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Synthesis and thermal stability of Cr_2AlC

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Abstract

A new reaction route with $AlCr_2$ and C as starting materials has been developed to produce Cr_2AlC. A Cr_2AlC bulk ceramic was achieved by hot pressing the $AlCr_2$ and C powders at 1400 °C with 20 MPa for 1 h in Ar. The mechanism to form Cr_2AlC in a temperature range of 1050–1400 °C was studied. It was confirmed that Cr_2AlC is formed directly by a reaction between C and $AlCr_2$. The reaction process, phase composition and microstructure were characterized with differential thermal analysis, X-ray diffractometry and scanning electron microscopy. The produced Cr_2AlC ceramic is stable up to 1500 °C in an Ar atmosphere, but decomposes into Al_8Cr_5 and $Cr_{23}C_6$ above 1500 °C.

Keywords: Cr_2AlC; Carbides; Hot pressing; Microstructure; Thermal properties

1. Introduction

The Cr_2AlC ternary carbide displays both ceramic and metallic behaviour. This MAX phase material exhibits a combination of attractive properties.[1–5] It has a high strength and yet is relatively ductile. The material is a good electrical and thermal conductor. Due to its oxidation and corrosion resistance as well as to thermal shock resistance, it can be used at high temperatures and in aggressive environments. Unlike conventional ceramics, Cr_2AlC is easily machinable.

The mechanical and electrical properties, together with the self-lubricity of Cr_2AlC make this material not only a suitable alternative coating to expensive metallic plating on electrical connectors, but also a good candidate for some applications where graphite or graphite–metal composites are widely used such as bipolar plate in fuel cells, pantographs and electrical brushers. In addition, with the combination of high strength, non-susceptibility to thermal shock, and high temperature oxidation and corrosion resistance, Cr_2AlC is also considered as a promising candidate for structural ceramic components, electrodes, and gas burner nozzles.

So far, several methods have been used to synthesize Cr_2AlC ceramics from mixtures of Cr/Al/C, $Cr/Al_4C_3/C$, or $CrC_{0.5}/Al$ powders including mechanically activated hot pressing,[4] hot isostatic pressing,[6] hot pressing,[3,7,8] and pulse discharge sintering.[9,10] One of the suggested reaction mechanisms to form Cr_2AlC, involves a reaction route between C and an intermediate phase, viz. $AlCr_2$ during sintering.[4,7,11] However, no direct experimental evidence has been provided yet to support such a reaction route.

In this work, $AlCr_2$ was used as a starting material to produce Cr_2AlC. The advantages of a direct synthesis of Cr_2AlC from C and $AlCr_2$ are obvious: (i) the reaction process is simple and more controllable for an $AlCr_2$/C mixture compared with that for the Cr/Al/C or $Cr/Al_4C_3/C$ mixtures upon sintering, (ii) the formation of impurities such as Al_4C_3, Cr_7C_3 and Cr–Al phases in the final product may be avoided, and (iii) pure Cr_2AlC powders and/or bulk materials can be produced on a large scale. The synthesis of a Cr_2AlC ceramic from a mixture of C and $AlCr_2$ will be reported. Results of detailed composition and microstructure analysis of the final product will be presented.

For high temperature applications, some properties for Cr_2AlC have been studied extensively,[1–4,8,9] however, its thermal stability is still unknown. It is well known that MAX phase materials may decompose at very high temperatures. For example, Ti_3SiC_2 becomes unstable at temperatures above 1400 °C in vacuum or Ar atmosphere,[12–14] Ti_3AlC_2 decomposes at above 1400 °C in vacuum atmosphere,[15,16] and Ti_2SnC decom-

