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Grain Boundary Segregation in Sintered Materials: Effect on Densification and Grain Growth

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Abstract

Dopants are often included in the composition of powders to elaborate sintered materials. They have various effects as facilitating sintering, improving microstructure, stabilizing crystalline phases or enhancing properties of materials. The exact role of these additives is often not fully understood thus microstructural characterization is required to elucidate this issue, especially the composition of grain boundaries (GB). Two materials are presented in this study: binderless WC with addition of VC or Cr₃C₂ and Al₂O₃-ZrO₂ composites. In each case, structural and microstructural characterization was performed at different scales. The distribution of V and Cr elements was determined in WC. In the oxides, Y and Zr segregate in GB so the effect of the sintering process –natural or microwave sintering (MWS)- on GB segregation is investigated as MWS is proposed to enhance diffusion. The effect of GB segregation is related to the densification behavior and grain growth in sintered materials.

Keywords: grain boundary, TEM, segregation, WC, ZrO₂

1. Introduction

So-called dopants or minor amounts of elements are often added to raw materials to facilitate their elaboration or to improve their properties. Their exact effect is often not well understood and studying their influence on the constitution and microstructure of the material is an essential step. Owing to the small quantity of additives, transmission electron microscopy (TEM) and associated analytical techniques at the nano-scale are powerful ways to determine the distribution of the elements. In this work, two materials are considered, binderless WC and Al₂O₃/ ZrO₂ composites. Binderless WC has favourable properties when it comes to high hardness and resistance to corrosion. Sintering WC powders without liquid binder to full density is obtained at high temperature and high pressure while field assisted techniques are also being studied and developed. Small additions of carbides like VC or Cr₃C₂ are also used to prevent abnormal grain growth, as in WC-Co alloys [1-4]. In these latter, grain growth occurs by Oswald ripening mechanism, involving WC dissolution in Co and WC precipitation at the WC/Co interfaces. VC and Cr₃C₂ were shown to segregate to WC/Co interfaces, so grain growth inhibition would be linked to the presence of a carbide layer (VC or CrC) at the WC/Co interfaces. The role of such carbides in binderless WC may be questioned. Here it was observed that Cr₃C₂ is more efficient to prevent grain growth and allows the densification to be achieved at lower temperature than with VC [2]. In what follows, the distribution of Cr and V in binderless WC materials is studied at the nanometer scale to get a better insight of their role during the sintering process. Ceramics processing by sintering is another field in which grain boundaries and segregation effects play an important role. In alumina, it has been shown that densification and grain growth are dominated by grain boundary diffusion of Al³⁺ ions [5]. Zr and Y are known to segregate in grain boundaries [6]. Y segregation has an effect on the diffusivity of the grain boundaries [7], and 1000 ppm of Y₂O₃ is enough to significantly delay densification and increase the activation energy for densification in Al₂O₃ [8]. Field effects in microwave sintering of ceramics are expected to particularly enhance interface and grain boundary mechanisms [9]. An Al₂O₃/ ZrO₂ composite containing a very small amount of yttria-doped ZrO₂ (3%) was used to study the relationship between grain boundary segregation and specific effects of microwave sintering. Zr and Y distribution was determined after microwave and natural heating.

2. Experimental

The binderless WC samples used in this study are part of a work devoted to the sintering behavior and grain growth of these materials [1,2,4]. The powders used were WC DN3.0 (D_{BET} of 115 nm, C content of 6.10 wt.% and O content of 0.40 wt.%), VC 160 (D_{BET} of 470 nm, C content of 17.71 wt.% and O content of 0.90 wt.%) and Cr₃C₂ 160 (D_{BET} of 320 nm, C content of 13.03 wt.% and O content of 0.68 wt.%), all from H.C. Starck Germany. WC powders were milled with either 1 % VC or 1% Cr₃C₂ (wt.

