Advantages of combined μ -XRF and μ -XRD for phase characterization of Ti–B–C ceramics compared with conventional X-ray diffraction

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Received: 31 October 2007 / Revised: 19 March 2008 / Accepted: 25 March 2008 / Published online: 6 May 2008
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Abstract Design and processing of new materials with improved high-temperature properties is one of the most challenging tasks of modern engineering. Among such materials, nonoxidic ceramics hold an important place. When optimizing the synthesis conditions of these new materials in an largely empirical manner, the use of analytical methods that can fully document the resulting phase compositions is of great importance. In this paper, we demonstrate the advantages of using combined microbeam X-ray diffraction and X-ray fluorescence over conventional X-ray diffraction as the characterization method in the specific case of Ti–B–C ceramics. Ceramic samples were synthesized by the pulse plasma method starting from high-purity powders of titanium, boron, graphite, and nickel. Different mixtures were heated in a pulsed fashion and sintered by combustion synthesis at various temperatures and time durations, as is the case during empirical optimization of a synthesis procedure. Conventional X-ray diffraction showed the presence of two phases at the end of the sintering process, TiB_2 and TiC , irrespective of the conditions employed. Scanning μ -XRF/ μ -XRD on the other

hand allowed one to detect and visualize the distribution of additional phases present in the sintering products, during which a dependence on sintering conditions was apparent. The μ -XRD results showed that three phases (TiB_2 , TiC , and TiB) instead of two were present in samples sintered during a short time interval. The addition of metallic Ni to the initial mixture as a sintering facilitator resulted in the formation of a Ni_3B phase. All phases proved to have strongly heterogeneous distributions above the 15- μm level with the presence of TiB_2 anticorrelated to that of TiC and TiB , emphasizing the necessity of the use of laterally resolved methods of characterization.

Keywords X-ray diffraction (XRD) · X-ray fluorescence (XRF) · Synchrotron radiation · Ceramics · Pulse plasma sintering · Boron · Titanium

Introduction

Owing to their high melting point, hardness, high corrosion resistance, good thermal shock resistance, and high-temperature stability, titanium diboride-based and titanium carbide-based materials are promising candidate materials for manufacture of cutting tools, wearproof parts, and armored vehicles [1]. These properties and their light weight make them also attractive for use in aircraft propulsion systems and space vehicle thermal protection materials [2]. In addition, because of their high electrical conductivity, they can be used as materials for new types of electrodes [3].

Conventional synthesis and fabrication methods of titanium-based ceramics involve the use of costly procedures with unavoidable high energy consumption. Since its development the technique of combustion synthesis [4] has

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proved to be an efficient and energy-saving method for obtaining some high melting point materials, see for instance [5–8]. The principle of this technique is that the initial reagents, when ignited, spontaneously transform into products due to the exothermic nature of reaction. The major advantages of this technique are the very high reaction rates and the elimination of the need for high-temperature furnaces as used in conventional material fabrication due to self-generation of energy. An essential disadvantage of the materials produced by the combustion synthesis is their high porosity; however, this can be obviated when the material being synthesized is simultaneously loaded and thereby consolidated by utilizing the pulse plasma sintering (PPS) method [9]. Additionally in the PPS method the reaction is initiated by high-current electric pulses applied during the process. Under these conditions, the synthesis and sintering of the powder proceed in a specific way, namely by the release of a few kilojoules of energy during a period of several hundred microseconds. This technique of heating combined with an external pressure exerted upon the powder mixture permits the synthesis ignition temperature to be achieved within the entire powder volume in a very short time [10].

By utilizing the pulse plasma sintering method in combination with combustion synthesis, it is possible to produce ceramic composites from a mixture of titanium, boron, graphite, and nickel powders. The optimization of this method of synthesis largely takes place in an empirical fashion. Conventionally, bulk X-ray diffractometry is employed to determine the phase composition of the sintered materials and guide the optimization procedure. However, a more-detailed documentation of the composition and heterogeneity of the synthesized and sintered ceramics at the microscale may be important in order to further optimize the fabrication process with the aim of eventual industrial implementation. In order to visualize the distribution of some of the elemental components of the ceramic together with the distribution of the corresponding crystal phases, measurements were carried out by means of a high-energy ($E=21.44$ keV) microbeam of 15- μm diameter that was scanned over $1\times1\times0.5\text{-mm}^3$ -sized samples of sintered ceramic. While in transmission, two-dimensional Debye–Scherrer patterns were recorded, whereas in reflection, the spectrum of X-ray fluorescence radiation emitted from the sample surface was simultaneously collected.

