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Electrical and Thermal Properties of Ti_3AlC_2 at High Temperature

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Abstract

In this paper, we report on the electrical and thermal properties of predominantly single-phase Ti_3AlC_2 ceramics (96.7 wt%) as a function of temperature. The results show that Ti_3AlC_2 is a good electrical and thermal conductor at high temperature. From 300 to 1173 K, the electrical resistivity of Ti_3AlC_2 increases linearly from 3.4×10^{-5} to 1.1×10^{-4} $\Omega \cdot m$, which indicates that Ti_3AlC_2 ceramic is a metallic conductor. In the 473 to 1473 K temperature range, the coefficient of thermal expansion of Ti_3AlC_2 yields an average value of 9.3×10^{-6} K^{-1}, which is comparable with the coefficients of Ti_2AlC and Ti_3SiC_2. The thermal conductivity increases from 22.6 to 26.4 $W \cdot m^{-1} \cdot K^{-1}$ with rising temperature from 473 to 1473 K. It is found that the electronic contribution to the thermal conductivity is the dominant mechanism. The molar heat capacity of Ti_3AlC_2 is 138.6 $J \cdot mol^{-1} \cdot K^{-1}$ at 473 K and extrapolates to 168.5 $J \cdot mol^{-1} \cdot K^{-1}$ at 1473 K.

Keywords: Ceramics, thermal conductivity, thermal expansion, electrical properties

I. Introduction

Ti_3AlC_2 is an important member of $M_{n+1}AX_n$ phase ($n = 1-3$), where M = early transition metal, A = an A-group element (mostly IIIA and IVA), and X = C or N [1–4]. And it has been proven that Ti_3AlC_2 combines the unique properties of both ceramics and metals. Similar to ceramics, Ti_3AlC_2 is oxidation resistant [5–8], high-temperature stable up to 1360 °C [9, 10] and lightweight with a measured low density of 4.21 g/cm^3 [11]. Similar to metals, Ti_3AlC_2 is elastically stiff with a Young's modulus of 297 GPa, damage- and thermal-shock-tolerant [12], and it behaves quasi-plastically under compression at temperatures above 1000 °C [2, 13]. Such salient properties make Ti_3AlC_2 suitable for potential applications in high-temperature areas. The electrical properties [13] and the thermal properties of Ti_3AlC_2 [14] at low temperatures (< 285 K) have been well studied. However, as far as we are aware, there are no reports about the electrical and thermal properties of Ti_3AlC_2 at high temperature. In this paper, Ti_3AlC_2 fabricated by means of self-propagating high-temperature synthesis (SHS) and its electrical resistance was investigated at 300 – 1173 K. The coefficient of thermal expansion, thermal conductivity and the heat capacity of Ti_3AlC_2 were also reported for the 473 – 1473 K range.

II. Experimental

Polycrystalline Ti_3AlC_2 was fabricated by means of the SHS technique; the experimental details can be found elsewhere [3]. In brief, Ti, Al and C elemental powders were adequately ball-milled in a nylon jar using WC balls. After mixing and drying, the powders were cold-compressed into a cylindrical compact of 55 mm diameter × 25 mm height with a compact density of 60 % of the theoretical density. The SHS experiments were performed in a stainless-steel combustion chamber. The Ti-Al-C compact was ignited from one end by a tungsten heating element, and then the combustion wave quickly propagated. As soon as the combustion wave extinguished, a pressure of 200 MPa was applied for 20 s to obtain densified samples. To avoid oxidation, the resultant samples were then quickly transferred into sand and cooled down to room temperature. XRD quantitative results [15] show that there is a predominant percentage of Ti_3AlC_2 (96.7 wt%) and very low impurity of TiC (3.3 wt%). XRD results also demonstrate that there is no preferential orientation. The relative density is calculated to be 97 % according to the Archimedes' principle. SEM results show the grain size of Ti_3AlC_2 is of the average order of 10 μm.

