(Ti,Cr)C Synthesized *In Situ* by Spark Plasma Sintering of TiC/Cr₃C₂ Powder Mixtures

Hanjung Kwon, Sun-A Jung and Wonbaek Kim*

Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources,
Yuseong-gu, Daejeon 305-350, Korea

(Ti,Cr)C was synthesized and consolidated *in situ* by spark plasma sintering (SPS) of two TiC/Cr₃C₂ powder mixtures of distinctly different particle sizes. SPS of both mixtures successfully produced single-phase (Ti,Cr)C in two minutes at 1800°C. It was found that the nano-scale mixture consists of fine and uniformly dispersed TiC/Cr₃C₂ particles while the micron-scale mixture consists of particles aggregated and unevenly distributed. The (Ti,Cr)C consolidated using nano-scale mixture retained an equilibrium grain structure linear grain boundaries thanks to the fine and uniform elemental distribution. On the contrary, the grain boundaries of (Ti,Cr)C consolidated using micron-scale mixture were heavily serrated with Cr-rich composition. It is believed that Cr₃C₂ melts and forms networks where it starts to react with TiC to form solid solution leaving serrations along the grain boundaries because of its non-uniform distribution. The higher fracture toughness of (Ti,Cr)C consolidated from nano-scale mixture may be attributed to its uniform microstructure. [doi:10.2320/matertrans.M2014327]

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1. Introduction

Titanium carbide has been used as structural materials because of its high hardness, excellent wear resistance, and high chemical stability.¹⁾ A cermet (titanium carbide-metal composite) is the typical application of titanium carbide. The cermet was formulated as an alternative of tungsten carbide because titanium is cheaper than tungsten. As a matter of fact, the replacement of tungsten carbide with titanium carbide was not very successful due to the low toughness of titanium carbide compared to that of tungsten carbide.

Unsurprisingly, many researchers have been endeavored to improve the low toughness of titanium carbide based cermets. The methodologies have been two folds. First was the addition of second carbides with higher toughness. Transition metal carbides such as tungsten carbide, molybdenum carbide, and chromium carbide were added to improve the properties of the titanium based cermet.²⁻⁶⁾ More recently, second approach was realized through the formation of solid-solution carbide in the form of (Ti,M)C (M = W, Mo, and V, etc.).⁷⁻¹¹⁾ In this case, the solid-solution carbide plays the role of the tougher phase which is relevant to the solid-solution strengthening. The improvement of the toughness of the titanium-carbide based cermet was demonstrated for (Ti,W)C, (Ti,V)C, and (Ti,Zr)C solid-solution carbides.

Various techniques has been employed to synthesize the solid-solution carbides such as mechanical alloying of metals and carbon,^{7,10)} carbothermal reduction of amorphized oxides mixture,^{8,9)} and SPS (spark plasma sintering) of carbides mixture^{11,12)} were employed. Among the methods, the mechanical alloying and carbothermal reduction methods require the additional sintering processes to produce bulk materials because the solid solution carbides are in the form of powders.

Among them, SPS has an obvious advantage in the fact that the synthesis and consolidation of the solid-solution

carbide phase could be achieved simultaneously. Nevertheless, the synthesis of a single phase solid-solution by SPS is not easy and usually results in the mixture of two solid-solution phases.¹²⁾ This is because SPS is accomplished in a very short time (typically within few minutes) and thus the time for solid-state diffusion of elements is not enough for the synthesis of a single-phase solid solution. Therefore, a subsequent annealing at higher temperature is inevitable to produce a single-phase solid solution.¹²⁾

In this work, we report the synthesis and consolidation of a single-phase (Ti,Cr)C by SPS using two different TiC/Cr₃C₂ powder mixtures; The first mixture was prepared by milling commercial TiC and Cr₃C₂ powders. The second mixture was composed of nano-scale TiC/Cr₃C₂ powders which were manipulated by milling and subsequent heat treatment of Ti-Cr alloy and graphite powders. The microstructure and mechanical properties of (Ti,Cr)C were investigated and compared in terms of the TiC/Cr₃C₂ mixtures.

