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Novel insight into the chemical analysis of light elements in oxycarbides

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ABSTRACT

Pure powders of $TiC_xO_{(1-x)}$ solid solution were synthesized through the carbothermal route. The chemical analysis of the light elements in the as-obtained $TiC_xO_{(1-x)}$ oxycarbides powders were performed by Instrumented Gas Analysis (IGA). The cell parameters of the samples were determined with an accuracy of about 2% by means of X-ray powder diffraction and the internal standard method. As a result, a model correlating the cell parameters to the chemical composition was established. These reference $TiC_xO_{(1-x)}$ oxycarbides powders were then sintered in order to obtain pellets of dense ceramics. After having determined that the sintering process does not change the chemical composition of the starting powder, chemical analysis of the different samples of the solid solution were successfully undertaken by Ion Beam Analysis techniques (IBA). The Nuclear Reaction Analysis (NRA) method - that was used to analyse light elements with very high sensitivity - was coupled with Rutherford Back Scattering (RBS) analysis in order to accurately determine the metallic over light elements ratio and to determine the stoichiometry of the phase on massive samples. Exhaustive simulations of the NRA spectra were performed and demonstrated that discrete compositions of the $TiC_xO_{(1-x)}$ can be efficiently measured locally for bulk samples. Compared to IGA results, the relative amounts of carbon and oxygen of bulk materials were determined with a bias lower than 5%. This protocol being implemented for the $TiC_xO_{(1-x)}$ system was then tested on $HfC_xO_{(1-x)}$with the same success.

1. Introduction

The quantitative analysis of light elements remains one of the ongoing issues in the field of ceramic materials. As an example, this topic is commonly a pending issue for searchers working in the field of carbide based ceramics as carbo-nitrides (MC_xN_y: M = Si, Ti, Zr, Hf …) or oxycarbides (MC_xO_y) for which macroscopical properties depend strongly on their respective amounts of light elements [1]. In the present paper, we report and compare different investigation techniques aiming at characterizing directly or indirectly the chemical composition of both powders and bulk samples of MC_xO_y oxycarbides compounds.

The oxycarbide is a frequently encountered compound. Indeed, as the most used route to elaborate carbides, the carbothermal reduction reaction which consists in the progressive reduction of dioxides with carbon generally leads to an oxycarbide final product [2–4] whose composition is largely dependent on the synthesis conditions. Besides, these ultrarefractory carbides are ideally suited for ultra-high temperature applications [5], thanks to their favorable properties: high hardness, good wear resistance and high decomposition temperature [6]. These properties allow them to be used for example as barriers retaining the fission products in nuclear reactors [7], or as wear-resistant coatings [8]. However, the application field of zirconium carbide is limited under air due to its low oxidation resistance [9]. As a consequence, they are progressively transformed into oxycarbides during their use through carbon-oxygen substitution [10–12]. Therefore, the accurate quantification of light elements (C and O) in heavier matrices is a topic of significant interest in order to define the actual stoichiometry of the studied oxycarbides and to connect these

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compositions to their expected properties.

The analysis of oxycarbides meets two different kinds of issues depending on whether the sample is a powder or a bulk-type ceramics. When assuming homogeneous samples, powders are generally characterized by coupling X-ray powder diffraction (XRD) and X-Ray Fluorescence (XRF) or Instrumented Gas Analysis (IGA), which provide information averaged over macroscopic sample volumes only. This is for example the case with commercial powders that are mostly considered as homogeneous starting raw materials. The case of bulk type carbide ceramics is, however, more complicated. The high hardness of bulk type carbide materials makes complicated their quantitative analysis because the crushing of ceramics can lead to the incorporation of some impurities. In addition these samples are most often encountered under the form of composite materials and in this case, the global techniques of chemical analysis by IGA or XRF are no longer valid as they will solely provide an average analysis of the sample. For these reasons, numerous fields of research on ceramics could, however, take advantage of analytical methods allowing to perform accurate quantitative analysis of light element at local scale (micrometer to nanometer scale). In this paper, the Nuclear Reaction Analysis (NRA) method was used on bulk type oxycarbides to locally analyse light elements such as carbon and oxygen with very high sensitivity in transition metal oxycarbides of the IVb-group. NRA was associated with Rutherford Back Scattering (RBS) analysis which gives the ratio of metallic over light elements and makes it possible to determine the phase stoichiometry with good accuracy.

Concerning the choice of the chemical system, the focus was set on TiO_2-C. Indeed, the stability domain of the TiC_xO_y solid solution has already been investigated in the literature and it has been shown that the solid solution was complete between TiC and TiO [13,14], giving rise to a wide compositional range of TiC_xO_y compounds. This chemical system was also retained because some of the authors of this publication share a long standing experience in synthesis and characterization of these compounds [3,15,16]. In the present study, the synthesis of the starting powders was achieved through the carbothermal reduction of TiO_2 by carbon black [3]. After having controlled the phase and purity of each synthesized powder sample by XRD and Transmission Electron Microscopy (TEM) and their chemical composition by Instrumented Gas Analysis (IGA) with an accuracy of a few atomic percent, the high purity powders obtained were considered as reference materials to test the accuracy of the Ion Beam Analysis techniques (IBA) on bulk samples that were obtained from the powders.