Experimental

Material preparation

Ceramic samples were synthesized starting from high-purity, commercially available powders of titanium, amor-

phous boron, graphite, and nickel, manually mixed in a mortar. Nickel was chosen as a metallic sintering additive; it is commonly used to reduce the sintering temperature of Ti–B–C ceramics. The composition of the mixture was selected so as to suit the reaction:

- (a) $3\text{Ti} + 4\text{B} + \text{C} \rightarrow 2\text{TiB}_2 + \text{TiC}$
(in the case of samples T1, T2, and T3)
- (b) $3\text{Ti} + 4\text{B} + \text{C} + 5 \text{ vol\% Ni} \rightarrow 2\text{TiB}_2 + \text{TiC} + 5 \text{ vol\% Ni}$
(in the case of sample TNi)

The Ni powder is considered to function as a relatively soft adhesive phase, improving the adherence between the much harder TiB_2 and TiC grains.

The mixtures were heated in a pulsed fashion and sintered by combustion synthesis at different temperatures and heating and dwell times, as detailed in Table 1.

Characterization

Conventional X-ray powder diffraction patterns of the sintered materials were obtained with a Philips PW 1140 X-ray diffractometer equipped with a PW 1050 goniometer using $\text{Co} - \text{K}\alpha_1$ radiation ($\lambda=1.78897$ Å). At this relatively low energy, XRD measurements were performed in reflection geometry. The X-ray tube was operated at 35 kV and 35 mA. During the 2θ scans, an angular increment of 0.02° and dwell time of 3 s per angle were employed.

Beamline L of the HASYLAB synchrotron laboratory (Hamburg, Germany) was used for the microbeam investigations. A quasimonochromatic X-ray microbeam of 15- μm diameter, produced by means of Mo/Si 1:1 multilayer monochromator and focused with a single-bounce elliptical capillary [11], was used to perform a combined scanning $\mu\text{-XRF}/\mu\text{-XRD}$ experiment on the sintered materials. A Bruker 1000 CCD camera positioned in transmission geometry and a silicon drift chamber detector (SDD) at 90° to the primary beam allowed simultaneous collection of diffractograms and XRF spectra while the sample was mounted on a motorized xyz -stage for scanning.

The frames collected containing diffraction rings were processed using the XRDUA program [12]: XRD peaks were identified by matching them to JCPDS-ICDD data cards.

Table 1 Process parameters of the synthesis of the TiB_2/TiC composites

Sample	Initial powder	Sintering parameters		
		t_{heating} (min)	t_{dwell} (min)	T ($^\circ\text{C}$)
T1	Ti/B/C	5	0	800
T2	Ti/B/C	20	20	1450
T3	Ti/B/C	20	20	1350
TNi	Ti/B/C/Ni	20	10	1150

During the conventional XRD and μ -XRD experiments, the samples were exposed to the beam in the form of $1 \times 1 \times 0.5\text{-mm}^3$ blocks of sintered material. The relative high energy employed during the synchrotron experiment allows one (a) to penetrate the strongly absorbing and relatively thick ceramic specimen and (b) to capture a larger number of Debye–Scherrer rings by the CCD camera positioned at a distance of ca. 15 cm behind the sample while not having negative implications on the angular resolution of the resulting 2θ patterns.

Results and discussion

Since different process parameters and a different initial composition were used, it was expected that the samples T1, T2, T3, and TNi would show a different phase composition; more specifically that the composites might contain additional compounds such as TiB, Ti_3B_4 or Ni, Ni_3Ti , Ni_3B in the case of the nickel-containing sample. However, as is shown in Fig. 1a, the X-ray diffraction results obtained by means of a conventional X-ray diffractometer indicated that only two phases were present: TiB_2 and TiC. Furthermore, no significant difference between the XRD profiles obtained from samples sintered under different conditions was observed; also between sample TNi on the one hand and samples T1, T2, and T3 on the other hand, no such difference was discernable.