The electrical resistance and its temperature dependence were measured using a 2 mm × 2 mm × 15 mm sample with a four-point probe method at 300 – 1173 K using self-designed equipment. The coefficient of thermal expansion (CTE) was measured with a Unitherm™ 1252 ultra-high temperature dilatometer (Anter Corp., Pittsburgh, USA) in the temperature range of 473 – 1473 K in an argon atmosphere. The thermal conductivity and thermal diffusivity were measured using a disk sample measuring ∅12.7 mm × 3.14 mm with a Flashline TM 5000 thermal properties analyzer (Anter Corp., Pittsburgh, USA).

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The heat capacity, C_p ($J\cdot mol^{-1}\cdot K^{-1}$), was calculated according to the following equation:

$$C_p = \frac{k}{\alpha\rho} \quad (1)$$

where *k* is the thermal conductivity ($W\cdot m^{-1}\cdot K^{-1}$), α thermal diffusivity ($cm^2\cdot s^{-1}$) and ϱ the density ($g\cdot cm^{-3}$).

III. Results and Discussion

(1) Electrical properties

Fig. 1 shows the electrical resistivity and the conductivity as a function of temperature from 300 to 1173 K. The relationship between electrical conductivity and electrical resistivity is

$$\rho = \frac{1}{\sigma} \quad (2)$$

where ϱ is the electrical resistivity (Ω·m), σ is the electrical conductivity ($\Omega^{-1}\cdot m^{-1}$). At room temperature, the electrical conductivity of Ti_3AlC_2 is 2.9×10^6 $\Omega^{-1}\cdot m^{-1}$, which is close to that of Ti_2AlC (2.8×10^6 $\Omega^{-1}\cdot m^{-1}$)[16], but less than that of Ti_3SiC_2 (4.5×10^6 $\Omega^{-1}\cdot m^{-1}$) [17]. At a higher temperature of 750 K, our calculated data yield an electrical conductivity of 1.29×10^6 $\Omega^{-1}\cdot m^{-1}$, in good agreement with the previous result of 1.23×10^6 $\Omega^{-1}\cdot m^{-1}$ [1]. This testifies to the reliability and accuracy of our measurement. With increasing temperature from 300 to 1173 K, the electrical resistivity of Ti_3AlC_2 increases linearly from 3.4×10^{-5} to 1.1×10^{-4} Ω·m. Based on the Bloch-Grüneisen law, it is known that the electrical resistivity of a metal shows a direct proportionality with the temperature greater than 0.5 Debye temperature. The reported Debye temperature of Ti_3AlC_2 is 764 K [14]. Therefore, from the viewpoint of electrical conduction, Ti_3AlC_2 exhibits the same conducting mechanism as a metal and therefore is a metallic conductor. A least square fit of data in Fig. 1 yields the expression:

$$\rho = \rho_0[1 - \beta\Delta T] = 11.49[1 - 0.0082(1173 - T)] \quad (3)$$

where ϱ_0 is the electrical resistivity at 1173 K (μΩ·m), β the temperature coefficient of resistivity and *T* the absolute temperature (K).

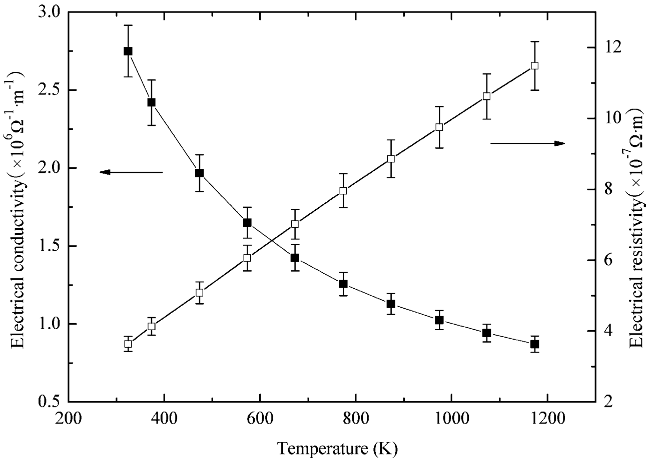

Fig. 1 Electrical resistivity and conductivity of Ti_3AlC_2 as a function of temperature.