2. Experimental Procedure

TiC/Cr₃C₂ powder mixture for SPS was prepared using commercial powders. The first mixture was prepared by the conventional mixing of TiC (purity: 99.5%; average particle size: 2 μm, Alfa) and Cr₃C₂ (purity: 99%; particle size < 6 μm, AMERICAN ELEMENTS) powders. The second mixture was prepared from Ti-Cr alloy powders (weight ratio of Ti : Cr = 8 : 2; 99.9% purity; particle size < 180 μm), and graphite (purity > 99%; average particle size: 7–10 μm) powders. The amount of graphite was adjusted such that TiC-Cr₃C₂ could be formed after reacting with the alloy. For the purpose of clarification, the first mixture and second mixture will be referred as “micron-scale mixture” and “nano-scale mixture”, respectively. The powder mixtures were subjected to high-energy milling using a planetary mill (Pulverisette 5, Fritsch, Germany). Tungsten carbide balls were mixed with the mixture powders in a ball-to-powder weight ratio of 20 : 1. A stainless steel bowl was used, and the powders were milled at 250 rpm in an argon atmosphere

*Corresponding author, E-mail: wbkim@kigam.re.kr

for 10 h. Then the milled powder was heat treated at 1200°C for 2 h in a graphite furnace under vacuum. The phase of the synthesized powder was analyzed using X-ray diffraction (XRD) analyses (SmartLab, Rigaku, Japan). Monochromatized Cu K α radiation ($\lambda = 0.15418$ nm) was employed during the analyses, and Si was used as a standard to calibrate the diffractometer. Energy-dispersive spectrometry (EDS) performed using a system with a field-emission transmission electron microscopy (FE-TEM) attachment (JEM-2100F, JEOL, Tokyo, Japan) and a field-emission scanning electron microscopy (FE-SEM) attachment (Quanta 650, FEI, Oregon, USA) was used to analyze the dispersion of elements in the synthesized powder.

The powder mixtures were placed in a graphite die (outside diameter, 35 mm; inside diameter, 10 mm; height, 40 mm) and introduced into the SPS system (Eltek, South Korea). The sintering was conducted typically in four stages. The system was evacuated (stage 1) and subjected to an uniaxial pressure of 80 MPa (stage 2). An induced current was activated and maintained until densification occurred as indicated by a linear gauge measuring sample shrinkage (stage 3). The temperature was measured by an optical pyrometer that was focused on the surface of the graphite die. The sintering continued until the shrinkage reached a constant value at 1800°C. The heating rate was very fast reaching at 1800°C in 2 minutes. Afterwards the compact was cooled to room temperature (stage 4). Vickers hardness was measured with an indenter load of 1 kg, and fracture toughness was calculated using the expression derived by Shetty *et al.*¹³ After the hardness measurement, the sample was broken and the fracture surface was examined under FE-SEM.