The first part of this paper is devoted to the establishment of a model that can be further on used by the readers to correlate the evolution of the cell parameter of the solid solution with the oxygen and carbon content. In this part, a special attention has been paid to accurately determine the cell parameters by minimizing systematic errors related to X-ray powder diffraction measurements. In the past, several models linking the oxycarbide cell parameter with its chemical composition had already been proposed in the literature [13,14,17]. However, none of these works used an internal standard to correct for sample positioning errors, which results in large uncertainties in the measurement of the cell parameters. In addition, in none of these previous works the targeted compositions were checked by elemental analysis, so that the mentioned compositions are not fully reliable.

The second part of the paper deals with the local analysis of bulk ceramic materials by IBA. In this work, bulk oxycarbides sintered by Spark Plasma Sintering (SPS) from well controlled powders are used as references in order to evaluate IBA capabilities for light elements quantification in ceramics. The expected results were first simulated and discussed and the obtained results were then compared to those obtained by IGA on powder samples.

The methodology was first implemented on TiC_xO_y and was further on applied to an HfC_xO_y sample.

2. Synthesis of powders and SPS sintering of bulk samples

2.1. Synthesis and characterization of powders

The synthesis protocol of powders was described in a previous paper [3]. Summarily, TiO_2 powder (99.9% wt.%, Anatase, Alfa Aesar) and carbon black (Prolabo, France, ashes < 0.75% wt.%) were weighted to the desired final composition of oxycarbide according to the global reaction:

$$TiO_{2(s)} + (1+2x)\,C_{(s)} \rightleftarrows TiC_xO_{1-x(s)} + (1+x)\,CO_{(g)} \tag{1}$$

The theoretical targeted compositions were calculated assuming that the sum of the C/Ti and O/Ti ratios is equal to 1. In such a condition the amount of possible vacancies is neglected and in the following the general formulae of the oxycarbide will be written as $TiC_xO_{(1\text{-}x)}$. Eight different samples with theoretical formulae were synthesized (Table 1) and two sets of samples were performed: one at 1500 °C and the other at 1600 °C. The initial powders of carbon black and titanium dioxide were mixed in various proportions using a low speed planetary ball mill (Pulverisette 7, Fritsch, Germany). The blending sequence was composed of 5 pulses of 1 min at 200 rpm interrupted by pauses of 5 min to avoid heating up the materials. Each mixture was then treated for 4 h in a graphite furnace (V.A.S. furnace, Suresnes, France) under flowing argon (grade U, Air Products and Chemicals Inc., Allentown, USA - 30 $L\,h^{-1}$). The heating rate was fixed at 20 $°C.min^{-1}$ up to the targeted temperatures (1500 °C or 1600 °C). The sample was then maintained 4 h in temperature in order to reach the maximal extent of the reaction ($\xi = 1$) as previously defined in Ref. [3]. Oxygen richest compositions were more difficult to obtain as pure powders so that $TiC_{0.40}O_{0.60}$, $TiC_{0.30}O_{0.70}$ and $TiC_{0.20}O_{0.80}$ samples required two complete runs of heating treatment as specified in Table 1 in order to reach the maximal advancement of the reaction ($\xi = 1$). Between heating treatments, the powders were homogenized by crushing in an agate mortar.

Finally and as an extension of this study, powder samples of $HfC_{0.85}O_{0.15}$ were synthesized (Table 1) to elaborate bulk ceramics to check the methodology implemented on $TiC_xO_{(1\text{-}x)}$. In a second step, this system will allow to test the relevance of the IBA technique for quantitative analysis of light elements in other oxycarbides showing contrasted Z values.

2.2. Shaping of pellet-type bulk materials and comparison with powders

With regards to their high melting point and their related low self-diffusion, the complete densification of carbides powders requires extremely high sintering temperature [18]. In such conditions, high relative densities of samples are usually obtained by using pressure-assisted sintering methods (Hot Isostatic Pressing or Hot Pressing). Fully dense samples are then obtained at very high temperature and/or by using sintering aids such as metallic elements [19]. As a consequence of the high temperature used, the microstructures of the samples so obtained are generally coarse and contain noticeable residual porosity. In this context, the Spark Plasma Sintering (SPS) represents one possible way to densify ceramic materials, keeping fine microstructures (i.e. microsized) without sintering additives even for poorly sinterable compounds [20,21]. According to the SPS procedure, the raw powders are firstly put into a graphite die before being uniaxially pressed while a D.C. pulse voltage is applied to the compact. In the case of electrically