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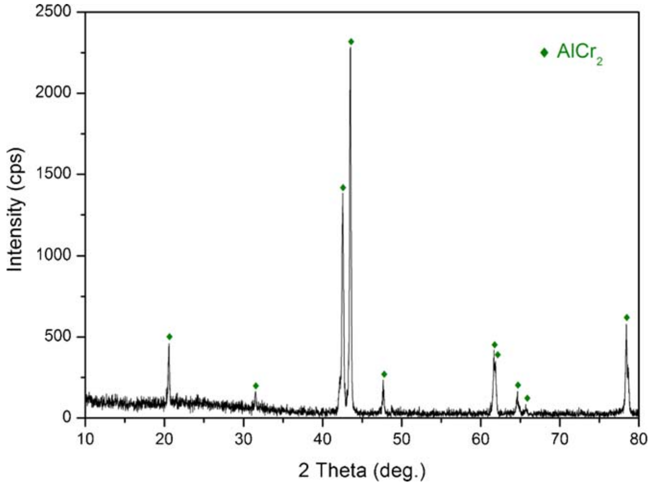

Fig. 1. XRD pattern of 2Cr/1.2Al mixture after pressureless sintering at 1100 °C for 1 h in Ar. ICDD card number for $AlCr_2$ is 03-065-6360.

poses at above 1200 °C in Ar atmosphere[17] and at 1250 °C in vacuum atmosphere,[18] respectively. In this study, the thermal stability of Cr_2AlC was investigated and the results were presented.

2. Experimental procedures

Powders of Cr (particle size <75 μm, 99.5 wt.% purity), Al (particle size <5 μm, 99.5 wt.% purity) and C (graphite, particle size <45 μm, 99.5 wt.% purity) were used as the starting materials.

To produce $AlCr_2$, the Cr and the Al powders with a mole ratio of 2:1.2 (denoted as 2Cr/1.2Al) were mixed for 5 h and then pressurelessly sintered at 1100 °C for 1 h in an Ar atmosphere. Next, the sintered $AlCr_2$ sample was pulverized to a powder and sifted with a 200-mesh sieve.

Subsequently, the designed Cr_2AlC material was prepared from the $AlCr_2$ and C powders with a molar ratio of 1:1 (denoted as $AlCr_2$/C) by pressurelessly sintered at 1050–1400 °C for 15 min in an Ar atmosphere. This mixture was also hot-pressed at 1400 °C for 1 h with 20 MPa in Ar to synthesize a Cr_2AlC bulk ceramic.

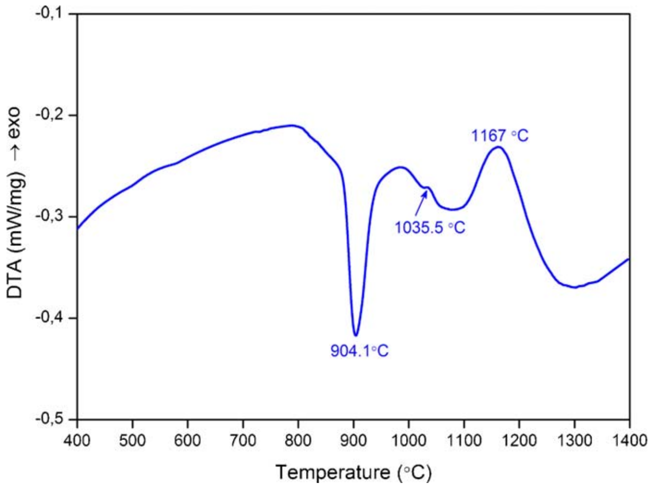

Fig. 2. DTA curve recorded of an $AlCr_2$/C mixture with a heating rate of 15 °C/min in Ar.