3. Results and Discussion

3.1 Preparation of nano-scale and micron-scale TiC/Cr₃C₂ powder mixtures

The nano-scale TiC/Cr₃C₂ powder mixture was obtained by milling and subsequent heat treatment of Ti-Cr alloy and graphite powders. Figures 1(a)(b)(c) are the X-ray diffraction patterns illustrating the phase evolution. Here, (a) is the pattern for the Ti-Cr alloy raw powder, (b) is the pattern after milling for 10 h with the addition of graphite, (c) is the pattern after annealing sample (b) at 1200°C for 2 h. Ti-Cr alloy powder was composed of a series of Ti-Cr intermetallic compounds (Ti₄Cr, TiCr₂, and Ti_{0.95}Cr_{0.05}) and pure Ti (See Fig. 1(a)). Among the constituents, Ti and Ti_{0.95}Cr_{0.05} reacted with graphite, forming a B1-structured (i.e., a NaCl-like structure) phase as shown in Fig. 1(b). In the meantime, the broadening of Ti₄Cr and TiCr₂ peaks implies that their particle sizes were reduced considerably. Finally, during the heat treatment, they reacted completely with graphite leaving only the B1-structured phase and Cr₃C₂ (Fig. 3(c)). Cr₃C₂ has two isomorphs. Here, Cr₃C₂ phase synthesized matches JCPDS 65-089 having the symmetry of space group Cmc₂m. The lattice parameter of the B1-structured phase (0.43075 nm) is smaller than that of pure TiC phase (0.43274 nm). This suggests that its lattice parameter was reduced by the substitution of Cr since the atomic radius of Cr (176 pm) is smaller than that of Ti (166 pm).¹⁴

Fig. 1 X-ray diffraction patterns of nano-scale TiC/Cr₃C₂ mixtures prepared from Ti-Cr alloy and graphite powders. (a) as-received Ti-Cr alloy, (b) Ti-Cr alloy/graphite mixture high-energy milled for 10 h, (c) after heating sample (b) in vacuum for 2 h at 1200°C.

Fig. 2 X-ray diffraction patterns of micron-scale TiC/Cr₃C₂ mixtures. (a) TiC/Cr₃C₂ mixture, (b) TiC/Cr₃C₂ mixture high-energy milled for 10 h, (c) after heating sample (b) in vacuum for 2 h at 1200°C.

For the comparison experiment, micron-scale TiC/Cr₃C₂ powder mixture was also subjected to the identical processes (i.e. 10 h milling and 1200°C anneal). We previously reported that the same mixture produced a single-phase (Ti,Cr)C after the high-energy milling of 20 h.^{15,16} Figures 2(a)(b)(c) are X-ray diffraction patterns showing the phase evolution in micron-scale mixture. In this case, no phase change occurred either during milling or annealing. Here, Cr₃C₂ phase matches JCPDS 35-0804 which has the symmetry of space group Pnam. The milling introduced only the particle size reduction as can be seen from the peak broadening (Fig. 2(b)). However, it was recovered during annealing returning to its original state (Fig. 2(c)).

Originally, it was anticipated that the uniform and fine distribution of constituent elements would be advantageous for the solid-solution reaction to occur fast. It would be more important in the fast-sintering processes as SPS. Figures 3(a)–(d) show SEM and EDS mapped images of the mixture powders. Here, (a)(c) are images for nano-scale mixture and (b)(d) are images for micron-scale mixture powders. At a glance, it is obvious that the nano-scale mixture consists of a much finer size and uniform distribution of TiC and Cr₃C₂. This suggests that the solid-state diffusion distance between Ti and Cr in the nano-scale mixture can be

Fig. 3 SEM micrographs and corresponding EDS mapping images. (a) and (c) nano-scale TiC/Cr₃C₂ mixture powder after heat treatment for 2 h at 1200°C, (b) and (d) micron-scale TiC/Cr₃C₂ mixture powder prepared by conventional mixing.

significantly shorter than that in the micron-scale mixture. The fine size and uniform distribution of Ti and Cr was retained after the subsequent heat treatment as shown in TEM micrographs (Fig. 4). The particles sizes of the nano-scale mixture are seen to be about few tens of nanometers. The EDS mapped images also illustrate the fine and uniform distribution of Ti and Cr atoms in nano-scale TiC/Cr₃C₂ mixture.

