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Non-isothermal oxidation kinetics of nano-laminated Cr_2AlC MAX phase

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ABSTRACT

A highly pure Cr_2AlC MAX phase is prepared through the sintering method by varying the aluminum content. The non-isothermal oxidation kinetics of the Cr_2AlC phase is examined through a TGA/DTA technique, at variable heating rates (10, 20, 30, 40 °C/min). The TGA/DTA results show that the oxidation of the Cr_2AlC phase occurred in two stages. The multi-stage kinetic analysis is performed to establish the nature of the oxidation process. The activation energy is calculated by following the Kissinger-Akahira-Sunose (KAS) and the Friedman (FR) iso-conversional kinetic methods. The reaction mechanism involved during the oxidation process is proposed through the integral master-plots method.

1. Introduction

In the current scenario, the MAX phases have received significant attention from the scientists for their promising practical applications [1]. The reason behind the growing demand of the MAX phases is their extraordinary combination of properties which include both metals and ceramics. The properties include the high thermal and electrical conductivity, excellent machinability, good damage tolerability, high oxidation and corrosion resistance at higher temperatures, and superb thermal shock resistance [2]. These interesting properties have placed, the MAX phases as a potential candidate for the higher temperature applications [3,4]. Furthermore, etching of A element in MAX phases leads to the formation of new class of materials, i.e., MXenes (two-dimensional transition metal carbides). MXenes are the potential candidate for energy conversion and storage applications [5].

Among these phases, the chromium aluminum carbide (Cr_2AlC) possess better oxidation and corrosion resistance [6–8]. Sun and co-workers [8] conducted theoretical studies on the elastic properties of the five M_2AlC phases (M: V, Cr, Ta, Ti, Nb). They suggested that the Cr_2AlC phase exhibits the highest Bulk Modulus, the Shear Modulus and the Young's Modulus among the V_2AlC, Ta_2AlC, Ti_2AlC and Nb_2AlC phases [8]. Recently, Pei and co-workers testified that the Cr_2AlC possesses a self-crack healing property at elevated temperatures [9]. In addition, Cr_2AlC MAX phase emerges as a potential candidate for concentrated solar power (CSP) applications. Sarwar et al. [10] studied the thermal performance, flux transmission performance and optical properties of Cr_2AlC and Ti_2AlC MAX phases. They suggested that Cr_2AlC is a better solar receiver as compared to Ti_2AlC. All these unique properties of the Cr_2AlC significantly depend on the phase purity. However, no pure Cr_2AlC phase has been reported to date. There is always a formation of Cr_7C_3, Cr_2Al phases along with the Cr_2AlC phase as evident from the X-ray diffraction patterns in the published literature [11,12]. Hence, there is a need to investigate the optimum synthesis condition for the formation of a highly pure Cr_2AlC MAX phase.

Also, the isothermal oxidation kinetics of Cr_2AlC MAX phase has been well investigated by several researchers because of the ease of the theoretical interpretation of the data [13–16]. However, non-isothermal oxidation study of Cr_2AlC MAX phase is scarce in the literature. In fact, a non-isothermal heating process is practically involved during oxidation of Cr_2AlC [17]. The non-isothermal oxidation study will provide guidelines for the practical application of Cr_2AlC MAX phase. Also, the isothermal oxidation experiments suffer from certain limitations such as leakage of gas and sudden variation in temperature, time, and gas flow rate [17]. These parameters significantly affect the accuracy of the isothermal oxidation process. So, it is crucial to investigate non-isothermal oxidation of Cr_2AlC MAX phase.

Various research group adopted thermal analysis techniques to

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investigate the oxidation of material under non-isothermal heating process [18–22]. They performed experiments at multiple heating rates and studied the kinetics involved during the oxidation process by following iso-conversional kinetic methods. The kinetic analysis provides detailed information associated with the oxidation process. Various kinetic parameters are evaluated such as activation energy, pre-exponential factor, and the reaction mechanism by following different kinetic models [23–28]. The kinetics involved in the non-isothermal oxidation process is essential to predict the thermal behavior of a material, which could be used for higher temperature applications.

In the current study, the impact of the aluminum concentration on the formation of a highly pure Cr_2AlC was conducted at 1200 °C and 1300 °C. The thermal stability of the Cr_2AlC MAX phase was estimated through the Thermogravimetry Analysis (TGA) and the Differential Thermal Analysis (DTA) techniques. The focus of the present work is to evaluate the optimum condition for the synthesis of Cr_2AlC phase and to study its oxidation behavior under non-isothermal conditions. The kinetic parameters are calculated by following the Kissinger-Akahira-Sunose (KAS) and the Friedman iso-conversional kinetic methods. The reaction mechanism involved during the oxidation process has been proposed by using the integral master plots method.

2. Experimental details

The bulk Cr_2AlC powder samples are prepared by varying aluminum (Al) content (10–50 mol%) from the stoichiometry ratio. Firstly, the size of the Chromium metal powder (Loba Chemie) is reduced to ≤ 45 μm through a PM-100 Retsch Ball Mill. In this step, the ball milling is performed at 400 rpm for 4 h with the charge ratio of 14:1. Afterwards, all the starting materials, i.e., the milled chromium (≤45 μm, Loba Chemie), the aluminum (<45 μm, SD fine), and the graphite (<20 μm, Sigma Aldrich) are mixed in the five different molar ratios (Cr: Al: C = 2:1.1:1, 2:1.2:1, 2:1.3:1, 2:1.4:1 and 2:1.5:1) for 30 min in a ball mill at 200 rpm with the charge ratio 14:1. These five powder samples are named CAC-1, CAC-2, CAC-3, CAC-4, and CAC-5, respectively. The mixed powder samples are pelletized (10 mm Dia. X 5 mm Thickness) by using a Hydraulic Press. The Pressure-Less sintering of all the pellets is carried out in a Lenton Tubular Furnace (LTF 18/75/300). The sintering of the pellets is performed in two sets of experiments. In the first set, the prepared pellets are sintered at 1200 °C for 1-h dwell time, and the samples are named 12CAC-1, 12CAC-2, 12CAC-3, 12CAC-4, and 12CAC-5. While, in the second set, the pellets are sintered at 1300 °C for 1-h dwell time and named as 13CAC-1, 13CAC-2, 13CAC-3, 13CAC-4, and 13CAC-5. The complete synthesis process is performed under the high purity argon atmosphere.

