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Phase formation sequence of Cr_2AlC ceramics starting from Cr–Al–C powders

Wu-Bian Tian [a,b], Pei-Ling Wang [a,*], Yan-Mei Kan [a], Guo-Jun Zhang [a], Yong-Xiang Li [a], Dong-Sheng Yan [a]

[a] *State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China*

[b] *Graduate School of Chinese Academy of Sciences, China*

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Abstract

The reaction process of Cr_2AlC ceramics was analyzed, in which the samples were prepared for composition Cr:Al:C = 1:1.2:1 by hot-pressing in argon in the range of 850–1450 °C using Cr, Al and graphite powders as the starting materials. X-ray diffraction (XRD), electron probe microanalysis (EPMA) and energy dispersive spectrum (EDS) were employed for identification of phase assembly and analysis of reaction route of the samples. The phase formation sequence of Cr_2AlC was finally analyzed based on phase diagram of the Cr–Al binary system combined with the results of differential thermal analysis (DTA) and XRD. It was found that Cr_5Al_8, Cr_2Al and Cr_7C_3 were the intermediate phases appearing in turn in the heating process. The amount of Cr_2AlC phase was gradually increased with increase in temperature by the reaction between Cr–Al intermetallic compounds, un-reacted Cr and graphite, and it became a pure phase in the sample with disappearance of intermediate phases above 1250 °C.

Keywords: Ceramics; Differential thermal analysis (DTA); Electron probe microanalysis (EPMA); X-ray diffraction (XRD); Intermetallic compounds

1. Introduction

The $M_{n+1}AX_n$ system (where $n = 1, 2, 3$, M is an early transition metal, A is a IIIA or IVA element and X is C or N, abbreviated as MAX) provokes much attention for its excellent mechanical, thermal, electrical and chemical properties [1–15]. For a long time, the formation of the pure MAX phase in bulk ceramics has been a key topic in the projects related to MAX materials. The difficulty to obtain pure MAX phase in the material has become a big obstacle for further investigation. For example, after Barsoum and El-Raghy made the breakthrough in the synthesis of pure Ti_3SiC_2 bulk material in 1996 [1], research on its properties and application has been able to develop widely.

The ternary carbide Cr_2AlC was first identified by Nowotny in 1970 [16]. However, systematic study of Cr_2AlC has not yet been available in the literature. As a member of the $M_{n+1}AX_n$ system, it has excited great expectation for its potential high elastic modulus, high room-temperature plasticity and excellent oxidation resistance [17–20]. The excellent high-temperature oxidation resistance of Cr_2AlC ceramics reported in the recent years [21] further confirmed that Cr_2AlC might be a promising material for high-temperature applications.

Study on synthesis of Cr_2AlC bulk ceramics and their characterization was carried out in our previous work [22]. It was found that the sample has comparable properties with $Ti_3Al_{1.1}C_{1.8}$ and the final phase assemblage, bulk density and properties of sintered samples were affected by composition and process parameters, such as sintering temperature, dwell time and atmosphere. The synthesis parameters could be further optimized to fabricate the material with improved properties. The corresponding research is going on. On the other hand, we are lack of the knowledge of reaction sequence of Cr_2AlC using Cr, Al and graphite as the starting materials when the sample is sintered. It is clear that the reaction process would be encouraged after melting point of aluminum, however, the knowledge of whole reaction sequence of Cr_2AlC is helpful to understand the effect of composition, processing conditions on densification behavior and properties of the material. The phase formation sequence of the sample starting from Cr, Al and graphite powders was therefore investigated in the present work. The identification of phase

* Corresponding author. Tel.: +86 21 5241 2324; fax: +86 21 5241 3122.
E-mail address: plwang@sunm.shcnc.ac.cn (P.-L. Wang).

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assembly and analysis of reaction route of the samples were performed by X-ray diffraction (XRD), electron probe microanalysis (EPMA) and energy dispersive spectrum (EDS). And the phase formation sequence of Cr_2AlC was finally analyzed based on binary phase diagram of the Cr–Al system combined with the results of differential thermal analysis (DTA) and XRD.

2. Experimental procedure

Chromium (200 mesh, 99.95%, Shanghai Chemical Reagent Company of National Medicine Group), aluminum (100–200 mesh, 99.95%, Shanghai Chemical Reagent Company of National Medicine Group) and graphite (3200 mesh, 99%, Shanghai Colloid Chemical Plant) powders were used as the starting materials. The powders were weighed according to the designed composition (Cr:Al:C = 2:1.2:1) and milled in absolute alcohol for 24 h, using Si_3N_4 milling media. Pellets of dried powders were hot-pressed under 20 MPa in the ranges of 850–1450 °C for 1 h in argon atmosphere.