%) for 48 h in a WC-Co vessel with WC-Co balls. It resulted in a small contamination of the powder with Co (~0.05 wt. %). After milling the grain size was in the 50-200 nm range from microstructural observations and the d_{BET} size was 80 nm. Specimens were sintered at 1900°C using a sinter-HIP furnace with a 100 bar Ar pressure.

Al₂O₃/ZrO₂ composites were prepared in the framework of A. Guyon's PhD work [10,11]. A mixture of alumina and 3 % (vol%) of ZrO₂ (with 3 mol% Y₂O₃) powders with sub-micrometer size were sintered for comparison in a dilatometer for natural sintering (NS) and in a microwave (MW) single mode cavity up to 1500°C with a heating rate of 25°C/min with no holding stage.

The microstructure of the samples after the sintering stage was observed using the JEOL 3010 or with the JEOL 2100 F transmission electron microscope (TEM) that is equipped with an energy dispersive X-ray spectrometry (EDS) device.

3. Results and discussion

3.1. Binderless WC

Before sintering, XRD patterns of the milled powder with and without additives only show WC peaks. Cr₃C₂ and VC are not detected. After sintering, M₂C (M=W, V or Cr) peaks are present due to a slightly understoichiometric composition [1,2,4]. For the specimens investigated here, peaks of the M₂C phase were only detected in the sample containing Cr₃C₂.

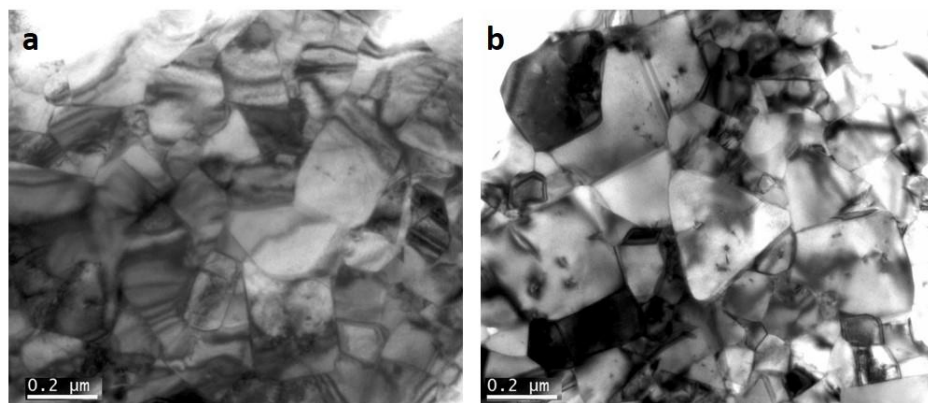


Figure 1. TEM images of binderless WC sintered with Cr₃C₂ (a) and with VC (b)

The microstructure of the samples after the sinter-HIP stage are shown in Fig. 1. Grain size measurements conducted on scanning electron microscopy images indicate a coarser but a more homogeneous microstructure in regard to grain size with Cr₃C₂ addition as compared to the sample with VC addition [2]. This is in agreement with the TEM images. Most grains have a size ranging between 100 and 400 nm. In both samples, WC grains have a distinctive faceted shape with basal and prismatic habit planes.