The phase formation in the samples is examined through a PANalytical X'Pert PRO with the Ni filter. The voltage and the current of the machine are kept at 40 kV and 45 mA, respectively. The scan angle (2θ) is varied from 10° to 90° for all the prepared samples. All the crystalline peaks observed in the diffractograms are analyzed by the X'Pert High Score and the Origin software. The International Centre for Diffraction Data (ICDD) standard cards are used in matching the phases present in the prepared samples. Rietveld Refinement analysis is performed by using Fullprof software and the atomic position of Cr (0.333, 0.666, 0.086), Al (0.666, 0.333, 0.25), C (0, 0, 0) are used during refinement [29,30]. The morphological and the microstructural features of the synthesized Cr_2AlC MAX phase is examined through the Field-Emission Scanning Electron Microscope (FE-SEM) (Hitachi SU8010) and the Transmission Electron Microscope (TEM) (JEOL 2100 F) operating at 15 kV and 200 kV, respectively. The surface chemical composition and the valency states in the Cr_2AlC are examined through the X-ray Photoelectron Spectroscopy (XPS) with the Auger Electron Spectroscopy (AES) Module (PHI 5000 Versa Prob II, FEI Inc.). The oxidation kinetics of the Cr_2AlC is analyzed through the Thermogravimetry Analysis (TGA) and the Differential Thermal Analysis (DTA) by using the EXSTAR TG/DTA 6300 instrument. The thermal analysis is performed at multiple heating rates (10, 20, 30, 40 K/min) in the air atmosphere (200 ml/min).

3. Results and discussions

3.1. The X-Ray diffraction analysis

Fig. 1a shows the XRD patterns of 12CAC-1 – 12CAC-5 samples heated at 1200 °C for an hour. The percentage composition of the distinct phases observed in these samples are estimated through the XRD data and given in Table 1. It is visible from Fig. 1 and Table 1 that the variation of the aluminum content influences the formation of a pure hexagonal Cr_2AlC MAX phase. The samples heated at 1200 °C (Fig. 1a) reveal the formation of three distinct phases Cr_2AlC, Cr_7C_3, and Cr_2Al. It is observed in a 12CAC-4 sample (Fig. 1) that the intensity of the secondary phases (Cr_7C_3 and Cr_2Al) decreased with an increase in the aluminum content up to 40 mol%. This indicates that the formation of the Cr_2AlC phase is favored with an increase in the aluminum content. Comparable results are also reported for the synthesis of the other MAX phases by increasing the aluminum content from the stoichiometry ratio [31,32]. However, any further increment in the aluminum content in a 12CAC-5 sample leads to an increase in the peak intensity the secondary phases (Cr_7C_3 and Cr_2Al). This could be ascribed to the excessive aluminum present in the system, which favors the formation of the Cr_2Al phase and results in more residual carbon. This residual carbon reacts with the chromium and forms a carbon-deficient chromium carbide (Cr_7C_3) phase [33]. At 1200 °C (Fig. 1a), the maximum purity of the Cr_2AlC phase (96.3%) is observed in a 12CAC- 4 sample. The presence of the intermediate phases in all the samples sintered at 1200 °C (Fig. 1a) reveals that the reaction temperature is not enough for the formation of a highly pure Cr_2AlC MAX phase. It could be possible at the higher temperature (>1200 °C), where the intermediate phases (Cr_7C_3 and Cr_2Al) react with one another to form the Cr_2AlC MAX phase.

Further, 13CAC-1 – 13CAC-5 samples are sintered at the higher temperature (1300 °C). Fig. 1b shows the XRD patterns of all these samples. In Fig. 1b, there are two distinct phases, i.e., Cr_2AlC and Cr_7C_3 are present in all the samples. It is observed that an increase in the temperature favors the formation of the Cr_2AlC phase. However, no peak associated with the Cr_2Al phase is observed. An increase in the amount of the aluminum content up to 40 mol% results in the decrease in the intensity of the secondary phase (Cr_7C_3). However, the increment in the aluminum content to 50 mol % again increases the intensity of the Cr_7C_3 phase. It is observed from Fig. 1 and Table 1 that the hexagonal Cr_2AlC MAX phase is having the purity of 96.3%, and 98.2% is observed in 12CAC-4 and 13CAC-4, respectively. Moreover, Fig. 1c shows Rietveld refinement plots of 13CAC-4 sample and the lattice parameters along with cell volume for all the samples is presented in Table 1.

3.2. The X-Ray line profile analysis

The X-Ray Line Profile Analysis is performed to estimate the volume weighted domain size, the surface weighted domain size and the root mean square (RMS) strain present in the synthesized samples. In this analysis, the Pseudo-Voigt function is employed to fit every individual peak associated with the Cr_2AlC phase present in all the samples. This function combines the Lorentzian (L(x)) function and the Gaussian (G(x)) function [34,35]: