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Oxidation of titanium carbide–graphite hetero-modulus ceramics with low carbon content

II. Physico-chemical interpretation of the ridge effect

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Abstract

Hetero-modulus ceramics (HMC) present the combination of a ceramic matrix with the inclusions of a dispersed phase with considerably lower Young's modulus, resulting in a material with significantly improved properties. An interpretation of the so-called "ridge effect" observed during the isobaric-isothermal oxidation of 93 vol% TiC–7 vol% C (graphite) HMC at temperatures of 400–1000 °C and oxygen pressures of 0.13–65 kPa is given. Established in Part I of this study, the meanings of a ridge temperature and ridge oxygen pressure, which are served as boundaries between prevailing oxidation mechanisms in phenomenological kinetics model, are considered on the basis of X-ray diffraction (XRD) and microscopy analyses. The oxidation mechanisms, essentially different within the studied ranges of temperatures and oxygen pressures are identified according to the developed general model. These results can be used for the preparation of special protective coatings on the surface of refractory carbide–carbon HMC parts applied in severe environments, e.g. chemically active, high-enthalpy gaseous flows.

Keywords: Composites; Chemical properties; Carbides; Carbon; Hetero-modulus ceramics; TiC

1. Introduction

Hetero-modulus ceramic–ceramic composite materials (HMC) present the combination of ceramic matrix having a high-Young's modulus (300–600 GPa) with inclusions of a dispersed phase with significantly lower values (15–20 GPa), such as sp^2-structured graphite and graphite-like hexagonal boron nitride.[1–8] Typical representatives of this sub-class of ceramics are compositions of group 4 transition-metal refractory carbides with excessive carbon,[3,7,8] present in a variety of micro- and nanostructures. In addition to the excellent thermal shock resistance and remarkable machinability inherent to all kinds of HMC, this group of ultra-high-temperature ceramics has another significant advantage: during oxidation at elevated temperatures, the refractory carbides form high-melting scales, which (at least theoretically) could protect the material from further corrosion damage. Carbon–carbon composites (CCC), currently widely used in aerospace engineering as thermal protection for aerodynamically heated surfaces and critical cross-sections of nozzles for rocket engines, demonstrate low gas-corrosion resistance at higher temperatures, so this type of composites needs to be coated with special materials, although this is frequently impractical due to weak adhesion with the substrate.

If the scales formed on HMC possess protective properties and prevent corrosion propagation, the chemical stability of carbide–carbon HMC in active gaseous and melt media will become significantly higher than those for CCC. The advanced physical properties inherent to ceramic matrices, along with high gas-corrosion resistance, provide a good justification for replacement of such carbon composites with HMC. Nevertheless, in spite of the fact that oxide phases individually have good physico-mechanical properties as well as excellent chemical stability in oxidative atmospheres, the oxide scales resulting from the interaction between carbide and oxygen often do not effectively inhibit the oxidation process of the bulk material and provide the corrosion resistant properties that are so desirable. This situation increase the importance of studies devoted to the oxidation processes in the carbide–carbon HMC with different compositions and carbon content. During the comprehensive phenomenological kinetics analysis of the oxidation process for 93 vol% TiC–7 vol% C (graphite) HMC, carried out in Part I

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of this work[8] at temperatures of 500–1000 °C and oxygen pressures of 0.13–65 kPa, it was revealed that the behaviour of this material, described using a linear–paralinear model, is unusual, as there was no steady increase of oxidation rate from the lowest temperatures and pressures to the highest ones. However, within the range of studied oxidation temperatures and pressures, there was a clearly defined maximum interaction between solid and gas, which corresponds to critical values of the oxidation parameters. These critical, so-called "ridge" temperatures and pressures mark a change in the prevailing oxidation mechanism; while traversing these features, the values of apparent activation energies Q and orders of reaction m change their signs. This formalism clearly defines regions in parameter space with alternating values (negative and positive) of Q and m, modeling a rather unique phenomenon in solid-state chemistry.