On the other hand, even though the 2θ resolution of the CCD-based μ -XRD setup at HASYLAB is significantly lower than that of the conventional X-ray diffractometer, the μ -XRD results showed a clear difference between sample T1 and T2/T3. In sample T1 three phases, i.e., TiB_2 , TiC, and TiB were found, whereas in T2 and T3 only TiB_2 and TiC were found to be present. In order to investigate the occurrence of the additional TiB phase more in detail, an area of $120 \times 200 \mu\text{m}^2$ was scanned with $15\text{-}\mu\text{m}$ steps in each direction and a diffraction pattern recorded at each position. The resulting distribution of the integrated reflex intensities of TiB_2 , TiC, and TiB is shown in Fig. 1b. Some heterogeneity can be observed in the microstructure of the incompletely reacted composites: while the TiC and TiB_2 phases show a complementary distribution, to some extent the TiB phase appears to be spatially correlated with that of TiC. Also in phase maps obtained from other samples, an identical spatial complementarity between TiB_2 on the one hand and TiC (and TiB) on the other hand is observed.

In the two samples sintered for 20 min (T2 and T3), the μ -XRD results only revealed the presence of two phases, i.e., TiB_2 and TiC, indicating that in the T1 sample the TiB phase is present as an intermediate constituent. On the basis of Rietveld refinement calculations, which in this case are only approximate in nature, we estimate the average TiB weight percentage in the scanned area to be around 3%. It should be noted that this value is an estimate only since no complete powder rings for this phase are visible in the X-

Fig. 1 **a** XRD profiles of ceramic composites obtained from the Philips PW 1140 diffractometer by means of primary $\text{CoK}_{\alpha 1}$ radiation. ICDD peak positions for TiB_2 and TiC are shown as vertical lines. **b**

μ -XRD patterns and phase maps of the incompletely reacted TiB_2/TiC composite (T1) obtained from the Beamline L of the HASYLAB synchrotron laboratory

ray diffraction images. This low average abundance ratio may be the principal reason why the TiB phase is not visible by means of conventional XRD equipment, featuring relative detection limits at the 5% level.

A diffraction image of sample TNi in a location showing a high Ni – K_{α} X-ray fluorescence signal is shown in Fig. 2a. This pattern differs from the data derived from other samples in that it contains clear indications of the presence of an additional phase. The presence of extra diffraction peaks at 1.73, 1.86, 1.96, and 2.36 Å, together with the correlation of the intensity of this phase with that of the Ni- K_{α} fluorescence, leads us to the identification of Ni_3B as the extra phase (Fig. 2c).

To some extent, a spatial correlation can be observed between the Ni – K_{α} μ -XRF map (representing the

distribution of Ni near the surface of the sample) and the phase map of the Ni_3B phase, representing the projected distribution of this phase throughout the scanned area (Fig. 2b). Since both signals do not sample exactly the same specimen volume, a number of differences between both distributions can be observed.

Conclusions

By making use of a scanning μ -XRF/ μ -XRD combination, it was possible to detect and visualize the distribution of additional phases present in Ti/B/C sintering products. It could be observed that a powder mixture of Ti/B/C was not completely transformed to TiB_2 /TiC composite when

Fig. 2 **a** Diffraction image of sample TNi (arrows indicate reflections associated with the Ni-bearing phase at $d=2.36$ Å, 1.96 Å, 1.86 Å and 1.73 Å); **b** μ -XRD map of Ni_3B phase (summed intensity of (121),

(122), and (221) reflections) and Ni – K_{α} μ -XRF intensity map; **c** corresponding diffractogram showing diffraction peaks of the Ni_3B phase

sintered at 800 °C for only 5 min. An intermediate TiB phase, spatially correlated with TiC, was identified in the sample. This phase is no longer present when the sintering process is conducted during a longer time such as 20 min. When Ni powder is added to the reaction mixture, a new phase, i.e., Ni₃B, is formed.

It can be concluded that the use of synchrotron radiation-based scanning by μ -XRD allows one to obtain more-detailed information about the intermediate and final products of the sintering process as a function of its operational parameters and therefore that it is a more powerful way of analyzing the reaction products that will permit a more effective optimization of the fabrication process. A disadvantage of the use of synchrotron-based μ -XRF/ μ -XRD is the requirement to produce test materials separate in time and place from the analytical measurement without the possibility of direct online optimization of the production process.

Thus, in further work, the possibility of performing the sintering step online, i.e., during the synchrotron experiment, will be considered.

Acknowledgements This research was supported by the Interuniversity Attraction Poles Programme - Belgian Science Policy (IUAP VI/16). The text also presents results of GOA “Atom” (Research Fund

University of Antwerp, Belgium) and of FWO (Brussels, Belgium) projects no. G.0177.03, G.0103.04 and G.0689.06.

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