(2) Thermal properties

Fig. 2(a) shows the thermal expansion of Ti_3AlC_2 in the temperature range of 473 – 1473 K upon heating. It can be seen that the unit linear expansion increases with rising temperature. The CTE increases slightly at the initial and final stages, respectively, whereas it remains steady in the middle temperature range. The linear fit of the data yields a mean CTE of 9.3×10^{-6} K^{-1}, which is greater than the CTEs of Ti_2AlC (8.7×10^{-6} K^{-1}) [16] and Ti_3SiC_2 (9.2×10^{-6} K^{-1}) [18]. This value is in good agreement with the reported value of $(9.0 \pm 0.2) \times 10^{-6}$ K^{-1} for $Ti_3Al_{1.1}C_{1.8}$ over the 298 – 1473 K temperature range. The temperature dependence of the thermal diffusivity was plotted in Fig. 2(b). It is found that the thermal diffusivity basically remains the same with the increase in temperature. As shown in Fig. 2(c), the thermal conductivity of Ti_3AlC_2 increases from 22.6 to 26.4 $W\cdot m^{-1}\cdot K^{-1}$ with rising temperature from 473 to 1473 K. In general, the total thermal conductivity, k_{total}, is associated with both the electronic and phonon contributions, i.e.,

$$k_{total} = k_e + k_{ph} \quad (4)$$

where k_e and k_{ph} are the electronic and phonon contributions to the total conductivity, respectively. k_e can be calculated according to the Wiedemann-Frans law:

$$k_e = \frac{L_0 T}{\rho} \quad (5)$$

where ϱ and *T* have the same meanings as defined previously, and L_0 Lorenz number (2.45×10^{-8} $W\cdot\Omega\cdot K^{-2}$). To date, this expression has been found to be valid for many MAX phases [1]. At 1300 K, the calculated k_e of Ti_3AlC_2 is 23.7 $W\cdot m^{-1}\cdot K^{-1}$, which is very close to the total thermal conductivity, k_{total}, 26.4 $W\cdot m^{-1}\cdot K^{-1}$. Based on this observation, it can be concluded that for Ti_3AlC_2, the electron contributes greater to the thermal conductivity at high temperature. For comparison, the thermal conductivities of selected MAX phase materials are listed here [16], see Table 1. The highest k_{total} at 1300 K belongs to Ti_2AlC. Moreover, from the table, we can see that the electron plays a major role in the thermal conduction for the five MAX-phase compounds at high temperature.

Table 1: The thermal conductivities of selected MAX-phase materials.

Compound	k_{tot} ($W\cdot m^{-1}\cdot K^{-1}$)	k_e ($W\cdot m^{-1}\cdot K^{-1}$)	k_{ph} ($W\cdot m^{-1}\cdot K^{-1}$)
Ti_2AlC	36	19.7 (55 %)	15 (38 %)
Nb_2SnC	30	25 (82 %)	5 (18 %)
Ti_3AlC_2	25	23.7 (95 %)	1.3 (5 %)
Ti_3SiC_2	33	32 (97 %)	1 (3 %)
$Ti_4AlN_{2.9}$	20	10 (50 %)	10 (50 %)