3.2 Synthesis and consolidation of (Ti,Cr)C by SPS

The formation of (Ti,Cr)C from TiC/Cr₃C₂ mixture was very rapid. X-ray diffraction study revealed that TiC and Cr₃C₂ phases reacted instantly to form (Ti,Cr)C suggesting that the complete dissolution of Cr₃C₂ occurs in only two minutes. Figures 5(a)(b) are the XRD patterns of (Ti,Cr)C consolidated by SPS. Here, (a) is the pattern of (Ti,Cr)C prepared from the micron-scale mixture and (b) is the pattern of (Ti,Cr)C prepared from the nano-scale mixture. It is thus obvious that the reaction is exceptionally fast as a solid-state reaction especially in the case of the micron-scale mixture considering its aggregated and uneven distribution of TiC and Cr₃C₂ powders (See Fig. 3(d)).

Therefore, it was postulated that the (Ti,Cr)C forming reaction may be expedited by the melting of Cr₃C₂ phase. The melting points of TiC and Cr₃C₂ are 3160 and 1890°C, respectively. The temperature of SPS in this study was 1800°C which is the mold surface temperature. It is therefore possible that the actual sintering temperature could be higher

Fig. 4 TEM micrographs and corresponding EDS mapping images. (a) TEM micrograph of nano-scale TiC/Cr₃C₂ mixture powder after heat treatment for 2 h at 1200°C, (b) EDS mapping images of (a).

than 1890°C. In addition, it may also be plausible that Cr₃C₂ in nano-scale mixture could melt at a lower temperature than that in micron-scale mixture. It is well known that the melting

Fig. 5 X-ray diffraction patterns of mixture samples after SPS. (a) nano-scale TiC/Cr₃C₂ mixture powder, (b) micron-scale TiC/Cr₃C₂ mixture powder.

Table 1 Ti/Cr content in (Ti,Cr)C consolidated from the nano-scale mixture and micron-scale mixture.*

Location of measurement	Specimen	Amount/mass%		Ti/Cr
		Ti	Cr	
Original composition		80	20	4
Fractured surface	Nano-scale mixture	74.4 (1.1)	25.6 (1.2)	2.9
	Micron-scale mixture	71.0 (0.08)	29.0 (0.08)	2.4
Grain interior	Nano-scale mixture	87.8 (0.3)	12.2 (0.3)	7.2
	Micron-scale mixture	84.2 (0.4)	15.8 (0.4)	5.3

*Standard deviation in parentheses.

point of various metals decrease significantly in nano-sized particles. If this happens in this case, the evaporation loss of Cr₃C₂ could be higher in the nano-scale mixture. As a matter of fact, the amount of Cr in (Ti,Cr)C consolidated from the nano-scale was significantly lower than that in (Ti,Cr)C consolidated from the micron-scale mixture. It was 12.2 mass% and 15.8 mass% for nano-scale mixture and micron-scale mixture, respectively (Table 1). Therefore, it is probable that the nano-sized Cr₃C₂ melts at a lower temperature. In any case, the melting of Cr₃C₂ should expedite the reaction significantly.

The melting of Cr₃C₂ phase affected their grain structure significantly. Figures 6(a)(b) show the backscattered electron SEM images of the polished/etched surface of the sintered (Ti,Cr)C. (Ti,Cr)C consolidated from the nano-scale mixture shows a stable grain structure with linear grain boundaries. In contrast, (Ti,Cr)C consolidated from the micron-scale mixture reveals heavily serrated erratic grain boundaries. The grain structure of nano-scale mixture sample is almost linear suggesting an ideal grain growth minimizing the grain boundary area. In the meantime, the shape of the grains in micron-mixture sample is very awkward and energetically unstable due to the significantly enlarged area by serration.

This implies that it did not have enough time to obtain a stable grain structure by diffusion. The grain boundary serration was attributed to the melting of unevenly distributed Cr₃C₂. As soon as Cr₃C₂ melts, it forms a liquid network along grain boundaries which remains due to low solid-state diffusion rate in the short duration of SPS. The higher Cr content on the fracture surface appears to support the

Fig. 6 FE-SEM micrographs of the polished/etched surfaces of (Ti,Cr)C synthesized by SPS. (a) nano-scale TiC/Cr₃C₂ mixture powder (b) micron-scale TiC/Cr₃C₂ mixture powder.

