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Microstructure evolution during phase separation in Ti-Zr-C

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ABSTRACT

(Ti,Zr)C powder was synthesized by carbothermal reduction and subsequently aged at 1150–2000 °C. The phase composition and microstructure was investigated using X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, and electron backscatter diffraction. It was found that the as-synthesized (Ti,Zr)C particles have a concentration gradient with a higher concentration of Ti at the surface of the particles. Furthermore, during aging the (Ti,Zr)C decomposes into Ti-rich and Zr-rich lamellae. During aging at 1400 and 1800 °C for 10 h, most Zr-rich and Ti-rich domains precipitate at grain boundaries, inheriting the crystal orientation of the parent grain behind the growth front. When the precipitate grows into another (Ti,Zr)C grain, that grain adopts the same crystal orientation as the parent grain. The crystallographic misorientation between adjacent lamellae is 0–5°. Based on these microstructural observations it is hypothesized that the mechanism of decomposition is discontinuous precipitation.

1. Introduction

Miscibility gaps are found in many ternary transition metal carbide systems such as (Ti,Hf)C, (Ti,Nb)C and (Ti,Zr)C [1,2]. Many of these carbides have been reported to be harder than their corresponding binary carbides and phase separation has been suggested to contribute to the enhanced hardness [2]. There are several possible applications for these carbides within the field of hard material tools for metal cutting, for instance, as the second hard phase alongside WC in cemented carbides, as the hard phase in cermets or in wear-resistant coatings. Phase separation is today favorably utilized in the work-horse coating (Ti,Al)N within the machining industry, which decomposes into TiN and AlN nano-sized domains, at temperatures close to the service temperature, thus enhancing the hardness and wear resistance of the coating [3,4].

Phase separation in (Ti,Zr)C alloys has recently been investigated by different research groups [5–9]. Borgh et al. [5,6] synthesized near-single phase (Ti,Zr)C at 2200 °C using traditional powder metallurgical methods. The (Ti,Zr)C decomposed into Ti-rich and Zr-rich carbide lamellae upon aging at 1300 °C. As a continuation of the work by Borgh et al., Ma et al. [7] performed nanoindentation measurements on both as-synthesized and aged (Ti,Zr)C. It was found that the materials in both conditions were super hard. Li et al. [8] synthesized a single phase $Ti_{0.9}Zr_{0.1}C$ alloy by spark plasma sintering at 2100 °C, which decomposed into a $Ti_{0.97}Zr_{0.03}C$ matrix and $Ti_{0.06}Zr_{0.94}C$ nodules upon aging at 1300 °C. These authors reported an increase of both the hardness and fracture toughness due to the nodular structure. Thereafter, Li et al. [9] performed a systematic study on the phase separation in a series of alloys during aging at temperatures between 1200 and 2000 °C for 1 h. Alloys in the range $Ti_{0.9}Zr_{0.1}C$ to $Ti_{0.3}Zr_{0.7}C$ were found to decompose and the maximum hardness and fracture toughness were found for the $Ti_{0.8}Zr_{0.2}C$ alloy aged at 1600 °C for 1 h.

The mechanism of phase separation in the (Ti,Zr)C system and its dependence on temperature, composition etc. have not been comprehensively discussed in the literature, but hypotheses can be found. Knotek and Barimani [10] attributed the Ti-rich and Zr-rich nano-particles formed in magnetron-sputtered (Ti,Zr)C films to spinodal decomposition. Xu et al. [11] investigated the decomposition of $(Ti_{0.4}Zr_{0.4}W_{0.2})C$ sintered with WC and Co, and they also suggested a spinodal mechanism due to the existence of side bands in the X-ray diffraction (XRD) pattern. Borgh et al. [6] argued that the rather large coherency strain between Ti-rich and Zr-rich carbide lamellae would suppress the coherent miscibility gap to low temperatures and thus stabilize the mixed (Ti,Zr)C. However, they discussed the possibility that the existence of imperfections could relax the coherency strains and thus enable phase separation, in line with the theory of spinodal decomposition suggested by Cahn [12].