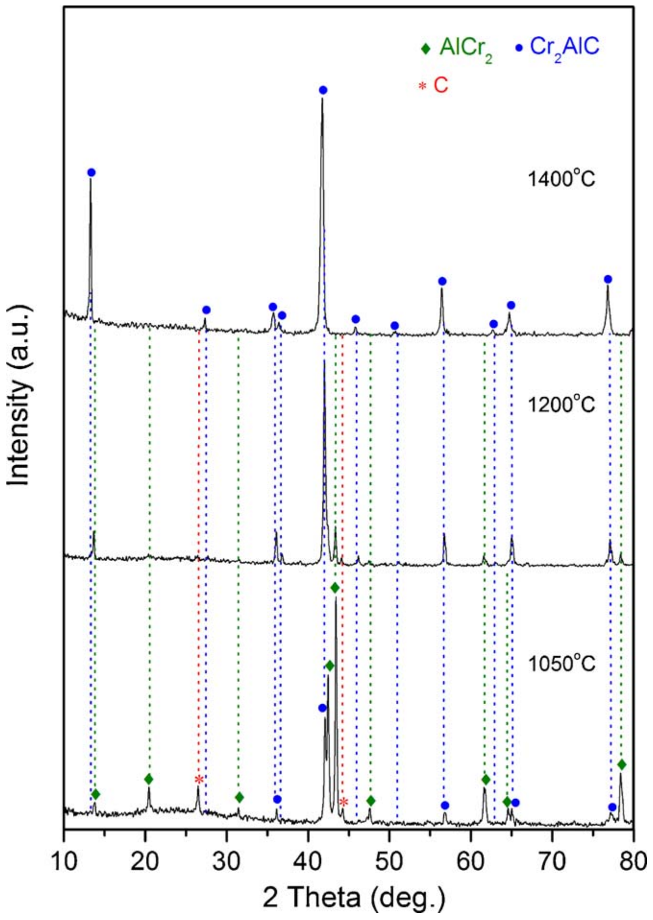

Fig. 3. XRD patterns of $AlCr_2$/C powders after pressureless sintering for 15 min in Ar at 1050 °C, 1200 °C, and 1400 °C, respectively. ICDD card numbers for Cr_2AlC, $AlCr_2$, and C are 01-089-2275, 03-065-6360, and 01-075-1621, respectively.

The phase composition and microstructure of the synthesized materials was identified with X-ray diffractometry (XRD) analysis using a D/Max 2200 PC diffractometer (Tokyo, Japan) operating with Cu Kα radiation, scanning electron microscopy (SEM) using a JEOL JSM 6500F scanning electron microscope (Tokyo, Japan)) equipped with a NORAN System 7 X-ray Microanalysis (XMA) including an Ultra Dry silicon drift detector (SDD) 10 mm^2 (Thermo Scientific, USA), and optical microscopy (OM) using a Neophot 30 optical microscope (Carl Zeiss, Germany).

Differential thermal analysis (DTA) was performed with the $AlCr_2$/C mixture under flowing Ar in a thermal analysis instrument (Netzsch STA409C, Germany) with a heating rate of 15 °C/min in a temperature range of 25–1400 °C. DTA was also used to investigate the thermal stability of Cr_2AlC under flowing Ar in a temperature range of 25–1600 °C with a heating rate of 15 °C/min. The decomposed sample was characterized by XRD, SEM and XMA.

