

Synthesis of a Cr₂AlC-Ti₂AlC ternary carbide

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The Cr₂AlC ternary carbide is excellent in chemical and oxidation resistances as well as mechanical properties at high temperatures. Therefore it satisfies most requirements for as an interconnector material in solid oxide fuel cells (SOFCs). However, its thermal expansion coefficient is higher than those of the anode and cathode so that a high thermal stress is generated unavoidably between them during heating and cooling SOFCs. Thus we attempted to reduce the thermal expansion coefficient through a solid solution with Ti₂AlC which has a lower thermal expansion coefficient. Dense and single phase (Cr_{1-x}Ti_x)₂AlC solid solutions with a relative density of 99.5% or more were synthesized by hot pressing a mixture of Cr_x, Ti₂C, Al powders at 1250 °C for 4 h. The limitation of Ti substitution was found to be less than 20 mol%. When Ti substitution exceeded this limit, unreacted Ti₂C, Cr₇C₃, and Cr₃C₂ remained as second phases. The grain size decreased with Ti substitution. With 5 mol% Ti substitution, the thermal expansion coefficient could be lowered by 5% compared with the case without substitution in the temperature range of 700–800 °C.

Key words: Cr₂AlC, Ti₂AlC, solid solution, thermal expansion coefficient, oxidation resistance.

Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices that efficiently generate clean energy. Their operation temperatures are above 700 °C, which is quite high compared with the other fuel cells such as polymer electrolyte membrane fuel cells or molten carbonate fuel cells. The unique operation and performance characteristics of SOFCs are suitable to distribute on-site cogeneration of heat and power [1]. However, the components of SOFCs, electrolytes, cathodes, anodes, and interconnects, are placed in a severe operating environment chemically and mechanically because of the high operation temperature. Among them, interconnect materials must be chemically and mechanically stable both in oxidizing and reducing conditions at the high operation temperatures. In addition, they must have good electrical conductivity and an adequate thermal expansion coefficient to avoid the generation of thermal stresses between the adjacent components, the cathode and anode, during heating and cooling [2].

Ternary carbide compounds represented by M_{n+1}AC_n (where n is 1, 2, or 3; M is an early transition metal; A is an A-group element) display unique properties such as high electrical conductivity, high elastic modulus, excellent thermal shock resistance and easy machinability similar to metals. Also they have excellent chemical resistance and

heat resistance similar to covalent-bonded ceramics [3–5], and can be strong candidates for interconnect materials of SOFCs. Ti-based ternary carbides such as Ti₃SiC₂, Ti₃AlC₂, and Ti₂AlC had been studied intensively by other researchers [6–8]. However, it has been reported that Ti-based ternary carbides do not have a good high temperature oxidation resistance above 1100 °C [9, 10].

Recently it has been reported that the Cr-based ternary carbide Cr₂AlC displays a higher oxidation resistance owing to protective α -Al₂O₃ and α -Cr₂O₃ films on the surface [11, 12]. Tian *et al.* reported that it is not easy to synthesize high purity Cr₂AlC by hot pressing a Cr, Al, and graphite powder mixture since Al, as a starting material, readily evaporated during hot pressing [13]. The evaporation of Al seemed to be accelerated by the exothermic reaction between the Cr and graphite. Han *et al.* synthesized high purity Cr₂AlC by hot pressing a Cr_x and Al powder mixture at 1200 °C [14]. They suggested that the exothermic reaction could be eliminated by using Cr_x and Al as starting materials.

From the viewpoint of oxidation resistance, Cr₂AlC seems to be the best candidate for an interconnect material amongst the ternary carbides. However, the thermal expansion coefficient (TEC) of Cr₂AlC ($13.3 \times 10^{-6} \text{ K}^{-1}$) is high compared to the adjacent components. The TEC of LaMnO₃, which is widely used as a cathode, is in the range of $11.3\text{--}12.4 \times 10^{-6} \text{ K}^{-1}$ and the TEC of Ni/YSZ which is used as an anode is in the range of $11.6\text{--}13.2 \times 10^{-6} \text{ K}^{-1}$ [15, 16]. In this study, we tried to substitute Ti for Cr in Cr₂AlC to reduce the TEC of Cr₂AlC because the TEC of Ti₂AlC is quite low ($8.2 \times 10^{-6} \text{ K}^{-1}$). Cr_x, TiC_x and Al powder mixtures were used as starting materials to avoid the