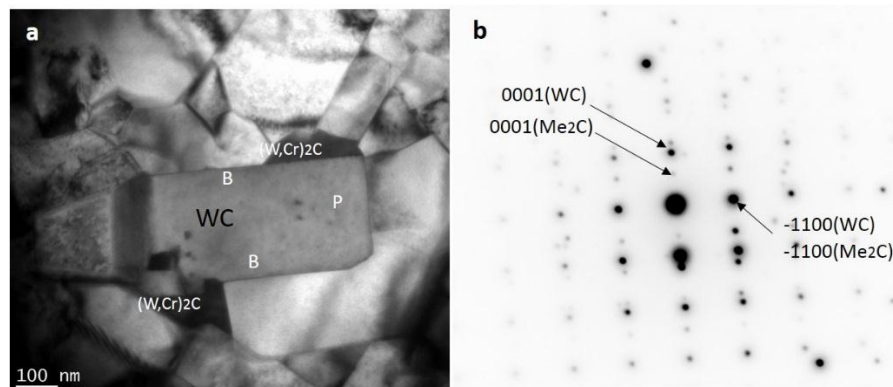


Figure 2. (a) WC grain viewed along [11-20] direction in the sample sintered with Cr₃C₂. The grain shows facets with basal (B) and prismatic (P) habit planes. Two small (W,Cr)₂C compounds are observed at the basal interfaces of the WC grain as revealed by the associated diffraction pattern (b).

In the WC sample with Cr₃C₂, M₂C compounds were found in contact with the basal facets of WC grains (Fig. 2). They adopt a special orientation relationship regarding the WC grain: (0001)M₂C // (0001)WC with [11-20]M₂C // [11-20]WC. In the sample with VC, no M₂C phase could be detected even at the basal facets of the WC grains.

Analytical investigations were conducted in the samples first at small magnification to image the Cr and V rich phases then at higher magnification to detect grain boundary segregation. In the sample sintered with Cr₃C₂, Cr rich areas that are likely the (W,Cr)₂C compound are numerous and are dispersed in the material (Fig. 3a). They are easily visible as their size attains 300 nm. At the opposite, V rich phases are smaller and more seldom. They are very often located at triple junctions where they form small triangular grains less than 50 nm in size (Fig. 3b).

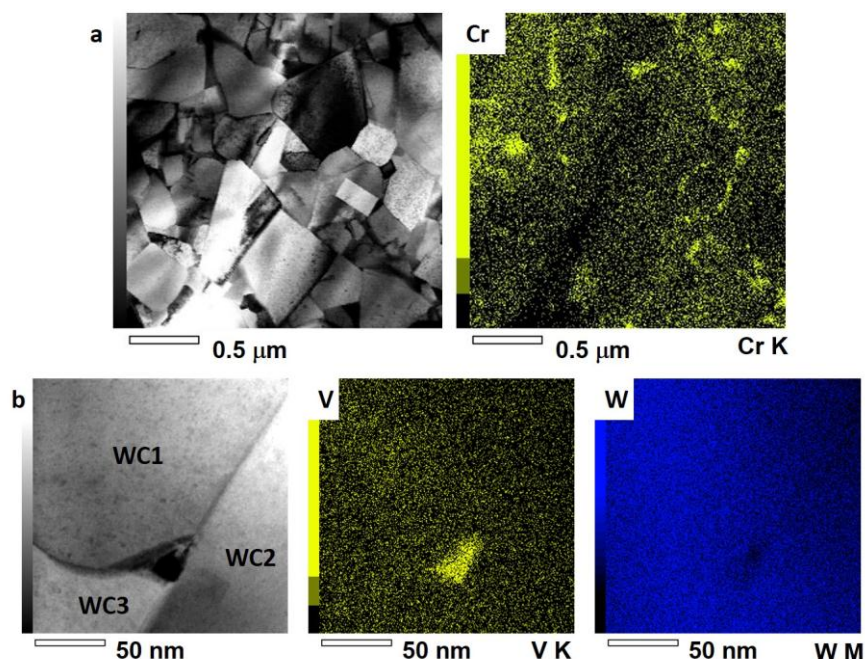


Figure 3. EDS maps performed in the binderless carbides. (a) Image of the sample sintered with Cr₃C₂ and corresponding Cr map. (b) Image of the junction of 3 grain boundaries in the sample sintered with VC and corresponding V and W maps. A deficit in W is found at the level of the V rich compound.

Further investigations were performed in the grain boundaries using a probe size of 0.7 nm or 1 nm. In the sample with Cr additive, segregation of Cr in the grain boundaries is visible (Fig. 4). On the EDS spectrum of the whole map, a significant peak of Co is visible. However, no concentration of Co is observed on the Co map. This peak could result from the deposition of Co onto the TEM specimen during the ion milling step by contamination from the milling chamber. A tiny V peak is also present on the spectrum while no V rich film is detected on the map. It could be due to the contamination of the starting powder during the milling process.

