Materials Science-Poland, *Vol. 27*, *No. 4/1*, *2009*

On the synthesis and properties of bulk ternary Cr_2AlC ceramics

W.B ZHOU[1, 2*], B.C. MEI[2], J.Q. ZHU[1]

[1]School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, P.R. China

[2]State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, P.R. China

Dense bulk Cr_2AlC was synthesized by hot-pressing of Cr, Cr_3C_2 and Al powders as starting materials. The phase composition was determined by X-ray diffraction (XRD), the microstructures of the samples were observed with a scanning electron microscope (SEM) and thermal, electrical as well as the mechanical properties at and above room temperature were determined. The results showed that Cr_2AlC grains have columnar and plate-like shapes, and that it is a good electrical and thermal conductor.

Key words: *ceramics; chromium aluminum carbide; hot-pressing*

1. Introduction

Layered ternary carbide Cr_2AlC has received considerable attention because of an unusual combination of good properties which makes it a candidate for many high temperature applications [1]. Like metals, it is an excellent electrical and thermal conductor, easily machinable, plastic, relatively soft, and not susceptible to thermal shock at higher temperatures. Like ceramics, it is oxidation resistant, refractory and has a high tensile strength, a high melting point and good thermal stability. Due to these unique properties, it is expected to have applications in various fields such as a substitute for machinable ceramics, kiln furniture, heat exchangers, and so on.

Even though Cr_2AlC has so many excellent properties, it has not received much attention until recent years, because it is difficult to synthesize bulk samples of Cr_2AlC with high purity. Schuster et al. [2] synthesized Cr_2AlC power by sintering Cr, Al and C powder through arc melting, then the sample was sealed in an evacuated quartz tube, annealed at temperatures between 600 and 1200 °C (170–500 h), and quenched in water. This method is limited to laboratory scale by its low efficiency. Recently, Manoun et al. [3] have successfully fabricated single-phase, fully dense, polycrystal-

*Corresponding author, e-mail: jsyczwb@hotmail.com

line samples of Cr_2AlC by reactive HIPing of Cr, Al and graphite powders. However, the preparation process was very complicated. Tian et al. [4] obtained bulk Cr_2AlC by hot pressing of Cr, Al and C powders at 1350 °C for 1 h, together with a small amount of Cr_7C_3. Further increase in temperature or extension of dwell time did not change the phase assemblage in an obvious way. More recently, Lin et al. [5] also have successfully fabricated single phase bulk Cr_2AlC through a solid–liquid (S–L) reaction by sintering Cr, Al and C powders at 1400 °C and 1350 °C for 60 min and 30 min, respectively. The relative density of the sample is 95% of the theoretical value.

In our previous work, we successfully obtained high purity Ti_3SiC_2 and Ti_3AlC_2 using TiC, instead of Ti and C as raw materials [6, 7]. Thus in the present research, we fabricated bulk Cr_2AlC by hot-pressing of Cr, Cr_3C_2 and Al powders. Additionally, the mechanical properties, thermal and electrical properties of the obtained Cr_2AlC sample were also investigated.

2. Experimental

High purity powders of Cr (99.9% pure, 4.3 μm), Al (99.8% pure, 12.8 μm) and Cr_3C_2 (99.8%, 5.5 μm) were used as raw materials. They were mixed in ethanol for 24 h and then compacted uniaxially under the pressure of 20 MPa in a graphite mold pre-sprayed with a layer of BN. The compacted mixture was first heated in an Ar atmosphere at the rate of 5 °C/min from room temperature to 600 °C, under the pressure of 10 MPa. Then it was heated up to and maintained at a temperature of 1350 °C for 2h, at which time the pressure was gradually increased to 30 MPa. Finally, the sample was cooled down to room temperature. Before examination, the surfaces of the sintered samples were machined to remove the layer contaminated by the carbon sheet, using a fine grit high speed diamond wheel.