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exothermic reaction. Crystallographic and microstructure analyses were performed using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Experimental

Cr ($< 45 \mu\text{m}$, 99.9% purity, Junsei Chemical Co. Ltd., Japan) and graphite ($10 \mu\text{m}$, 99.95% purity) powders were mixed at a molar ratio of Cr : C = 2 : 1 in a SPEXTM mill for 20 minutes in air and then formed into a disc type green pellet by uniaxially pressing it at 20 MPa. The mixture was heated at 1550°C for 3 h under an Ar flow to obtain CrC_x . TiC_x was also prepared using Ti ($< 40 \mu\text{m}$, 99.9% purity, High Purity Chemicals, Japan) powder in the same synthesis procedure as used for CrC_x . Synthesized and partially sintered CrC_x and TiC_x were ground, and screened to a diameter of $< 45 \mu\text{m}$. CrC_x , TiC_x , and Al ($< 45 \mu\text{m}$, 99.7% purity, Strem Chemicals, Inc., USA) powders were weight to be compositions of $(\text{Cr}_{1-x}\text{Ti}_x)_2\text{AlC}$ ($x = 0, 0.05, 0.1, 0.2$) and were mixed using a SPEXTM mill for 20 minutes in air. The mixtures were then hot pressed at 1250°C for 4 h under a pressure of 25 MPa to form $30 \text{ mm}\phi \times 10 \text{ mm}$ bulk specimens in flowing Ar gas.

The bulk specimens were cut into $5 \times 5 \times 12 \text{ mm}^3$ bars to measure a TEC using a dilatometer (Model 402, Netzsch, Germany) in the temperature range between 400 and 1000°C . The phase analysis and microstructures of specimens were investigated with an X-ray diffractometer (Model D-8, Bruker, Germany) and a scanning electron microscope (Model S-3000H, Hitachi, Japan).

Results and Discussion

Cr_2AlC and Ti_2AlC have a hexagonal structure of space group, $\text{P6}_3/\text{mmc}$. They show good thermal and electrical conductivities, high elastic moduli, and machinabilities due to their layered structures [6, 13]. Table 1 listing their properties shows that Ti_2AlC has advantages such as a lower theoretical density, and higher thermal and electrical conductivities compared with Cr_2AlC . It also has a lower thermal expansion coefficient.

When carbon or graphite is used as a carbon source in the synthesis of Cr_2AlC and Ti_2AlC , intermediate products such as chromium carbides, titanium carbides and Al_4C_3

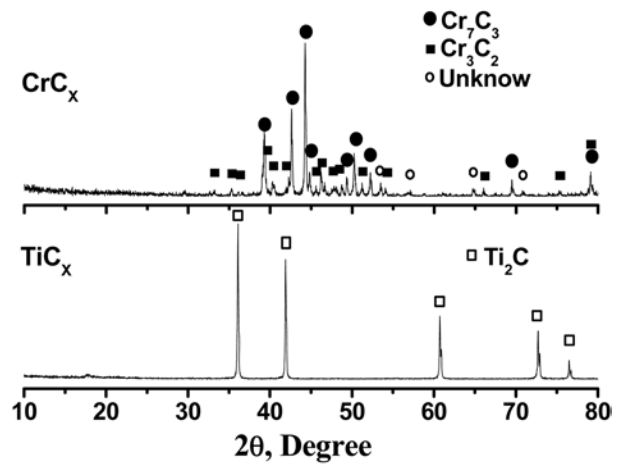


Fig. 1. XRD results from CrC_x and TiC_x .

are formed by exothermic reactions. As a result, some of Al in the starting materials evaporates and thus unreacted chromium carbides can remain in the sample [13]. Hence, in the present study, chromium carbides and titanium carbides were synthesized first and then mixed with Al powder to make Cr_2AlC - Ti_2AlC solid solutions.