In the sample sintered with VC, no V grain boundary segregation was evidenced by this method (Fig. 5). A small peak of Co was also recorded in the EDS spectra of this sample but gave rise to no detection of segregation. Only a tiny V rich compound is found at the triple junction of grain boundaries in the example of Fig. 5.

TEM and EDS investigations reveal that in the specimen sintered with Cr₃C₂, Cr segregates at all boundaries. Moreover the (W,Cr)₂C phase is homogeneously distributed in the specimen. These observations agree with the melting of the (W,Cr)₂C phase occurring at a temperature close to 1800°C that facilitates the spreading of the Cr rich phase in the WC skeleton and the segregation in WC grain boundaries [1]. On cooling, (W,Cr)₂C phase crystallizes with a special orientation on the basal facets of WC grains to minimize the interface energy. On the other hand, no evidence of (W,V)₂C phase formation is found in the specimen sintered with VC and in addition, no liquid phase is expected below 1900°C for (W,V)₂C. In addition, nanometric V rich compounds are found at triple junctions and never inside the grains. Both Cr and V addition are effective grain growth inhibitors. The effect of Cr is likely

due to Cr atoms segregated at all grain boundaries that hinder boundary migration. Unlike M₂C phase that has a large Cr solubility, the Cr solubility limit in WC is about 1.5 mol% and is expected to be reached within several minutes for sub-micrometer grains [12]. One can speculate that the migration of the boundary is difficult due to presence of Cr atoms and that Cr atoms cannot be left behind the boundary as the solubility limit would be exceeded.

No V rich grains were found inside WC grains. So small V compounds lying at triple junctions could hinder the boundary migration by anchoring the triple junctions, thus limiting grain growth. As the distribution of V rich grains is uneven in the specimen, grain growth could happen for some grains, resulting in a less homogeneous microstructure than for Cr addition.