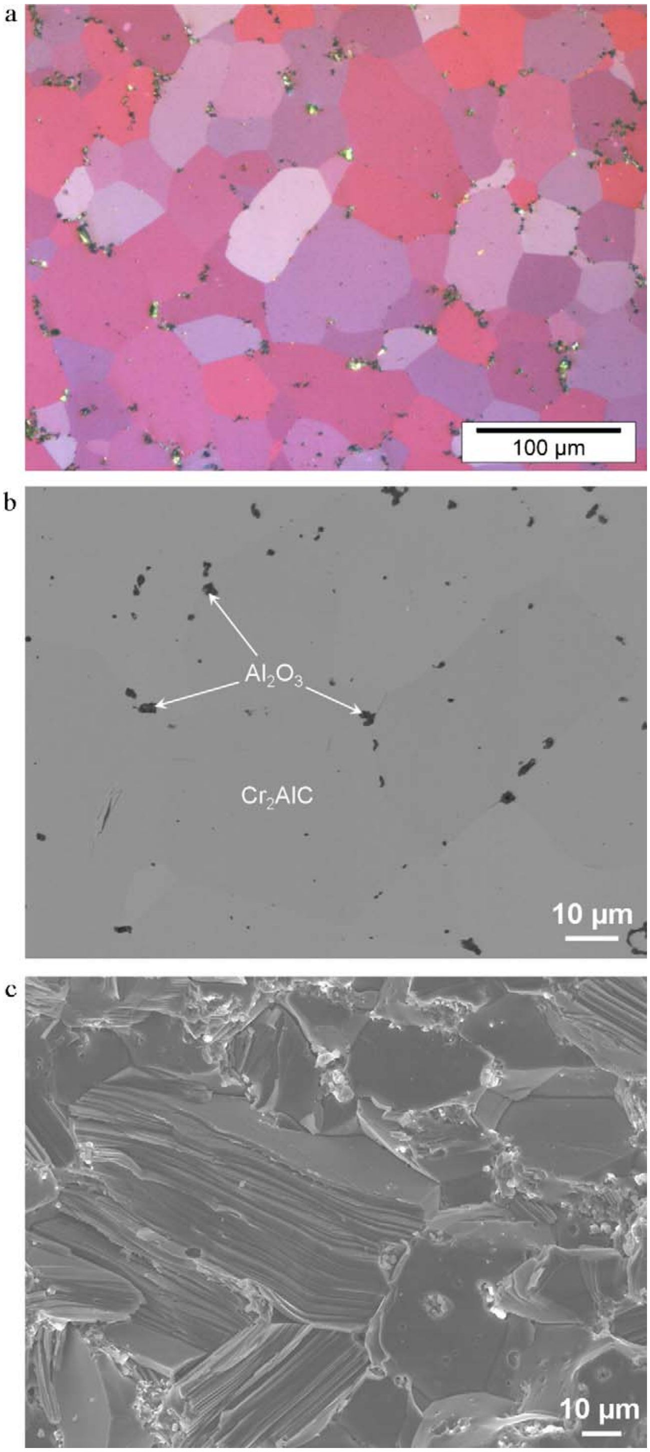

Fig. 4. Microstructure images of synthesized Cr_2AlC, (a) an optical microscope image of a polished surface, and (b) a backscattered electron image of a polished surface, and (c) a secondary electron image of a fracture surface.

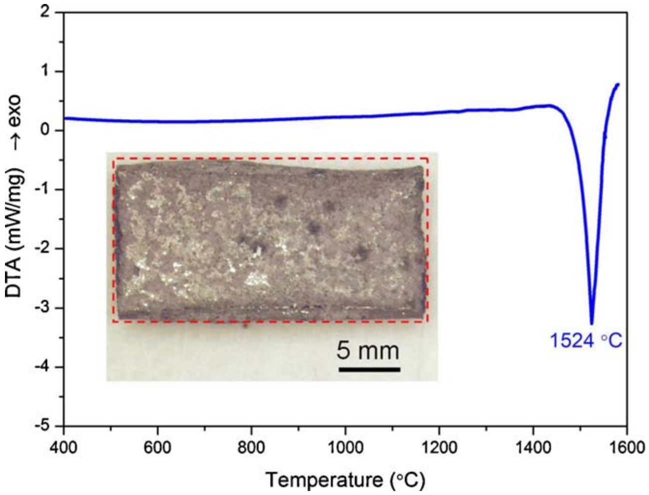

Fig. 5. DTA curve recorded of Cr_2AlC with a heating rate of 15 °C/min in Ar. The peak at 1524 °C corresponds to the decomposition of the material. The inset presents an image of the sample after the analysis. The dashed rectangle indicates the original sample dimension.