Fig. 1 shows the XRD results of the chromium carbides and titanium carbides synthesized. The titanium carbide was a single phase of Ti_2C , while the chromium carbides were composed of Cr_7C_3 and Cr_3C_2 . Bulk samples of Cr_2AlC - Ti_2AlC solid solutions with Ti substitutions of 5, 10, and 20 mol% were synthesized by hot pressing the mixture of CrC_x , Ti_2C , Al powders at 1250°C for 4 h at a pressure of 25 MPa. These synthesis conditions were determined from the results of preliminary experiments that Cr_7C_3 and Cr_3C_2 remained as a second phase with a synthesis temperature of Cr_2AlC lower than 1250°C , and a dense sintered body (relative density of 99.5% or more) with a well-developed layered structure could be obtained with the conditions of 1250°C for 4 h.

Fig. 2(a) is the XRD results of the samples of Cr_2AlC and solid solutions synthesized. In the case of the Cr_2AlC and the solid solutions with Ti substitutions of 5 and 10 mol%, only Cr_2AlC peaks were observed, indicating that Ti substituted for Cr. However, in the case of the sample with a Ti substitution of 20 mol%, peaks of unreacted Ti_2C , Cr_7C_3 , and Cr_3C_2 were observed, but Al peaks were not observed. This is similar to the results of Tian *et al.* [13] that some Cr_7C_3 forms by the evaporation of Al in the synthesis of Cr_2AlC . Fig. 2(b) is the enlarged part of the XRD patterns for 2θ between 38° and 46° . It can be seen that the (103) peak moved toward a lower angle as the Ti substitution was increased. Table 2 shows the lattice parameters of the solid solutions determined from the XRD results. Both lattice parameters a and c increased with the Ti substitution. However, the amount of these increases of the lattice parameters were very small compared with the difference of lattice parameters between Ti_2AlC and Cr_2AlC as shown in Table 1. This is different from the

Table 1. Comparison of the properties of Cr_2AlC and Ti_2AlC

| Property | Cr_2AlC [13] | Ti_2AlC [6] |
|--|------------------------------|-----------------------------|
| a (Å) | 2.863 | 3.051 |
| c (Å) | 12.814 | 13.637 |
| Theoretical Density (g/cm^3) | 5.229 | 4.113 |
| Coefficient of Thermal expansion (K^{-1}) | 1.33×10^{-5} | 8.2×10^{-6} |
| Thermal conductivity at 200°C W/(m K) | 17.5 | 41.7 |
| Electrical Conductivity (S/m) | 1.4×10^6 | 2.7×10^6 |
| Hardness (GPa) | 3.5 | 4.5 |

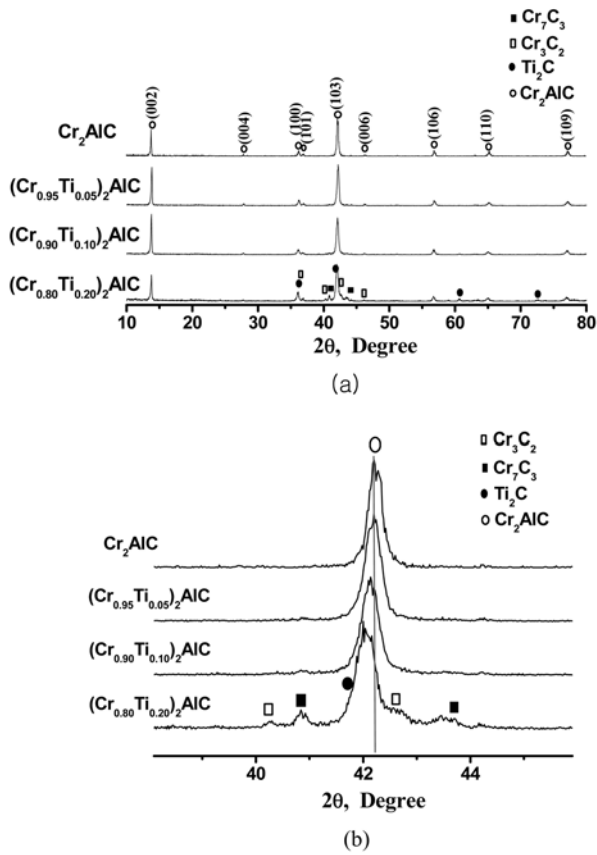


Fig. 2. XRD results(a) and enlarged (103) peaks(b) of Cr_2AlC and Cr_2AlC - Ti_2AlC solid solutions.