Phase assemblages were determined by XRD method derived from X-ray diffractometer (D/max 2550V, Japan). Microstructure observation of the sample was performed under an electron probe microanalyzer (JEOL JXA-8100F, Japan) that is equipped with energy dispersive spectrum (EDS, Oxford INCA energy). DTA was performed by Simultaneous DSC/DTA-TGA Analyzer (SDT Q600, America).

3. Results and discussion

3.1. X-ray diffraction analysis

XRD patterns illustrating the phase development of the samples hot-pressed at different temperatures in argon are shown in Fig. 1. Variation of phase assemblages of the samples versus the different sintering temperatures is listed in Table 1.

Although the strongest XRD peak of Cr_5Al_8 phase is overlapped with that of Cr_2AlC, it is found that Cr_5Al_8 and Cr_2Al are two phases appearing as the major and the second phase formed at 850 °C, while the existence of un-reacted Cr and graphite are obvious, especially the amount of Cr is higher than that of graphite. It is noted that formation of Cr_2AlC has been detected for the sample sintered at 850 °C from XRD pattern.

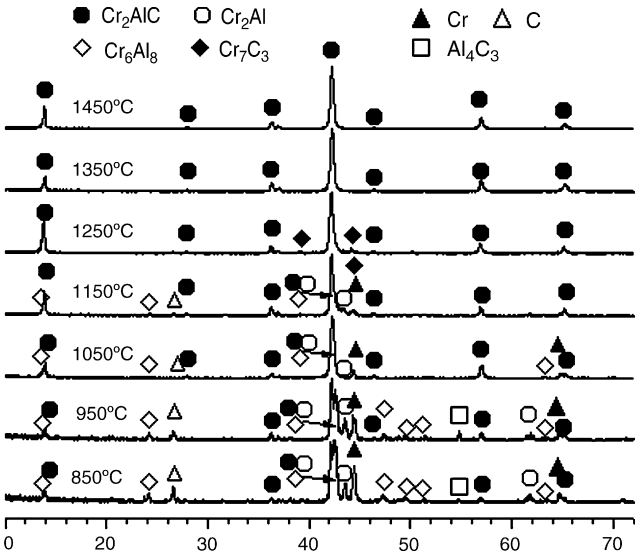

Fig. 1. XRD patterns of the samples hot-pressed at 850–1450 °C for 1 h. *Note*: The XRD peaks of Cr_4Al_9 are not shown in the figure.

At 950 °C, the amount of Cr_2AlC phase increases by expense of Cr_5Al_8, Cr and graphite, while amount of Cr_2Al has no obvious change. This result will also be discussed by means of EDS in the next section. There exists a weak XRD peak at $2\theta = 55°$ in the XRD pattern (see Fig. 1), which is even weaker at 850 °C and disappears at 1050 °C. By carefully checking the pattern, it is presumed that the XRD peak is possibly resulted from Al_4C_3 phase, but having (0 0 *l*) preference orientation. Few XRD peaks with very weak intensity are also found in the patterns at 850 and 950 °C that belong to Cr_4Al_9 phase, which is well agreed with the analysis of element mapping figure (see next section).

Although the variation in amount of phases for sample hot-pressed at 1050 °C shows mostly the same tendency as that at 950 °C, it is noted that the amount of Cr_5Al_8 and Cr_2Al phases reduces greatly and the quantity of Cr_2AlC phase climbs rapidly at that temperature.

The XRD results mentioned above reveal that the Cr–Al intermetallic compounds could have been formed after Al melts at 661 °C since Cr_5Al_8 and Cr_2Al are detected as two stronger phases than other phases formed at 850 °C. By further increase in temperature, the amount of these compounds decrease mostly, whereas the amount of Cr_2AlC increases. The corresponding reaction equations occurring in the temperature range of

Table 1
Variation of phase assemblages and densities of the samples vs. sintering temperatures

Temperature (°C)	Phase assembly[a]							
	Cr_2AlC	Cr_5Al_8	Cr_2Al	Cr_7C_3	Cr_4Al_9	Al_4C_3	Cr	C
850	m	s	mw		vw	vw	m	w
950	s	ms	mw		vw	w	m	w
1050	s	m	w				m	vw
1150	s	m	w	vw			m	vw
1250	s	m	vw	w			w	vw
1350	s							
1450	s							

[a] s = strong, m = medium, w = weak, vw = very weak.