The purpose of the present work is to carry out a careful investigation of the microstructure evolution during phase separation in (Ti,Zr)C, as an extension of the work by Borgh et al. [6] and Ma et al. [7]. The (Ti,Zr)C was synthesized by carbothermal reduction of a

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mixed oxide powder and the effect of temperature on decomposition is considered by aging at temperatures between 1150 and 2000 °C. The phases present are characterized by X-ray diffraction (XRD). The microstructure is investigated using a scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) and electron backscatter diffraction (EBSD).

2. Experimental procedures

In order to synthesize (Ti,Zr)C, a carbothermal reduction at 2200 °C for 2 h was performed, using a $TiZrO_4$ spherical nano-powder (30–100 nm in diameter) and carbon black powder as starting material (details of the synthesis have been provided in previous work [6]).

Different samples are prepared to study phase separation, by performing aging treatments at 1150, 1400, 1600, 1800 and 2000 °C with different durations. The aging was performed in different furnaces always using graphite crucibles with a slight overpressure of inert Ar gas. Different cooling methods were applied depending on the type of furnace and temperature used, see Table 1 for a compilation of the conditions used in the aging treatments.

To characterize the phases present, XRD was performed with a powder diffractometer (Panalytical X'Pert alpha 1) using pure Cu-$K_{\alpha 1}$ radiation produced by a focusing Johansson Ge monochromator. The tube voltage and current were set to 45 kV and 40 mA, respectively. The 2-theta scan range used was 28 to 65°, which includes the first three diffraction peaks, i.e. the 111, 200, and 220 peaks. The step size during the scans was 0.013°, and the acquisition time per step was 1.2 s. A Si powder was measured as a reference to verify the accuracy of the peak positions. Each XRD peak was fitted with a Gaussian peak function.

For the microstructure study the powder samples were mounted in a thermoset resin (Conductomet©) and subsequently polished using 9 and 1 μm diamond suspension followed by a final polishing using 0.02 μm colloidal silica. The imaging was performed using a Jeol-7800F (SEM) operated at 10 kV. EDS (Bruker Quantax) was employed to determine the concentration of Ti and Zr at different locations in the microstructure. Considering the requirement of a sub-micron spatial resolution for the EDS measurements, the ionization edge energies of L-shell electrons of Ti (0.45 keV) and Zr (2.04 keV) and a reasonable overvoltage, 5 kV was adopted as the accelerating voltage. The resulting spatial resolutions are estimated to be 230, 200 and 180 nm in TiC, $Ti_{0.5}Zr_{0.5}C$ and ZrC crystals respectively from Monte Carlo electron trajectory simulations [13,14]. EBSD measurements were conducted using a Bruker Quantax system at an SEM acceleration voltage of 10 kV and using a step size of 40 nm.

3. Results

3.1. X-ray diffraction (XRD)

XRD patterns of the as-synthesized and aged (Ti,Zr)C samples are shown in Fig. 1. For the as-synthesized (Ti,Zr)C (Fig. 1a) it can be seen that the main peak is broad and asymmetric and contains two overlapping peaks (Peaks 2 and 3), representing two different compositions. In addition, there are two rather small bulges at each side of the main peak, denoted Peaks 1 and 4 respectively. Therefore, four Gaussian peak functions were employed to fit the four experimental peaks. One example of the Gaussian fitting for the 111 peak is shown in Fig. 2. The lattice parameter of each phase was calculated from the fitted peak position, as the average of the lattice parameters determined from the 111, 200 and 220 peaks. However, it should be noted that Peak 3 is significantly broad (seen in Fig. 2), which creates uncertainty for the calculation of lattice parameters. The system is assumed to follow Vegard's law [5,6], and thus the lattice parameter is linearly dependent on the composition. The lattice parameter and composition of each phase, in both as-synthesized and aged samples, are listed in Table 2. As can be seen, the main phases obtained after synthesis have the compositions $Ti_{0.34}Zr_{0.66}C$ and $Ti_{0.5}Zr_{0.5}C$.