The sintered sample was polished and the density was measured by the Archimedes principle. Powders were drilled from the bulk of the samples for X-ray diffraction (XRD) characterization. The phase identification was made by XRD using a rotating anode X-ray diffractor (Model D/MAX-RB, RIGAKU Corporation, Japan). Scans were made with Cu K_α radiation (40 kV and 50 mA) at the rate of 1deg/min, using a step of 0.02°. The XRD data was refined for the lattice parameters by the Rietveld analysis. Pure silicon was added as an internal standard. The microstructures of the samples were investigated by the energy dispersive spectroscopy (EDS) method via scanning electron micrographs (SEM) (Model JSM-5610LV, JEOL Ltd., Japan). The microhardness was measured with a Leitz Microhardness Tester (Leitz Wetzlar, Germany) at 1 N with the loading time of 30 s. The hardness was calculated by averaging at least 10 measurements. Three-point bending tests were performed to measure flexural strength and fracture toughness (K_{IC}). The dimensions of the specimens subjected to flexural strength testing were 3×4×36 mm^3 and the crosshead speed was 0.5 mm/min. K_{IC} was measured by the single-edge notch beam (SENB) method with specimen dimensions of 4×8×36 mm^3. A notch 4 mm long and ca. 0.15 mm wide was

made by the electrical discharge method. The notch root radius was about 0.15 mm. The crosshead speed for fracture toughness testing was 0.05 mm/min. The thermal diffusivity α and heat capacity C_p were directly measured by a thermal constants measuring instrument (Sinku-Riko Model TC-7000) using the laser flash method. The thermal conductivity λ was calculated from the following equation:

$$\lambda = dC_p\alpha \tag{1}$$

where is the density (kg/m^3) of the sample, C_p its heat capacity (J/(kg·K)) and α – the coefficient of temperature conductivity (m^2/s).

The thermal expansion of the bulk polycrystalline samples was measured in air from room temperature to 1300 °C with a dilatometer. Electrical conductivity was measured using the four-probe method, from room temperature to 600 °C in vacuum. The Seebeck coefficient in vacuum was evaluated to 600 °C.

3. Results and discussions

3.1. Synthesis and microstructure of Cr_2AlC

Compared with the elemental chromium and chromium carbide, the melting point of aluminum is relatively low (ca. 933 K), so the weight loss of aluminum in the starting composition will inevitably occur, especially at elevated temperatures. Tian et al. [8] investigated Al content phase assemblage of Cr_2AlC and found that when the amount of additive Al is equal to or greater than 20 at. %, the Cr_2AlC phase becomes the only phase appearing in the final sample. Thus in the present research, samples initially having the molar ratio Cr: Al: C=2: 1.2: 1 were investigated.

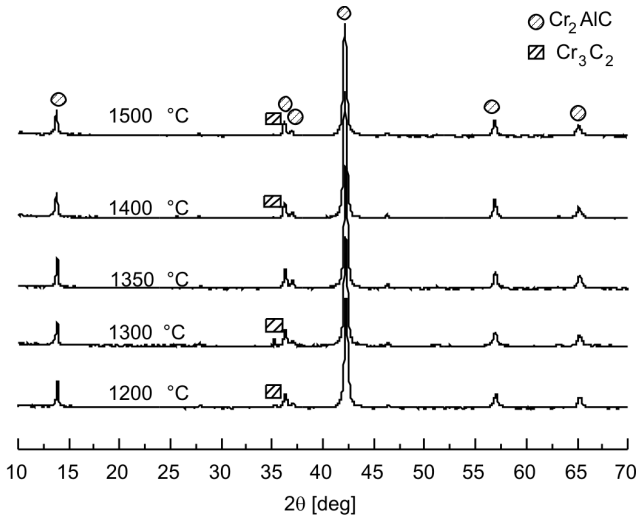

Fig. 1. X-ray diffraction patterns of the products sintered at various temperatures

Figure 1 shows the X-ray diffraction patterns of the products sintered at various temperatures from 1200 °C to 1500 °C. Between 1200 °C and 1300 °C, the main phase was Cr_2AlC, Cr_3C_2 phase was also found. When sintered at 1350 °C, no phase but Cr_2AlC was identified by X-ray diffraction, which indicated that the products were of high-purity. When the temperature was increased to 1400–1500 °C, the Cr_3C_2 peak appeared again, which indicated that Cr_2AlC could decompose into Cr_3C_2 and Al when the sintering temperature exceeded 1400 °C. The measured lattice parameters of sample (c) a = 0.2858±0.0002 nm and c = 1.2808±0.0002 nm were very close to those reported by other authors [2, 5].