3. Results and discussion

3.1. Reaction and phase composition

A pure $AlCr_2$ powder was successfully synthesized after sintering the 2Cr/1.2Al mixture at 1100 °C for 1 h in Ar, as evidenced by the X-ray diffractogram shown in Fig. 1. The $AlCr_2$ phase has a tetragonal crystal lattice and a melting point of at about 910 °C.[19] Thus, sintering of the $AlCr_2$/C mixture at temperature above 910 °C will result in a liquid environment that promotes the formation of Cr_2AlC. The reaction sequence between the synthesized $AlCr_2$ and C is reflected by the DTA curve, shown in Fig. 2. A sharp endothermic peak around 904 °C certainly corresponds to the melting of $AlCr_2$. The two other peaks, one at around 1035 °C with low intensity and the other around 1167 °C with high intensity, can be ascribed to the formation of Cr_2AlC. It is anticipated that the weak exothermic peak indicates the nucleation of the Cr_2AlC phase, whereas the stronger peak hints at an intensive reaction between $AlCr_2$ and C. In order to support this interpretation, the $AlCr_2$/C mixture was pressureless sintered at 1050, 1200 and 1400 °C for 15 min in Ar, respectively. Next, the resulting phases were identified with XRD.

The diffractogram of the material sintered at 1050 °C (see Fig. 3) shows peaks belonging to the following three phases: $AlCr_2$, C and Cr_2AlC. The presence of Cr_2AlC at this temperature confirms that already a reaction occurred between $AlCr_2$ and C, which explains the small exothermic peak around 1035 °C as shown in Fig. 2. The diffractogram of the material sintered at 1200 °C shows that the peak intensities corresponding to the $AlCr_2$ and C phases are much smaller, whereas the peak intensities corresponding to Cr_2AlC are much larger than those of the material sintered at 1050 °C. This implies that the reaction between $AlCr_2$ and C to form the Cr_2AlC phase is much more intensive at 1200 °C than at 1050 °C. This explains the strong exothermic peak around 1167 °C in the DTA curve (Fig. 2). The diffractogram of the material sintered at 1400 °C (see Fig. 3) only displays peaks corresponding to Cr_2AlC. Thus sintering at this temperature resulted in an almost pure Cr_2AlC material, due to a complete reaction between the $AlCr_2$ and C powders.