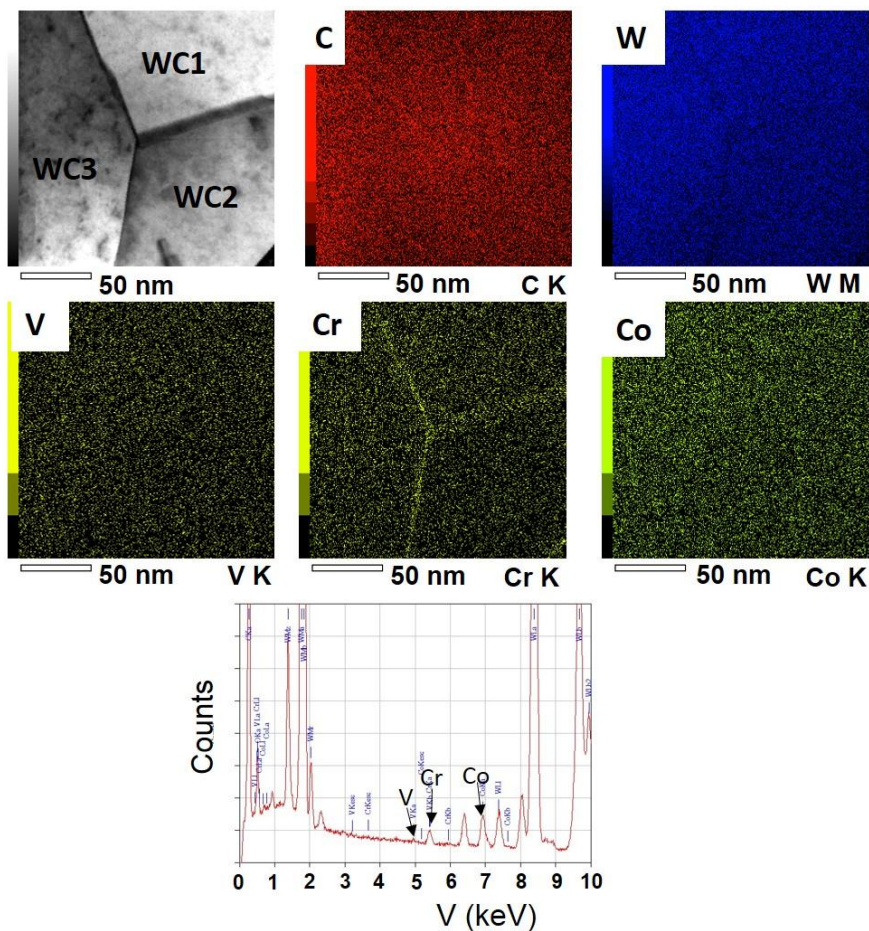


Figure 4. Image of a boundary triple junction in the Cr rich sample, corresponding EDS maps for C, W, V, Cr and Co, and spectrum of the whole map.

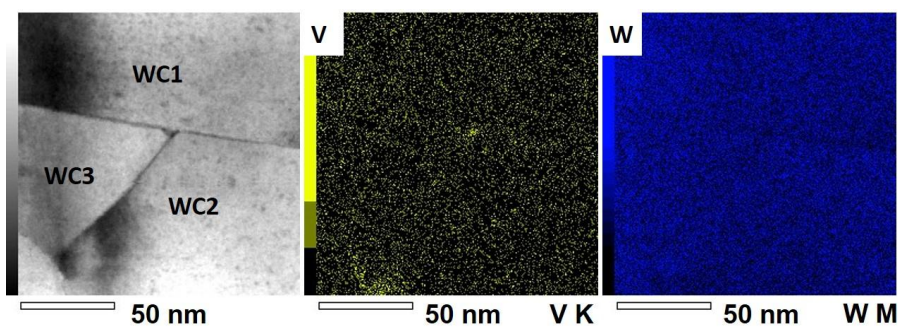


Figure 5. Image of a boundary triple junction and corresponding V and W maps. A small V rich compound is detected at the triple junction. No segregated V film is visible in the grain boundaries although a depletion of W is observed.

3.2. Al₂O₃/ZrO₂ composites

In spite of the very low amount of second phase in the composite (3vol%) after heating at 1500°C, the density only attains 92% in natural sintering (NS), which is far below the density obtained with pure alumina of the same type alone [10]. It reaches 98% in the MW sintered sample. Grain size measurements (intercept length method with $d=1.5\lambda$) carried out on FEG-SEM images indicate a larger grain size in the MWS sample (0.55 μm) than in the NS sample (0.45 μm). The observation of the microstructure by TEM shows the frequent presence of small ZrO₂ grains inside Al₂O₃ grains in the MS sample, in agreement with a more pronounced grain growth in this sample.

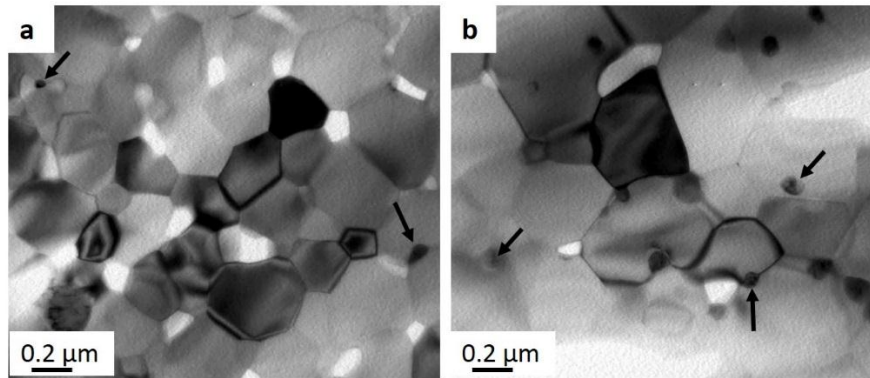


Figure 6. TEM images of Al₂O₃/ZrO₂ composite heated at 1500°C (a) by natural sintering and (b) by microwave sintering. Bright areas are pores and back arrows points ZrO₂ grains.