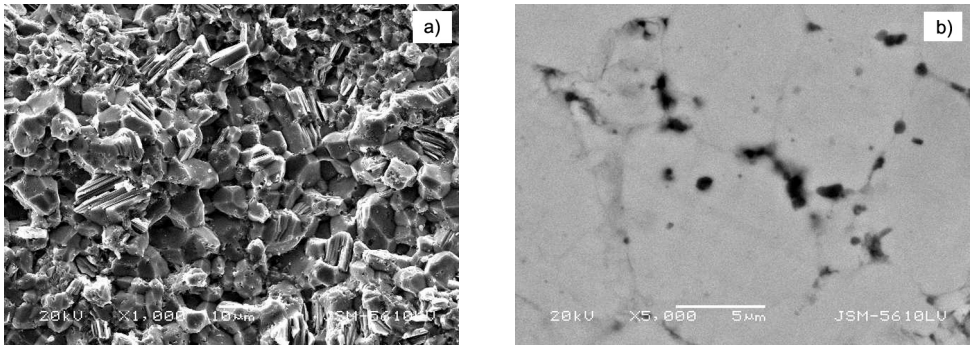

Fig. 2. SEM micrograph of the fracture surface for Cr_2AlC (a) and a typical BSE micrograph of the polished surface of Cr_2AlC (b)

Figure 2 shows the SEM micrograph of the fractured faces of samples sintered at 1350 °C for 2 h. The grains with the layered feature characteristic of Cr_2AlC can be clearly seen in the sample. The average grain size of Cr_2AlC is about 10 μm. A typical SEM micrograph, taken with back-scattered electron imaging, of the polished sample is shown in Fig. 2b. Some dark phases exist in the sample. Energy dispersive spectroscopy (EDS) analysis revealed that they were Cr_3C_2 phase. Cr_3C_2 phase could not be detected in the XRD spectrum due to its low content.

3.2. Mechanical properties of Cr_2AlC

The measured density of bulk material sintered at 1350 °C was 5200 kg/m^3, i.e. 99.4% of the theoretical value (5229 kg/m^3). The fracture toughness of Cr_2AlC is 5.8 MPa·m$^{1/2}$, being slightly lower than that of Ti_3AlC_2 and Ti_3SiC_2 but is still higher than that of conventional ceramics such as Al_2O_3, SiC, TiB_2, etc. The flexural strength of Cr_2AlC is 498 MPa, which is higher than that of Ti_3AlC_2 and Ti_3SiC_2. The compressive strength of the obtained sample was 627 MPa, which was lower than the value reported by Tian et al. Vickers indentation hardness was tested on the polished polycrystalline Cr_2AlC surface. The very highly polished surface of the sample showed metallic lustre. The measured Vickers hardness of Cr_2AlC sample was

5.2 GPa, which was similar to other reported values. More importantly, the material had the same machinability as that of graphite. It could easily be machined with ordinary mechanical machining tools, and holes could readily be drilled by using common steel drills, without adding lubricants.

3.3. Thermal and electrical properties

The average thermal expansion coefficient of the sample in the range 25–1300 °C was $1.31\times10^{-5}\,K^{-1}$, equal to that reported by Tian et al. [9] but a little higher than that of that Ti_3AlC_2 ($9.0\times10^{-6}\,K^{-1}$) [10].

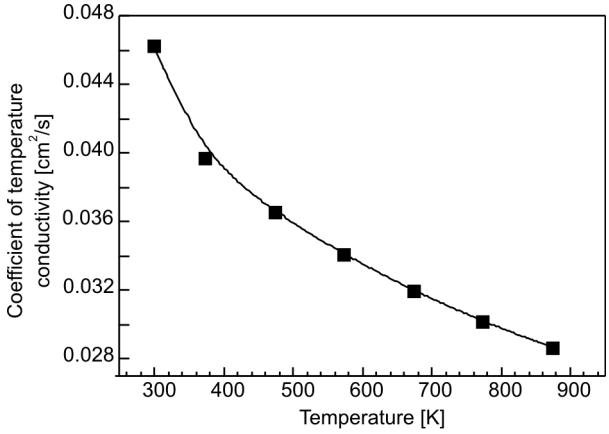

Fig. 3. Temperature dependence of the coefficient of temperature conductiity of Cr_2AlC