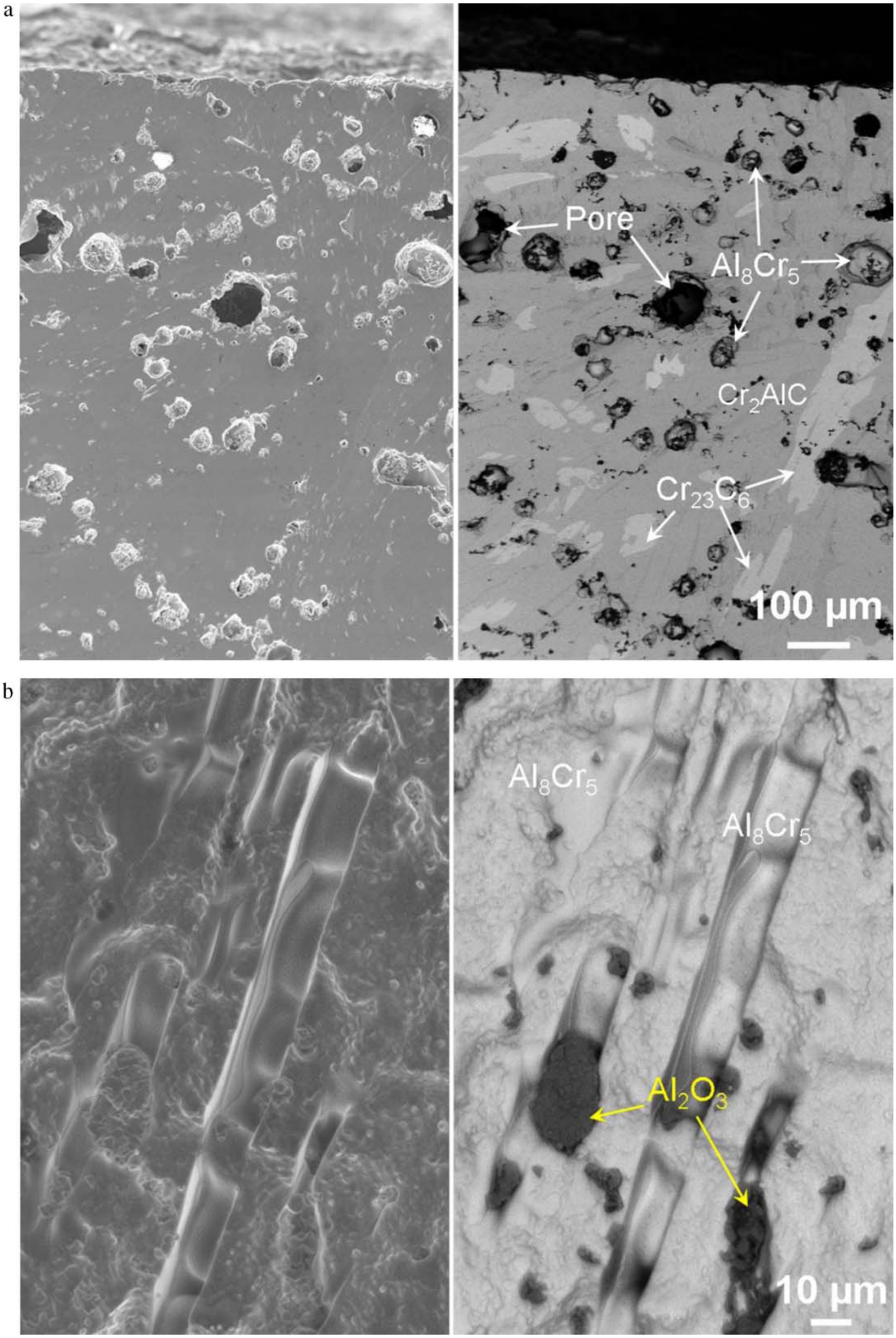

Fig. 6. SEM images of Cr_2AlC after decomposition taken from (a) a polished cross-sectional surface, and (b) the original surface. The micrographs at the left hand side in (a) and (b) are secondary electron images, and the micrographs at the right hand side are backscattered electron images.

3.2. Microstructure

The Cr_2AlC bulk ceramic, produced by hot-pressing the $AlCr_2/C$ powder mixture at 1400 °C for 1 h with 20 MPa in Ar, exhibits a coarse grained microstructure with an average size about 60 μm; see Fig. 4(a). A backscattered SEM image taken from a polished surface shows some small dark particles distributed within the grains and at the grain boundaries (Fig. 4(b)).

These particles were identified by XMA as Al_2O_3. This impurity is unfortunately always found in Al-containing MAX phases (i.e. Ti_3AlC_2, Ti_2AlC, Nb_2AlC, Cr_2AlC and $Cr_2Al(Si)C$),[4,5,20–22] due to reaction of Al with oxygen that is present as an absorbed species at the original powder surfaces.

The grain size of the Cr_2AlC produced from the $AlCr_2$/C mixture is larger than that produced from a conventional Cr/Al/C mixture after hot pressing at 1450 °C with 30 MPa for 1 h in Ar, i.e. 60 μm versus 35 μm.[4] This difference in grain size can be explained with the different amount of $AlCr_2$ liquid upon sintering of the various mixtures. During sintering of the $AlCr_2$/C mixture, the $AlCr_2$ phase with a melting point of 910 °C is liquid which promotes the reaction between C and $AlCr_2$ to form Cr_2AlC. Such a liquid phase is to a much lesser extent present during sintering of a conventional Cr/Al/C mixture and hence leads to a smaller grain size of the reaction product.

Fig. 4(c) shows that most of the Cr_2AlC grains fractured transgranular. This transgranular fracture results in layered features and/or smooth cleavage planes. The former feature is in response to the crack propagation perpendicular to the basal planes of Cr_2AlC, while the latter corresponds to the crack propagation along the basal direction.

