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Cyclic oxidation of Cr_2AlC between 1000 and 1300 °C in air

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Abstract

Fully dense, monolithic ternary Cr_2AlC compounds were synthesized via a powder metallurgical route, and their cyclic oxidation behavior was investigated between 1000 and 1300 °C in air for up to 100 h. At 1000 and 1100 °C, Cr_2AlC displayed excellent cyclic oxidation resistance by forming a less than 5 μm-thick Al_2O_3 oxide layer and a narrow Cr_7C_3 underlayer. At 1200 and 1300 °C, an outer (Al_2O_3, Cr_2O_3)-mixed oxide layer, an intermediate Cr_2O_3 oxide layer, an inner Al_2O_3 oxide layer, and a Cr_7C_3 underlayer formed on the surface. From 1200 °C, scale cracking and spalling began to occur locally to a small extent. At 1300 °C, the cyclic oxidation resistance deteriorated owing to the formation of voids and the spallation of the scales.

Keywords: Chromium; Aluminum; Carbide; Oxidation

1. Introduction

Cr_2AlC is one of the alloys, which belong to the so-called MAX-phases, where M is an early transition metal, A is an A group element (mostly IIIA or IVA), and X is C or N. Among many MAX compounds, Ti_2AlC and Cr_2AlC have recently attracted considerable interest, because of their excellent mechanical, thermal, electrical and chemical properties [1]. Cr_2AlC, which is the only ternary compound in the Cr–Al–C system, has a hexagonal crystal structure with a space group of $P6_3/mmc$, in which Cr_2C layers are interleaved with layers of Al. Like metals, Cr_2AlC is relatively soft, has good electrical and thermal conductivities, and good machinability. Like ceramics, it displays excellent heat resistance, elastic stiffness, and a high melting point [2–4]. It has been synthesized in the form of films via the magnetron sputtering method [5–7] or bulks via the powder metallurgical method [2,3,8–10]. In this study, monolithic, dense Cr_2AlC bulks were synthesized by hot pressing a new starting powder mixture consisting of CrC_X ($x = 0.5$) and Al. The simultaneous reaction and densification between CrC_x and Al powders produced monolithic, dense Cr_2AlC polycrystals.

To use Cr_2AlC as high-temperature structural components, it is important to study its high-temperature oxidation resistance. However, the oxidation properties of Cr_2AlC have not been extensively investigated, owing to the fact that it is a relatively new member of the ternary carbides. The isothermal oxidation kinetics of Cr_2AlC was briefly studied by Lin et al. at 1200 °C for 50 h in air [2]. They explained that Cr_2AlC had excellent oxidation resistance owing to the formation of protective α-Al_2O_3 and α-Cr_2O_3 oxide films on the surface. However, no further oxidation studies were performed. More information about the high-temperature oxidation behavior of Cr_2AlC is therefore needed. In this study, the high-temperature cyclic oxidation of Cr_2AlC was investigated between 1000 and 1300 °C in air. The aim of this study is to examine the oxidation kinetics, distribution and roles of Cr, Al and C around the scale, and the characteristics of the oxide scales formed on the Cr_2AlC bulk under cyclic oxidation conditions.

2. Experimental

Chromium (<45 μmϕ, 99.9% purity) and graphite (∼10 μmϕ, 99.95% purity) powders were mixed at a molar ratio of Cr:C = 2:1 in a SPEX™ shaker mill for 10 min in an Ar atmosphere. The mixture was pressed into a cylindrical green pellet by uniaxially pressing it at 20 MPa, and heated at 1550 °C for 1 h under a vacuum of 1.3 Pa to yield CrC_X ($x = 0.5$). The partially sintered CrC_X bulk was ground, and screened to a diameter of <45 μm. CrC_X and Al powders (<45 μmϕ, 99.7% purity) were mixed at a molar ratio of 2:1 in a SPEX™ shaker mill for 10 min in an Ar atmosphere. The resulting mixture was then hot pressed at 1300 °C to form 19 mmϕ × 10 mm bulk specimens under a pressure of 25 MPa for 1 h in flowing Ar gas. During the hot pressing, bulk Cr_2AlC was synthesized through the direct reaction between the CrC_X and Al powders.