Table 2. Lattice parameter changes in $(\text{Cr}_{1-x}\text{Ti}_x)_2\text{AlC}$ as a function of Cr/Ti contents

| | a (Å) | c (Å) |
|--|---------|---------|
| Cr_2AlC | 2.860 | 12.816 |
| $(\text{Cr}_{0.95}\text{Ti}_{0.05})_2\text{AlC}$ | 2.862 | 12.825 |
| $(\text{Cr}_{0.90}\text{Ti}_{0.10})_2\text{AlC}$ | 2.864 | 12.829 |
| $(\text{Cr}_{0.80}\text{Ti}_{0.20})_2\text{AlC}$ | 2.869 | 12.855 |

results of Salama *et al.* that the lattice parameters of a $(\text{Ti}_{0.47}\text{Nb}_{0.53})_2\text{AlC}$ solid solution have nearly intermediate values between those of Ti_2AlC and Nb_2AlC [17]. In the case of $(\text{Ti}_{0.47}\text{Nb}_{0.53})_2\text{AlC}$, the atomic radius of Nb (2.08 Å) is about the same as that of Ti (2.0 Å) so that there was no difficulty in forming a solid solution. On the other hand, in the case of the Cr_2AlC - Ti_2AlC solid solution, the atomic radius of Cr (1.85 Å) is quite different from that of Ti so that there seemed to be a limitation in forming a solid solution. When a Cr_2AlC - Ti_2AlC solid solution was synthesized by the present method, the limitation of the solid solution was found to be less than 20 mol%.

Fig. 3 shows the microstructures of the fracture surfaces of Cr_2AlC , $(\text{Cr}_{0.95}\text{Ti}_{0.05})_2\text{AlC}$, $(\text{Cr}_{0.90}\text{Ti}_{0.10})_2\text{AlC}$, and $(\text{Cr}_{0.80}\text{Ti}_{0.20})_2\text{AlC}$ sintered samples. As shown in Fig. 3, the greater the Ti addition to Cr_2AlC , the smaller the grain size of Cr_2AlC - Ti_2AlC solid solution becomes. The average grain size of Cr_2AlC was 15 μm and this decreased to 8 μm with a 20 mol% Ti substitution. For all the solid solution samples, a “comb teeth” pattern was observed,