3.3. *Thermal stability*

The decomposition temperature of MAX phase materials strongly depends on environments to which they are exposed.[12–18,23–25] In their crystal structure, the bond between “A” layers and “M–X” covalent bond chains is relatively weak. Hence, it is generally accepted that the outward diffusion of the “A” element occurs easily in the crystal structure, leaving a binary phase “MX”. This can be described by the following reaction:

$$\mathrm{MAX(s)} \rightarrow \mathrm{MX(s)} + \mathrm{A(gorl)} \qquad (1)$$

In practice, however, the decomposition is more complicated as also is the case for Cr_2AlC and thus the above reaction is not invariably followed. For example, the decomposition products for Ti_3SiC_2 when exposed to very high temperatures in a vacuum and/or argon atmospheres with a low oxygen partial pressure are nonstoichiometric $Ti_5Si_3C_x$ and TiC_x with TiO_2 and SiO_2.[12,14] Another example concerns the decomposition of Ti_3AlC_2 into TiC, Ti_2AlC and some other unknown phases at 1400–1550 °C in a high-vacuum environment.[15]

The thermal stability of the produced Cr_2AlC was analyzed with DTA. As can be seen in Fig. 5, only a significant endothermic peak at 1524 °C occurs and is associated with partial decomposition of Cr_2AlC. Thus Cr_2AlC can be stable at up to 1500 °C in Ar atmosphere.

The composition and microstructure of the decomposed material was investigated with SEM, XRD and XMA. Above 1524 °C, part of Cr_2AlC decomposes into two binary phases: Al_8Cr_5 and $Cr_{23}C_6$, see right micrograph in Fig. 6(a). These phases were also identified with both XRD and XMA (not shown here). The thermodynamically most stable binary carbide that can be formed is $Cr_{23}C_6$.[26,27] This phase is observed in cross sections of the decomposed material; see Fig. 6(a). At and above the decomposition temperature, Al_8Cr_5 with the melting point at about 1320 °C,[19] is a liquid phase. Apparently, this liquid phase was partially evaporated, leaving a large amount of micro-pores (size less than 100 μm) in the decomposed sample (Fig. 6(a)). Also this liquid phase easily flows to the sample surface, which explains the coverage of the decomposed sample by both small and extremely large Al_8Cr_5 particles (Fig. 6(b)). The different sizes of the Al_8Cr_5 particles may be due to nucleation and growth from a super saturated liquid on the surface upon cooling. Then most of nuclei developed into the small particles, while other nuclei grow abnormally into large particles. The formation and evaporation of the Al_8Cr_5 liquid phase at decomposition temperature also results in the contraction of Cr_2AlC sample, as shown in the inset of Fig. 5.

In addition to Al_2O_3 present as impurity in the as produced Cr_2AlC (cf. Section 3.2), also Al_2O_3 is observed in the surface of the decomposed sample (see right image in Fig. 6(b)) as a result of reaction with small amounts of oxygen and/or water vapor present in the Ar flow.

Based on the above results, the decomposition of Cr_2AlC in Ar with a low oxygen partial pressure maybe proceeds as follows:

$$\begin{aligned}14\mathrm{Cr_2AlC(s)} + \mathrm{O(g)} \rightarrow {} & \mathrm{Cr_{23}C_6(s)} + \mathrm{Al_8Cr_5(s)} \\ & + 3\mathrm{Al_2O_3(s)} + 8\mathrm{CO(g)} \end{aligned} \qquad (2)$$

4. Conclusions

A new recipe to produce Cr_2AlC has been developed using $AlCr_2$ and C as starting materials. During sintering of a mixture of $AlCr_2$ and C powders in the temperature range of 1050–1400 °C, Cr_2AlC starts to form at 1050 °C by a direct reaction between $AlCr_2$ and C. A Cr_2AlC bulk ceramic with only small amounts of Al_2O_3 as impurity was synthesized by hot pressing the $AlCr_2$/C mixture at 1400 °C with 20 MPa for 1 h in Ar. This synthesized Cr_2AlC ceramic has a coarse microstructure with a grain size of about 60 μm, which is larger than that produced from the conventional Cr/Al/C mixture, viz. about 35 μm. Cr_2AlC can be stable in Ar atmosphere up to about 1500 °C, but decomposes into Al_8Cr_5 and $Cr_{23}C_6$ at above 1500 °C.

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