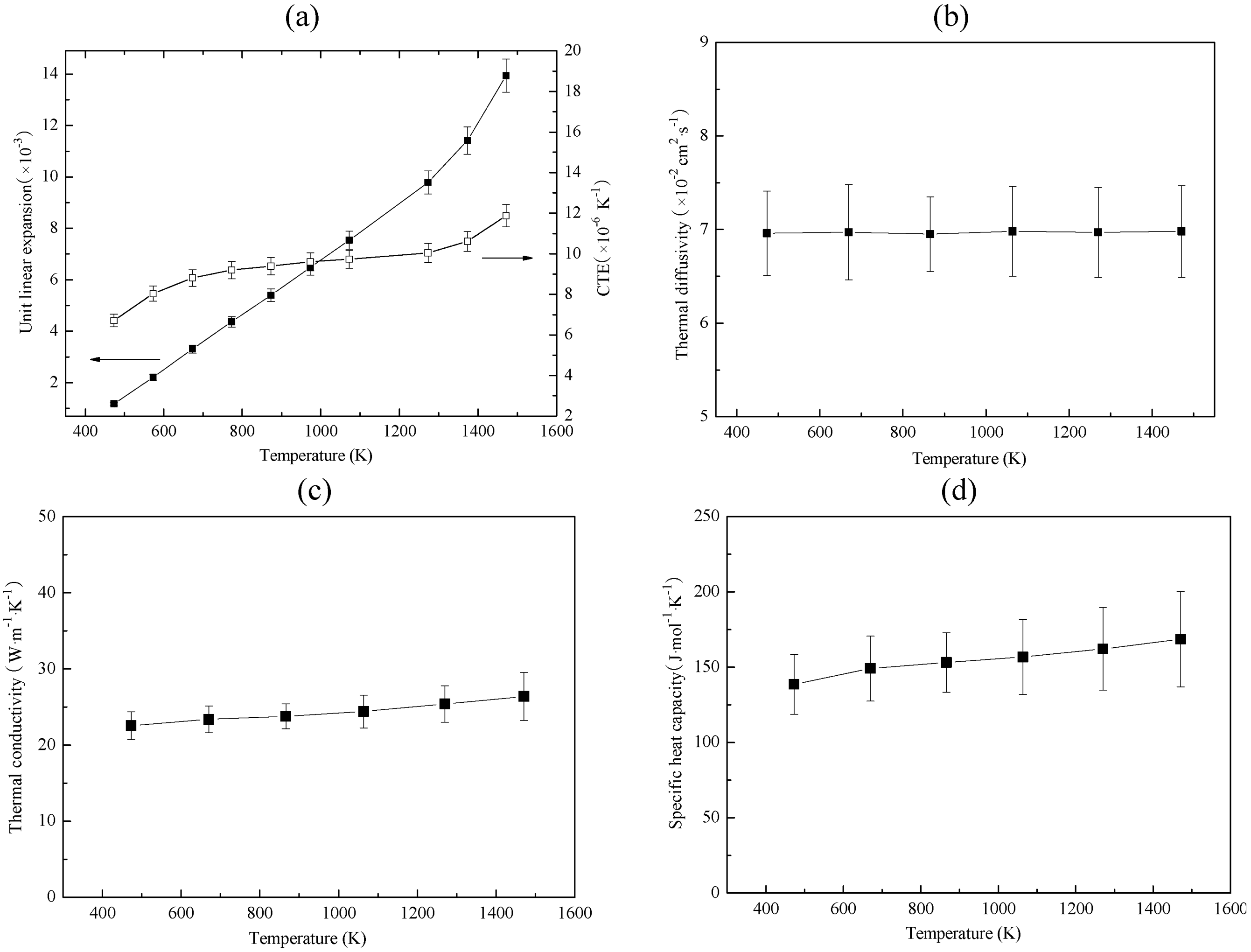

Fig. 2 Temperature dependence of (a) thermal expansion, (b) thermal diffusivity, (c) thermal conductivity and (d) molar thermal capacity of Ti_3AlC_2.

According to Eq. (1), the molar heat capacity of the sample was calculated at 473 – 1473 K. Fig. 2 (d) plots the temperature dependence of C_p. Like most MAX phases studied to date, it can be seen that the C_p of Ti_3AlC_2 increased with rising temperature. However, recent work on Ti_2AlC and Ti_2InC showed a decrease of C_p with increasing temperatures owing to the loss of A-group element, i.e. Al and In [16, 19], respectively. At 473 and 1470 K, the molar heat capacity of Ti_3AlC_2 is 138.6 and 168.5 $J{\cdot}mol^{-1}{\cdot}K^{-1}$, respectively, which is higher than those of Ti_2AlC (91.64 and 111.27 $J{\cdot}mol^{-1}{\cdot}K^{-1}$) [16].

IV. Conclusion

Ti_3AlC_2 is demonstrated to be a good electrical and thermal conductor. In the temperature range of 300 – 1173 K, the electrical conductivity decreases from 2.9×10^6 to $9.1\times10^5\ \Omega^{-1}\ m^{-1}$. In the 473 to 1473 K temperature range, the coefficient of thermal expansion yields an average value of $9.3\times10^{-6}\ K^{-1}$. The thermal conductivity increases from 22.6 to 26.4 $W{\cdot}m^{-1}{\cdot}K^{-1}$ and the molar heat capacity increases from 138.6 to 168.5 $J{\cdot}mol^{-1}{\cdot}K^{-1}$ in the 473 – 1473 K range.

Acknowledgements

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