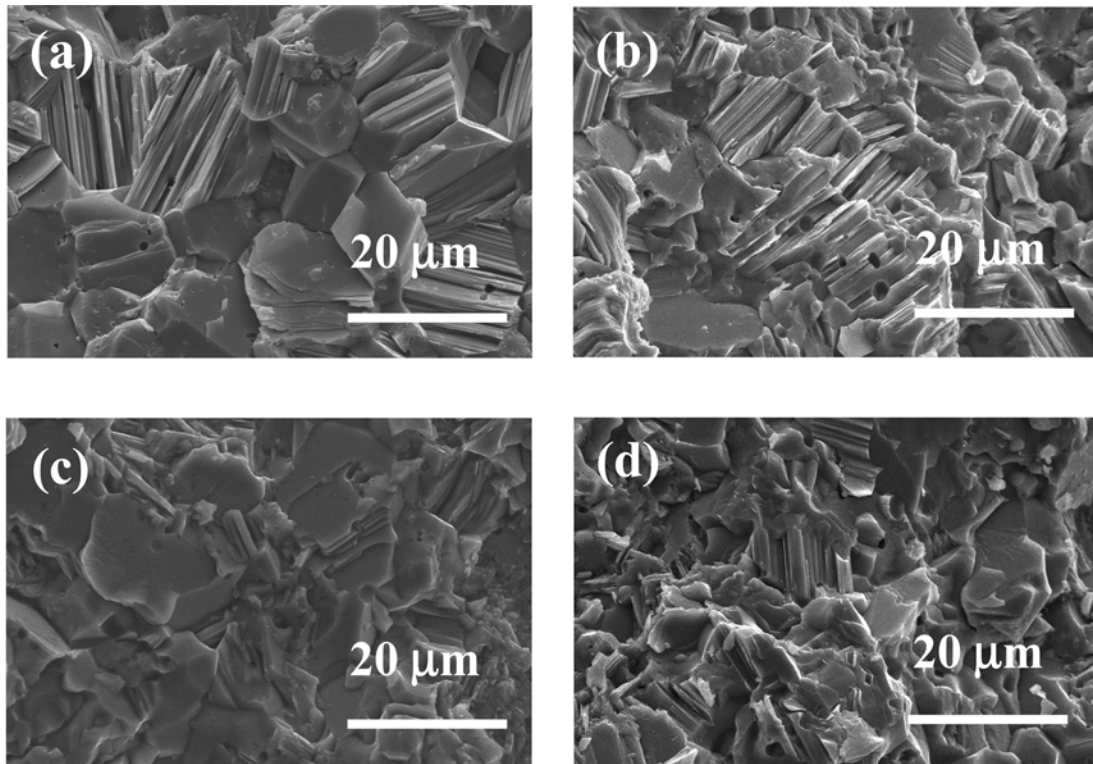


Fig. 3. SEM micrographs showing fracture surfaces of Cr_2AlC (a), and Cr_2AlC - Ti_2AlC solid solutions with 5 (b), 10 (c), 20 mol%(d) of Ti substitution.

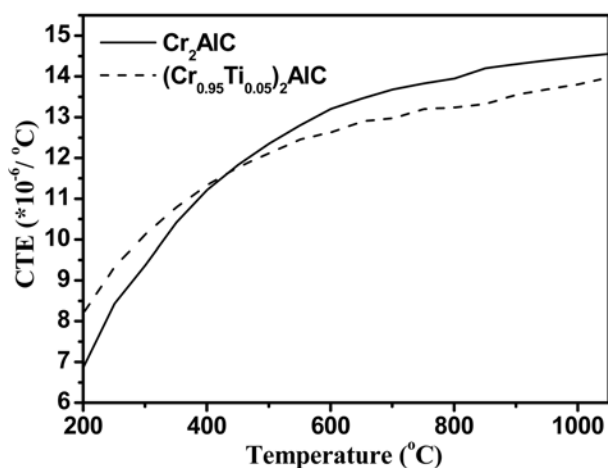


Fig. 4. The thermal expansion coefficient of Cr_2AlC and $(\text{Cr}_{0.95}\text{Ti}_{0.05})_2\text{AlC}$ solid solutions in the temperature range between 200 and 1000 °C.

which appears in the fracture surfaces of grains with the layered structure. From such microstructures, it is expected that these solid solutions also would be machinable.

Fig. 4 shows the variation of the thermal expansion coefficients of Cr_2AlC and $(\text{Cr}_{0.95}\text{Ti}_{0.05})_2\text{AlC}$ with temperature. From room temperature to 400 °C, the thermal expansion coefficient of Cr_2AlC was lower, but above 400 °C, $(\text{Cr}_{0.95}\text{Ti}_{0.05})_2\text{AlC}$ exhibited lower values. At temperatures above 700 °C, which corresponds to the operating temperature of SOFCs, the thermal expansion coefficient of $(\text{Cr}_{0.95}\text{Ti}_{0.05})_2\text{AlC}$ was 5% lower than that of Cr_2AlC . Ti_2AlC has a lower thermal expansion coefficient than Cr_2AlC . Therefore the thermal expansion coefficient of Cr_2AlC could be lowered by the substitution of Ti for Cr.

Summary

Dense $(\text{Cr}_{1-x}\text{Ti}_x)_2\text{AlC}$ solid solutions with a relative density of 99.5% or more were synthesized by hot-pressing a mixture of CrC_x , Ti_2C , Al powders at 1250 °C for 4 h. The limitation of Ti substitution was less than 20 mol%, and the grain size decreased with the Ti substitution. With 5 mol% Ti substitution, the thermal expansion coefficient could be lowered by 5% compared to the case without substitution in the temperature range of 700–800 °C.

Acknowledgements

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