The main aim of Part II of this work is to offer an explanation for this unusual behaviour, revealed while modeling the oxidation kinetics of 93 vol% TiC–7 vol% C (graphite) HMC, by means of an exploration of the physico-chemical transformations and phase transitions associated with this process. There have been few works on the oxidation of HMC containing TiC,[3,9,10] which mainly deal with the comparative evaluation of corrosion resistance for the materials without thorough consideration of the phases generated as reaction products, over the range of temperatures and pressures studied. In spite of the fact that transition-metal carbide phases in HMC possess a specific character[7] and differ from hypostoichiometric MeC_{1-x}, conventionally used in various studies on oxidation, it was impossible to ignore the results obtained from experiments on single-phase samples of TiC, reported by several authors, including recent complex research on oxidation of refractory carbides published by Shimada et al.[11–15] and Gozzi et al.[16,17] The most relevant data available in the literature on physico-chemical analysis of the oxidised materials based on TiC are collected in Table 1. A closer examination of these data shows that, even for the oxidation of individual carbide phases, there are few recognizable details of the underlying reaction mechanism: the formation of non-stoichiometric phases of oxycarbide TiC_xO_y and the presence of two modifications to the TiO_2 structure in the oxidation products with the anatase phase being observed at lower temperatures than the rutile. At the same time many details of the TiC oxidation process, which are connected in particular with carbide–oxide transformation and phase transitions in formed TiO_2, have not been well understood. The results of a number of published works not only differ markedly from those obtained in similar studies, but also have contradictory conclusions: for example, Voitovich and Pugach[24] attribute mutually exclusive effects to deposited carbon, proposing it promotes sintering of oxide scale and stabilises anatase simultaneously.

As a result, being a corollary to the main aim of study, an effort has been made to address the key issues associated with the oxidation of individual carbide phases such as a scheme for the carbide to oxide transformation, the temperature and oxygen pressure ranges of these transformations, also associated with the anatase to rutile transition, and the influence of carbon on these physico-chemical processes. Although the latter problem in the case of the oxidation of HMC is more complicated as an oxidised material can contain two different sources of carbon: "primary" carbon, this being the inclusions of graphite initially introduced as an ingredient of the composite, and "secondary" carbon, which is obtained as a reaction product, during the unique transformation of the oxidised carbide phase.

2. Experimental

The comprehensive details of the physico-chemical characteristics for the studied 93 vol% TiC–7 vol% C HMC (chemical and phase analysis, physical parameters for the components) as well as the full description of employed manufacturing method with a microphotograph of its structure were provided in the previous papers presented to this journal.[7,8] The details of the preparation of HMC samples, exposed to oxygen under different environmental conditions, are described in Part I of this study,[8] including the cutting-off scheme for the hot-pressed ceramic composite blank.

The samples, oxidised at temperatures of 500–1000 °C and oxygen pressures of 0.13–65 kPa, were investigated by the means of X-ray diffraction (XRD), optical and scanning electron microscopy (SEM) analyses as well as microanalysis by electron probe (EMPA) and energy-dispersive X-ray spectroscopy (EDX). The compositions of the sample scales were identified by XRD phase analysis, and the lattice parameters of these phases were measured by means of XRD structural analysis employing a diffractometer DRON-3.0 unit (Bourevestnik, Russia) with filtered Cu K_α radiation. Different cross-sections and surfaces of scale microstructures were investigated by different methods of optical microscopy in an Epitype-2 (Carl Zeiss Jena, Germany) using micro-photo equipment MFN-12 (LOMO, Russia), by SEM and EDX in a Philips XL30 with an embedded EDAX quantitative energy-dispersive spectrometer DX-4i. SEM images were obtained at accelerating voltage $U = 12–25$ kV, employing both secondary electron and back-scattered electron detectors. EMPA was carried out in a MS-46 analyser (Camebax, France).

3. Results and discussion

3.1. Physico-chemical transformations

The evolution of weight gain for the TiC–C HMC samples during the oxidation process, analysed in details in Part I of this work,[8] was accompanied with a change of the chemical composition of the surface layers of the samples. The XRD patterns taken from the surface of the samples, oxidised at lower and higher temperatures, respectively, are shown in Figs. 1 and 2.

No XRD peaks corresponding to the newly formed phases were found on the surface of the oxidised sample for values of weight gain per unit of surface area, $w < 8\ \mathrm{mg\,cm^{-2}}$ (Fig. 1b). However, for all samples oxidised under different conditions, the lattice parameter of the carbide phase changed slightly; for example, at the temperature of 500 °C and oxygen pressure of 1.3 kPa, the lattice parameter reduced from the initial 0.4326 ± 0.0001 to 0.429 ± 0.002 nm. This decrease of lattice