirconium nitride (ZrN) and titanium nitride (TiN). Some of these materials have also been investigated for use in PWRs (Pressurized Water Reactors) in order to enhance the tolerance to accidents and even more so since the station blackout events at the Fukushima Daiichi power plant in March 2011 [7–12]. Among these ceramics, TiC is studied because of its specific properties i.e. low cross-section for neutron absorption, high fusion temperature, high thermal conductivity and low damage to high ion irradiation doses [13–21]. Normal and especially accidental conditions in reactors can result in the exposure of core materials to oxidizing environments [12]. In the future generation of nuclear energy systems, known as Generation IV reactors, the coolant may contain oxidizing species [22] and the nominal operating temperature can reach 1000–1200 °C for some of the proposed concepts [1]. Several studies were therefore carried out on the oxidation of TiC material in various temperature and OPP conditions (see Table 1 [23–34]).

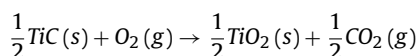
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Table 1
Summary of some important studies on TiC oxidation [23–34].

Microstructure	Temperature	Thermal treatment duration	Oxidizing atmosphere OPP	Oxide formed	Reference
Polycrystal	900 °C–1200 °C	1–30 h	Ar/O ₂ (950 mbar/5 mbar) Ar/O ₂ /H ₂ O (900 mbar/5 mbar/5 mbar)	TiO ₂ (R)	[23]
Single crystal	800 °C	8 h	Ar/O ₂ (999.82 mbar/0.18 mbar)	TiO ₂ (R)	[24]
Single crystal	800 °C	8 h	Ar/O ₂ (1999.73 mbar/0.27 mbar)	TiO ₂ (R)	[25]
Single crystal	800 °C	8 h	Ar/O ₂ (999.82 mbar/0.18 mbar)	TiO ₂ (R) TiC _x O _y	[26]
Polycrystal (Grain size ≈ 2 μm)	600 °C–1000 °C	6 h	Ar/O ₂ (1999.73 mbar/0.27 mbar)	TiO ₂ (R)	[27]
Single crystal	1500 °C	30 min	Ar/O ₂ (999.2 mbar/0.8 mbar)	Ti ₃ O ₅ + C and TiO ₂ (R)	[28]
TiC/Ti composite (5 wt.%–8 wt.% of TiC)	550 °C–600 °C	4 h	Air 1 bar	TiO ₂ (R)	[29]
TiC 93 vol.%–C 7 vol.% and TiC	400 °C–1000 °C	0–2 h	O ₂ 1 mbar < OPP < 650 mbar	TiO ₂ (A) and (R) TiC _x O _y	[30–32]
Polycrystal (Grain size ≈ 75 ± 10 μm)					
Stainless steel 304SS with 2 wt.% and 6 wt.% TiC	850 °C	96 h	Air 1 bar	TiO ₂	[33]
Polycrystal (Grain size ≈ 20 μm)	1500 °C	1 h	Air 10 ⁻⁶ mbar < OPP < 2.10 ⁻⁴ mbar	TiO ₂ (R) Ti ₃ O ₅ Ti ₂ O ₃	[34]
Polycrystal (Grain size ≈ 340 nm, 1.34 μm and 25 μm)	1000 °C	10 h	Degraded vacuum OPP ≤ 2.10 ⁻⁶ mbar	See results	Present study

Many oxides whose composition can be written Ti_xO_y (with $y/x \leq 2$) are potentially formed during the oxidation of TiC among which there are TiO, Ti₂O₃, Ti₃O₅, Magnéli phases (Ti_nO_{2n-1} with $4 \leq n < 10$) and TiO₂ (anatase or rutile), depending on the temperature and pressure conditions [35]. TiC and TiO are isomorphous compounds (lattice parameters: $a_{\text{TiO}} = 4.182 \text{ \AA}$ and $a_{\text{TiC}} = 4.328 \text{ \AA}$), so in an oxidation process, an intergrowth compound TiC-TiO is expected instead of pure TiO. To better understand the growth mechanisms of oxide on the TiC surface various models (linear, parabolic, logarithmic, etc.) have been used in the literature [23–33], and the following overall equation is often proposed to explain the formation of TiO₂:



However, many questions about the formation of intermediate phases, such as oxycarbides TiC_{1-x}O_y and unstable oxides still remain. The order in which the physico-chemical transformations and transitions occur during the oxidation is still not clearly understood as it could depend on many parameters such as the microstructure (porosity, grain size, etc) or the composition/stoichiometry of the carbide [32,34]. Recently, Shabalina et al. [30–32] proposed a multi-stage linear–parabolic model for the oxidation of TiC ($1.3 \text{ mbar} \leq \text{OPP} \leq 650 \text{ mbar}$ and $400 \text{ °C} \leq T \leq 1000 \text{ °C}$). The first stage is governed by a linear kinetics model connected to the formation of oxycarbide (also suggested by other authors [24–26]), and its subsequent decomposition into an oxide phase, in particular anatase, stabilized by residual carbon. The second stage follows a parabolic model associated with a solid state diffusion regime with oxygen diffusion through the oxide phase as the rate-determining process. The final linear stage would be due to the gasification of precipitated carbon. As indicated previously, each stage of this global kinetics model is likely to depend on various parameters and could thus result in oxide layers with particular properties, especially at low OPP because of the possible formation of many suboxides. The direct observation of the latter, and also residual carbon due to incomplete oxidation, is important to better understand the growth mechanisms and the properties of the oxide layer.

The oxidation resistance of 20 μm grain size sintered TiC under several OPPs was studied in previous work [34]. No sign of oxidation was detected on the surface of TiC after thermal treatment at 1500 °C for 1 h under a vacuum of 10⁻⁶ mbar (OPP ≈ 2.10⁻⁷ mbar). At higher oxygen pressure (OPP ≥ 2.10⁻⁵ mbar), oxidation of TiC was observed with the growth of scattered oxide islands on the surface. At OPP = 2.10⁻⁴ mbar, TiC surface was entirely covered with an oxide layer. This oxide, analyzed by X-ray diffraction (XRD), was mainly composed of a Ti₃O₅ phase also containing small quantities of Ti₂O₃ and TiO₂. The authors suggest that the protective effect of this oxide layer depends on its composition and also on the initial microstructure of the material.

The aim of the present work is to explore the growth mechanism and the properties of the oxide layer formed on a TiC surface under oxidizing conditions. Three different microstructures were obtained using spark plasma sintering (SPS). Sintered samples were then annealed at 1000 °C for several hours under low OPP. Prior to oxidation treatment, TiC pellets were implanted with a noble gas marker (xenon) to measure the distance of the range profile to the surface by Rutherford backscattering spectrometry (RBS). Xenon loss will also be measured by RBS to evaluate the gas-tightness of the material under oxidizing conditions.

2. Material and methods

2.1. Sintering cycles and resulting microstructures

The starting material is commercial TiC nanopowder (NanoStructured & Amorphous Materials Inc., USA) with a particle size of 40 nm and purity of 99% [36,37]. The main impurities of TiC are known to be oxygen and nitrogen [13]. The composition (major components) of the commercial powder was determined using elemental chemical analysis (see details in Ref. [37], powder Nano-2), and the following composition was found: TiC_{0.9}O_{0.23}N_{0.1}. SPS in vacuum (0.15 mbar) was used to obtain sintered bodies, and different cycles (Table 2) were implemented to obtain three distinct microstructures that will hereafter be called M1, M2 and M3. After sintering, the carbon content was found to be comparable

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