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The bulk Cr_2AlC was cut into $10 \times 5 \times 5\,mm^3$ sized coupons, ground to a 2000 grit finish, ultrasonically cleaned in acetone and methanol, and then oxidized cyclically at 1000, 1100, 1200 and 1300 °C in air. The test cycles involved exposing the specimens for 2 h, cooling them quickly to room temperature, measuring the weight changes, and returning them to the furnace. The heating and cooling rates were 350 and 150 °C/min, respectively. The specimens during cyclic oxidation were given a total exposure of 100 h (50 cycles). The oxidized specimens were investigated using a scanning electron microscope (SEM; Jeol 890), an X-ray diffractometer (XRD; Mac Science M18XHF-SRA) with Cu Kα radiation, and an electron probe microanalyzer (EPMA; Jeol JXA-8900R). The microstructure of Cr_2AlC was examined after electroetching it at 5 V dc in a (distilled water + 1% HF + 1% HNO_3) solution.

3. Results and discussion

Fig. 1 shows the cyclic oxidation curves of Cr_2AlC at 1000, 1100, 1200 and 1300 °C in air. Each data point indicates one thermal cycle. The displayed weight changes are the sum of the weight gain due to scaling and the weight losses due to scale spallation and carbon depletion from Cr_2AlC in the form of CO or CO_2. At 1000 °C, the weight changes were almost nil, indicating excellent oxidation resistance, without scale spallation. At 1100 °C, small weight gains were continuously measured, indicating that the rate of scaling was faster than the combined rate of spallation and carbon vaporization. Visual inspection indicated that little scale spallation occurred, which was mainly attributed to the formation of a quite thin scale. At 1200 °C, small initial weight gains occurred, followed by small weight losses, due to partial scale spallation and carbon loss at the later stage of oxidation. At 1300 °C, rather big weight losses occurred, due mainly to local spallation of the thickened oxide scale and an increased rate of carbon loss. Generally, the cyclic oxidation resistance of Cr_2AlC was acceptable up to 1100 °C, owing to the formation of thin, protective oxide scales.

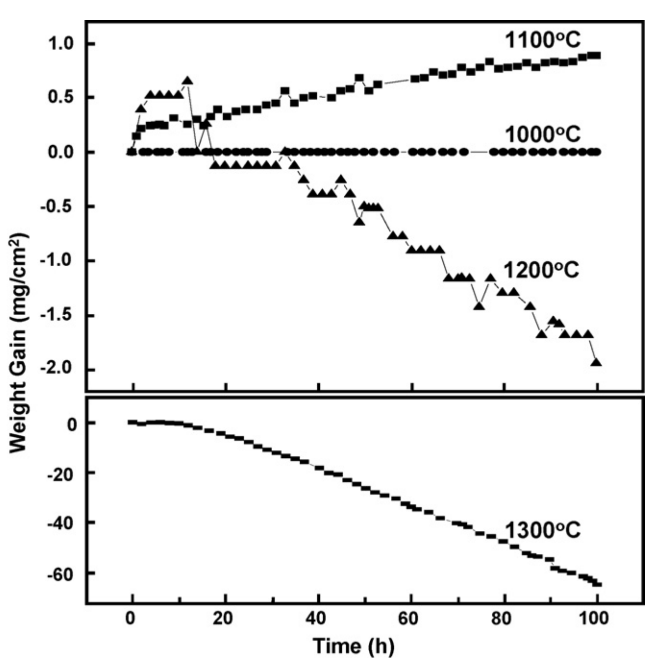

Fig. 1. Weight change vs. oxidation time curves of Cr_2AlC during cyclic oxidation for 100 h between 1000 and 1300 °C in air.