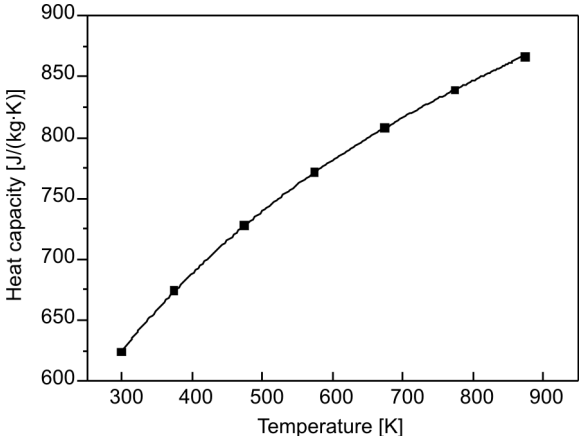

Fig. 4. Temperature dependence of the specific heat capacity of Cr_2AlC

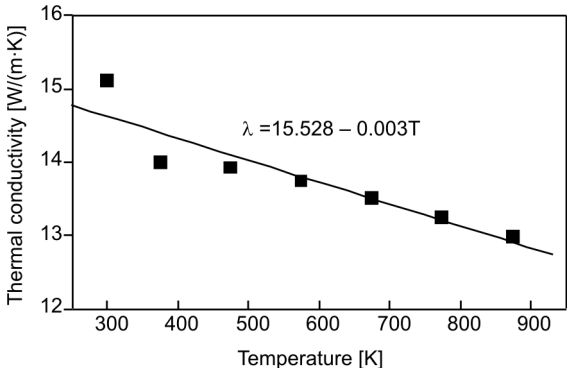

Fig. 5. Temperature dependence of the thermal conductivity of Cr_2AlC

The coefficient of temperature conductivity of each sample was determined in the range 25–600 °C. It decreased with the increase in temperature, as shown in Fig. 3. The specific heat capacity 624 J/(kg·K) of the sample obtained from Fig. 4 is higher than that of Ti_2AlC (581 J/(kg·K)) [11], and Cr_2AlC (590 J/(Kg·K)) [9].

The thermal conductivities of the sample λ between 25 °C and 600 °C can be calculated from Eq. (1). The thermal conductivity decreases slightly with the increase in temperature, as shown in Fig. 5. The least-squares fit of the data is shown as a straight solid line in Fig. 5.

The thermal conductivity of the sample in the range of 200-400 °C is from 13.84 W/(m·K) to 13.52 W/(m·K), which is lower than that of Cr_2AlC sample reported by Tian et al. [9]. The difference between the results of the two works is not clearly understood. It is probably due to the difference in particle sizes and impurities in the final samples.

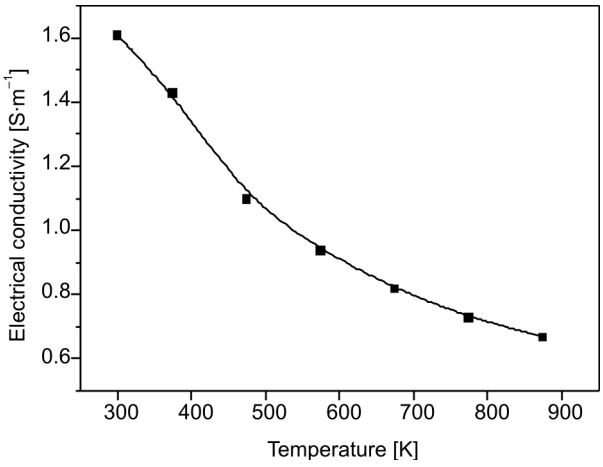

Fig. 6. Temperature dependence of the electrical conductivity of Cr_2AlC

The temperature dependence of the electrical conductivity of the Cr_2AlC sample is shown in Fig. 6 in the range 25–600 °C. The electrical conductivity of the sample decreases with the increase in temperature. At room temperature, the Cr_2AlC had an electrical conductivity of 1.6×10^6 S·m^{-1}, which is lower than that of Ti_3SiC_2 and Ti_3AlC_2.