Table 2 Mechanical properties of (Ti,Cr)C consolidated from the nano-scale mixture and micron-scale mixture.

Specimen	Vickers hardness, H _V /GPa	Fracture toughness, K _{IC} /MPa·m ^{1/2}
Nano-scale mixture	23.0	4.6
Micron-scale mixture	22.9	4.1

hypothesis. The Cr content on fracture surface was 29.0 mass% while that on grain interior was 15.8 mass% (Table 1).

3.3 Mechanical properties of (Ti,Cr)C

The mechanical properties of (Ti,Cr)C consolidated by SPS are summarized in Table 2. The hardness values of (Ti,Cr)C from both mixtures were almost identical. It was 23.0 and 22.9 GPa for the nano-scale and micron-scale mixtures, respectively. Meanwhile, the fracture toughness of (Ti,Cr)C from nano-scale mixture was 4.6 MPa·m^{1/2} while that from micron-scale mixture was 4.1 MPa·m^{1/2}. Figures 7(a)–(d) show FE-SEM micrographs of the fracture surfaces of (Ti,Cr)C. Here, (a)(c) and (b)(d) are the fracture surfaces of (Ti,Cr)C prepared by consolidation of the nano-scale mixture and micron-scale mixture, respectively. An intergranular fracture is most obvious when the sample was consolidated from the nano-scale mixture which had linear grain boundaries. However, the fracture surface of micron-sized mixture sample reveals more complicated morphology due to the presence of heavily serrated grain boundaries. The reason for the better toughness values for nano-scale mixture is not clear and may not allow a straightforward explanation. In general sense, it might be attributed to the uniform grain structure with clean grain boundaries. The increased fraction of the transgranular mode in micron-scale mixture sample may imply that the strength of grains is reduced to permit the transgranular fracture. It is possible that the higher Cr content on (Ti,Cr)C grains may reduce the strength of (Ti,Cr)C. The Cr content on (Ti,Cr)C grain was 12.2 mass% and 15.8 mass% for nano-scale mixture and micron-scale mixture, respectively (Table 1). The strength of (Ti,Cr)C may decrease with Cr content.

4. Conclusions

In this study, we developed a new method to synthesize

Fig. 7 FE-SEM micrographs of the fracture surfaces of (Ti,Cr)C. (a), (c) and (b), (d) are the fracture surfaces of (Ti,Cr)C prepared by consolidation of the nano-scale mixture and micron-scale mixture, respectively.

(Ti,Cr)C *in situ* by spark plasma sintering of TiC/Cr₃C₂ powder mixtures using SPS. To investigate the effect of TiC/Cr₃C₂, two distinctly different particle sizes were prepared by the combination of high-energy milling and the subsequent heat treatment. The first mixture was micron-scale mixture consisting of commercial TiC and Cr₃C₂. The second mixture was nano-scale mixture prepared using Ti-Cr alloy and graphite powders. SPS of both mixtures successfully produced the single-phase solid-solution (Ti,Cr)C in two minutes at 1800°C. The melting of Cr₃C₂ should expedite the reaction significantly. Nano-scale Cr₃C₂ melted at a lower temperature resulting in more Cr loss. The grain boundaries of (Ti,Cr)C consolidated from micron-scale mixture were heavily serrated by the melting of unevenly distributed Cr₃C₂. The hardness of (Ti,Cr)C was 22.9 and 23.0 GPa for the micron-scale and nano-scale mixtures, respectively. Meanwhile, the fracture toughness of (Ti,Cr)C from nano-scale mixture was 4.6 MPa·m^{1/2} while that from micron-scale mixture was 4.1 MPa·m^{1/2}. The higher fracture toughness of (Ti,Cr)C consolidated from nano-scale mixture was attributed to its comparatively uniform microstructure.

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