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Mechanical properties of low temperature synthesized dense and fine-grained Cr_2AlC ceramics

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Abstract

Mechanically activated hot-pressing technology was used to synthesize a fine-crystalline Cr_2AlC ceramic at relatively low temperatures. A mixture of Cr, Al and C powders with a molar ratio of 2:1.2:1 was mechanically alloyed for 3 h, and then subjected to hot pressing at 30 MPa and different temperatures for 1 h in Ar atmosphere. The results show that a dense Cr_2AlC ceramic with a grain size of about 2 μm can be synthesized at a relatively low temperature of 1100 °C. The synthesized fine-grained Cr_2AlC has a high density of 99%, which is higher than the 95% density for the coarse-grained Cr_2AlC (grain size of about 35 μm) as synthesized by hot pressing unmilled Cr, Al and C. The flexural strength, fracture toughness and Vickers hardness of the fine-grained Cr_2AlC were determined and compared with the values for the coarse-grained Cr_2AlC.

Keywords: Cr_2AlC; Carbides; Mechanically activated hot pressing; Microstructure; Mechanical properties

1. Introduction

MAX phase ceramics (where M denotes an early transition metal, A is an element mostly in IIIA or IVA group, and X is either C or N) exhibit many unusual combinations of attractive properties such as a high electrical conductivity, a low oxidation rate, resistance against corrosion, and high strength at high temperature as well as good machinability.[1,2] Moreover, these materials show autonomous crack healing at high temperatures in an oxidizing environment.[3] Out of the total MAX phase family, the systems Ti_3SiC_2, Ti_3AlC_2 and Ti_2AlC have been studied extensively because of their attractive properties and relative ease of fabrication. Recently it has been shown that Cr_2AlC has an even better oxidation and corrosion resistance than Ti_3SiC_2 and Ti_3AlC_2 at high temperatures.[4–6] So, Cr_2AlC is expected to be a more promising candidate for high temperature applications. In addition, the thermal expansion of Cr_2AlC is 12–13 × 10^{-6}/K, which is close to that of the superalloys.[7,8] Hence Cr_2AlC has potential applications in the field of ceramics/metals joining and protective coatings on the superalloys. The possibility of depositing large area Cr_2AlC coatings on steel substrates has already been demonstrated.[9]

There are several methods used to produce Cr_2AlC bulk ceramics. For example, Manoun et al.[10] synthesized Cr_2AlC bulk ceramic by hot isostatic pressing (HIP) of a mixture of 2Cr/Al/C elemental powders at 1200 °C under 100 MPa for 12 h. Lee and Nguyen[6] obtained Cr_2AlC bulk ceramic by hot pressing powders of $CrC_{0.5}$ and Al at 1300 °C under 25 MPa for 1 h. No information was provided on the presence of other phases. Lin et al.[11] made Cr_2AlC bulk ceramic with 95% density and containing Al–Cr phase as an impurity by hot pressing a mixture of 2Cr/1.05Al/C at 1400 °C under 30 MPa for 1 h. Tian et al.[12] fabricated Cr_2AlC bulk ceramic with Cr_7C_3 as the impurity by hot pressing a mixture of 2Cr/1.1Al/C at 1400 °C under 30 MPa for 1 h. They[13] also fabricated the ceramic by pulse discharge sintering (PDS) the same mixture at 1250 °C under 50 MPa for 30 min. Impurities of Al_2O_3 and Cr_7C_3 were detected in the matrix.

Generally, it is difficult to produce a pure Cr_2AlC ceramic from a mixture of Cr, Al and C powders, due to the formation of intermediate compounds, such as Al_4C_3, Cr_7C_3 and Cr–Al

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phases.[4–7,10–13] For high temperature structural applications a high density is prerequisite. The densities of Cr_2AlC ceramics synthesized by HP of a mixture of Cr, Al and C powders are about 95–97%.[11,12] To produce Cr_2AlC ceramics with a higher density, mechanically activated sintering (MAS) technology has been adopted. Then, the ceramic can be fabricated at relatively low temperatures as has been demonstrated for Ti_3SiC_2,[14] Ti_3AlC_2[15] and Ti_2SnC.[16] The MAS process makes use of mechanically alloyed powders with a superfine structure that are subsequently sintered. These pre-milled powders exhibit a high reactivity due to their high lattice defect density, large grain boundary area and large internal strains, which lead to a relatively low synthesis temperature. In addition, the MAS technology can be used to make fine powders and also obtain dense ceramics with nano-sized microstructure from low cost starting powders.

In this paper, the production of Cr_2AlC ceramic by mechanically activated sintering is described and the microstructure and mechanical properties of the produced dense materials are presented.