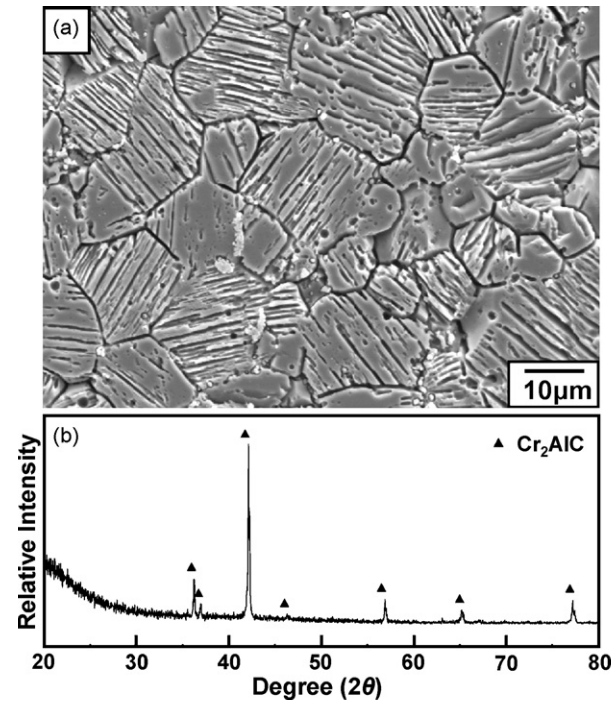

Fig. 2. (a) Etched SEM microstructure and (b) XRD pattern of Cr_2AlC.

Fig. 2(a) shows the SEM microstructure of the bulk Cr_2AlC that was prepared. The average size of the polyhedral grains was 18 μm. The layered grains were clearly observable. The measured density of Cr_2AlC was 5.2 g/cm^3, with a relative density of more than 99% of the theoretical value. Fig. 2(b) shows the XRD pattern of monolithic Cr_2AlC. In other studies, Cr_7C_3 was present as a major impurity in Cr_2AlC [3,9].

Fig. 3(a) shows the XRD pattern of the oxide scale formed on Cr_2AlC after cyclic oxidation at 1000 °C for 100 h. The Cr_2AlC matrix peaks were the strongest, owing to the small extent of oxidation. The oxidation of Cr_2AlC led to the formation of an α-Al_2O_3 oxide layer and a Cr_7C_3 underlayer. Al_2O_3 is highly stable, and exhibits low diffusivities for both cations and anions. Fig. 3(b) shows a dense, adherent oxide layer with a thickness of 1.3 μm. The consumption of Al on the matrix surface to form the α-Al_2O_3 oxide layer resulted in Al-depletion. Corresponding Cr-enrichment underneath the α-Al_2O_3 oxide layer resulted in the formation of the Cr_7C_3 underlayer. In Fig. 3(c), the Al-depletion and Cr-enrichment immediately below the Al_2O_3 layer were not distinct, due to the small extent of oxidation and well-known limited spatial resolution of the EDS employed.

Fig. 4(a) shows the XRD pattern of the oxide scale formed on Cr_2AlC after cyclic oxidation at 1100 °C for 100 h. The phases were identified as α-Al_2O_3, Cr_7C_3, and Cr_2AlC, in decreasing order of magnitude. The Cr_2AlC peaks became weak, owing to the growth of the Al_2O_3 layer and Cr_7C_3 underlayer. Fig. 4(b) shows an adherent, 4.5 μm-thick oxide layer. The origin of the cracks which developed around the scale-matrix interface is considered to be carbon loss from Cr_2AlC, growth stress due to the different volume expansion of the phases, and thermal stress due to the mismatch in their thermal-expansion coefficients. The EPMA mappings shown in Fig. 4(c–f) indicate the