Table 1
Regime of synthesis and aging treatment.

Temperature (°C)	Time (h)	Atmosphere	Cooling method
1150	10	Argon	Furnace cooling
1400	10, 100	Argon	Furnace cooling
1600	10	Argon	Quenched with argon
1800	10, 20, 30	Argon	Quenched with argon
2000	7	Helium	Quenched with helium
2200 (Synthesis)	2	Argon	High flow rate of argon

After aging at different temperatures for 7 to 10 h the mixed carbides decompose into Zr-rich (Peak 1) and Ti-rich (Peak 4) phases, see Fig. 1a. In the range from 1150 to 1800 °C, the decomposition rate increases with increasing temperature, due to the higher mobility of atoms at higher temperatures. However, during aging at 2000 °C, although the atomic mobility is high, the decomposition fraction is very small, which could be the result of a smaller driving force for phase separation following standard C-curve kinetics.

As expected, long term aging at 1400 °C for 100 h and 1800 °C for 20 and 30 h produces more pronounced decomposition than aging at 1400 and 1800 °C for 10 h respectively, see Fig. 1b and c. For instance, Peak 3 has completely disappeared after aging at 1800 °C for 30 h.

The composition of the as-decomposed Zr-rich and Ti-rich phases is compared with the calculated miscibility gap in Fig. 3. Since the as-decomposed phases are closer to equilibrium after longer aging, only the compositions from the longest aging in the present work are used, i.e. 1300 °C for 500 h, 1400 °C for 100 h, 1600 °C for 10 h, 1800 °C for 30 h and 2000 °C for 7 h. The data for 1300 °C have been previously reported in Borgh et al. [6]. It can be seen that the compositions obtained from the experiments are in good agreement with the compositions corresponding to the calculated miscibility gap. However, for the as-synthesized sample and the sample aged at 1150 °C, the Peaks 1 and 4 are too weak to accurately determine the composition, thus their compositions are not included in Fig. 3.

3.2. Scanning electron microscopy imaging

3.2.1. As-synthesized Ti-Zr-C

SEM backscatter images of the as-synthesized (Ti,Zr)C sample are shown in Fig. 4. The as-synthesized powder, shown in Fig. 4a, is composed of two different types of particles, light (Fig. 4b) and dark (Fig. 4c) porous particles. This difference in contrast is due to the difference in concentration of Zr and Ti, where dark particles have a higher concentration of Ti. Zr-rich light particles are predominant and two kinds of nanostructures are found in the vicinity of particle edges: one is nanoscale lamellae, as indicated by the red rectangle in Fig. 4b and magnified in Fig. 4d; the other type, white precipitates, is infrequent, and it is shown in Fig. 4e. In Fig. 4d early stages of decomposition can be seen close to two pores. It is in the form of embryos with alternating lamellae rich in Ti (black) and rich in Zr (white). It was found that during the aging treatments phase separation mainly takes place in Zr-rich light particles and therefore only light particles are considered below.

3.2.2. Ti-Zr-C aged at 1400 °C

After 10 h at 1400 °C alternating white and black precipitates have developed along most of the grain boundaries, see Fig. 5b. Upon extended aging for 100 h, many precipitates develop into cells with white and black lamellae, advancing into one or more adjacent grains, see Fig. 5d.

3.2.3. Ti-Zr-C aged at 1600 and 1800 °C

The microstructure after aging at 1600 and 1800 °C for 10 h is shown in Fig. 6. Small cells with short lamellae can be seen along grain boundaries. At certain grain boundary triple points, black or white small precipitates are found. Some larger cells with lamellae can be found close