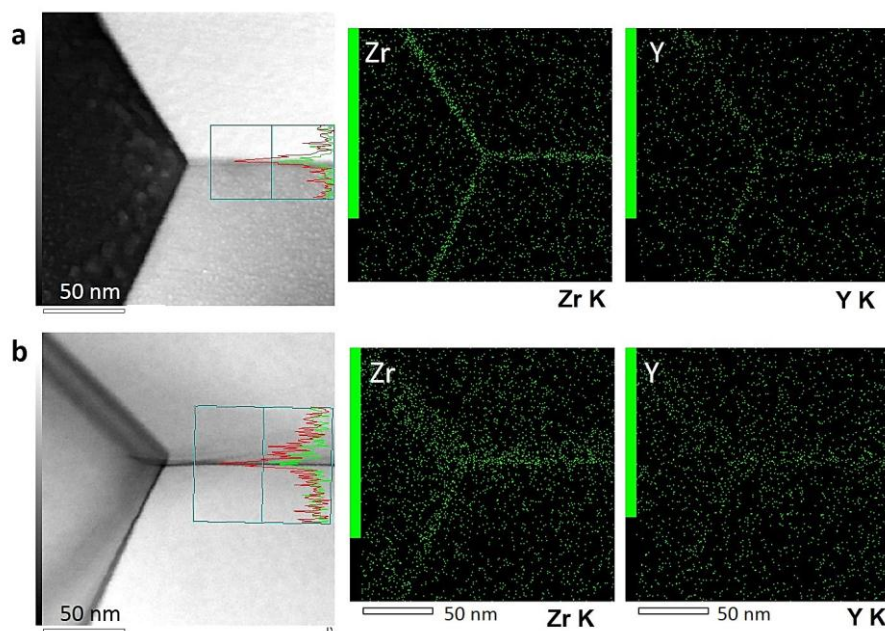


Figure 7. Image of a boundary triple junction and corresponding Zr and Y maps (a) in the NS sample, (b) in the MWS sample. The intensity profile of Zr (red) and Y (green) for a grain boundary are also drawn on the images.

In order to get a better understanding on the enhanced grain growth occurring in the MWS sample, investigations of the alumina grain boundaries were carried out. Both specimens after NS and MWS were characterized. As expected from the literature for NS sample, all grain boundaries contain a thin film of Zr and also of Y in a smaller quantity (Figure 7). In addition, the same observations were obtained for the MWS sample. This shows that both Y and Zr have migrated from zirconia particles to

the alumina grains surfaces and grain boundaries during the thermal process. The relatively low density attained in NS is therefore partly due to this segregation, as expected from literature [8]. No significant difference in segregation amount could be found between the samples, Microwaves therefore do not seem to affect the segregation itself but would enhance densification and grain growth, leading to the higher obtained values.

4. Conclusion

Chemical investigations at the nanoscale allow some assumptions on grain growth or sintering mechanisms to be proposed. After sintering of binderless WC with 1% Cr₃C₂, Cr is found to segregate in all WC grain boundaries (GB). After sintering WC with 1% VC, no segregation of the GBs is detected and small V rich nanometric grains are found at most grain boundary triple junctions. The grain growth inhibiting effect of Cr additive is likely related to GB segregation while the effect of V additive is likely due to the anchoring of GB triple junctions.

During the sintering of alumina containing 3% of yttria doped zirconia, Y and Zr were found to migrate towards alumina grain boundaries in similar ways during natural and microwave heating, but result in significantly different effects: while segregation tends to inhibit densification and grain growth in natural heating, this effect is balanced in microwave sintering. This could be due to the interaction of segregated species with the electromagnetic field.

5. References

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