2. Experimental procedures

Powders of Cr (particle size <75 μm, >99 wt.% purity, Beijing Reagent Company, Beijing, China), Al (particle size <75 μm, 99.5 wt.% purity, Beijing Reagent Company) and C (graphite, particle size <45 um, 99.5 wt.% purity, General Research Institute for Nonferrous Metals, Beijing, China) were used as the starting materials. The designed molar ratio of Cr, Al and C powders was Cr:Al:C = 2:1.2:1 to make Cr_2AlC samples. Extra Al was used to compensate for the loss of Al during the sintering process.

Mechanical alloying was performed in a QM-1SP4 planetary ball mill (Nanjing, China) using stainless steel containers and balls. The weight ratio of ball to powder was 20:1. The containers were evacuated to a pressure of 1×10^{-2} Pa. The rotation speed of the containers was set to 500 rpm. To avoid excessive heating during the milling process, the container surface was cooled in water for 10 min during milling at intervals of 0.5 h. A small amount of the milled powders was taken out of the containers after milling at various times for X-ray diffraction (XRD) analysis with a D/Max 2200 PC diffractometer (Tokyo, Japan) using Cu Kα radiation.

The mechanically activated powders were hot pressed at different temperatures for 1 h under 30 MPa in an Ar atmosphere. The heating rate was 30 °C/min. For comparison, unmilled Cr, Al and C powders were only mixed for 10 h and then hot pressed at 1450 °C under 30 MPa for 1 h in Ar.

The phase composition and the microstructure of the samples were identified with XRD and scanning electron microscopy (SEM) using a JEOL JSM 6500F field emission gun scanning electron microscope (Tokyo, Japan), which was equipped with energy-dispersive spectroscopy (EDS). Specimen for transmission electron microscopy (TEM) observation using a JEOL JEM 4000EX (Tokyo, Japan) was prepared by slicing, grinding and ion milling. The samples were polished using a JEOL SM09010 cross-section ion polisher (Tokyo, Japan) for SEM observation. The density of the samples was measured by the water immersion technique. The average grain size was obtained from the average linear intercept length comprising at least 100 grains in SEM micrographs taken of the fracture surfaces of the synthesized samples, multiplied with a statistical factor of 1.56.[17]

The Vickers hardness was determined with a Zwick/Z2.5 hardness tester (Ulm, Germany) in a load range of 1–50 kg and at a constant contact time of 15 s. The flexural strength of 3 mm × 4 mm × 36 mm specimens was measured by a three-point bending test using a Deben Microtester (Woolpit, UK). The span size and crosshead speed were 30 mm and 0.5 mm/min, respectively. The fracture toughness was measured using the single edge notched beam method. 2 mm × 4 mm × 36 mm specimens with a notch of about 2 mm in depth and 0.2 mm in width were used. Span size was 30 mm, and crosshead speed was 0.05 mm/min.

3. Results and discussion

3.1. Microstructure

The XRD patterns of the mixture of Cr, Al and C powders with a molar ratio of Cr:Al:C = 2:1.2:1 (denoted as 2Cr/1.2Al/C) before and after milling for 1–3 h are shown in Fig. 1. The mixture of powders before milling consists of bcc Cr, fcc Al and graphite C (see Fig. 1(a)). After milling this mixture for only 1 h, the peak in the diffractogram belonging to C (graphite) has completely disappeared, suggesting that either graphite is transformed to an amorphous structure or has already diffused into the surrounding metallic grains (see Fig. 1(b)). This observation is in agreement with those of the previous studies where

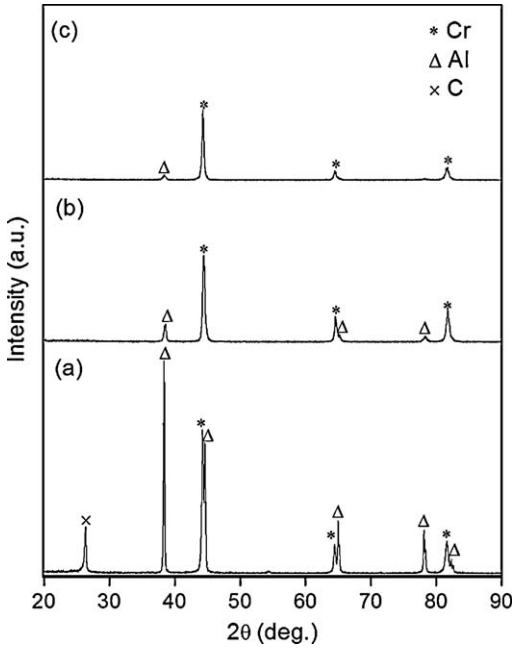

Fig. 1. XRD patterns of 2Cr/1.2Al/C mixture after milling for (a) 0 h, (b) 1 h and (c) 3 h. ICDD card numbers for Cr, Al and graphite are 01-085-1336, 01-089-2837 and 00-001-0640, respectively.