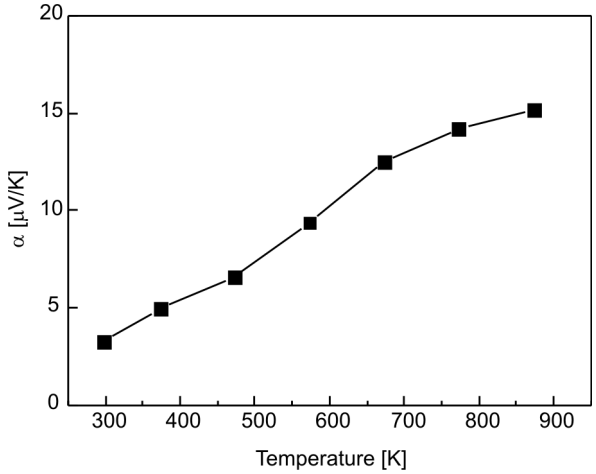

Fig. 7. Temperature dependence of the Seebeck coefficient of the Cr_2AlC sample

Figure 7 shows the Seebeck coefficient of Cr_2AlC in function of temperature. It changes in the range from 3.3 to 15.2 μV/K between room temperature and 873 K. This small positive value of the Seebeck coefficient and the metallic conductivity suggest that Cr_2AlC, similarly as Ti_3SiC_2 [12], is a semi-metal with hole carriers.

4. Conclusions

Dense polycrystalline Cr_2AlC can be obtained by hot pressing of the Cr, Al and Cr_3C_2 powders. A slight excess of Al is beneficial to synthesis of Cr_2AlC. The optimum temperature is 1350 °C. Cr_2AlC grains have an obvious, layered nature.

The flexural strength, fracture toughness and compressive strength of the obtained sample were 498 MPa, 5.8 MPa·m$^{1/2}$ and 627 MPa, respectively. It had the Vickers hardness of 5.2 GPa and could be easily machined by using ordinary mechanical machining tools.

The coefficient of thermal expansion of Cr_2AlC is 1.3×10^{-5} K^{-1} in the range 25 –1200 °C. The temperature coefficients of thermal conductivity and electrical conductivity decrease upon increase of temperature. The heat capacity of Cr_2AlC increases from 624 J/9kg·K) to 867 J/(kg·K) over the range of 25–600°C.

The Seebeck coefficient changed from 3.3 to 15.2 μV/K between room temperature and 873 K. These small positive values of the Seebeck coefficient suggest that Cr2AlC is semi-metallic with hole carriers.

Acknowledgements

The authors are grateful for the support given by the National Natural Science Foundation of China under Contracts No. 50572080, No. 20771088 and Doctoral Foundation of Wuhan University of Technology (No.471-38650142).

References

[1] BARSOUM M.W., Prog. Solid. St. Chem., 28 (2000), 201.
[2] BOUCHAIB M., Phys. Rev. B., 73 (2006), 024110.
[3] SCHUSTER J.C., NOWOTNY H., VACCARO C., J. Solid St. Chem., 32 (1980), 213.
[4] TIAN W.B., WANG P.L., KAN Y.M., ZHANG G.J., LI Y.X., YAN D.S., Mater. Sci. Eng. A., 3 (2007), 229.
[5] LIN Z.J., ZHOU Y.C., LI M.S.,WANG J.Y., Z. Metall., 6 (2005), 291.
[6] ZHU J.Q., MEI B.C., LIU J., XU X.W., J. Mater. Sci. Lett., 22 (2003), 1111.
[7] ZHOU W.B., MEI B.C., ZHU J.Q., Mater. Lett., 59 (2005), 1547.
[8] TIAN W.B., WANG P.L., ZHANG G.J., KAN Y.M., LI Y.X., YAN D.S., Mater. Sci. Eng. A., 454–455 (2007), 132.
[9] TIAN W.B., WANG P.L., ZHANG G.J., KAN Y.M.,LI Y.X., YAN D.S., Scripta Mater., 54 (2006), 841.
[10] TZENOV N.V., BARSOUM M.W., J. Am. Ceram. Soc., 3 (2000), 825.
[11] BARSOUM, M.W., SALAMA I., EL-RAGHY T., GOLCZEWSKI J., PORTER W.D., WANG H., SEIFERT H.J., ALDINGER F., Metall. Mater. Trans. A, Phys. Metall. Mater. Sci., 33 (2002), 2775.
[12] GAO N.F., MIYAMOTO Y., ZHANG D., J. Mater. Sci. Lett., 34 (1999), 4385.

Received 23 May 2008
Revised 26 February 2009