Advanced Powder Technology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Thermodynamic assessments and mechanically activated synthesis of ultrafine Cr_2AlC MAX phase powders

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ARTICLE INFO

Article history:
Received 18 October 2015
Received in revised form 19 July 2016
Accepted 3 November 2016
Available online xxxx

Keywords:
MAX phases
Powders
Milling energy
Enthalpy
Gibb's free energy

ABSTRACT

This work attempts to produce ultrafine powders and studies the effect of mechanical activation on reaction kinetics and thermodynamics of Cr_2AlC formation, which are essential to design the processing parameters. Cr_2AlC formation was found to be exothermic in nature, which occurred as soon as Al started melting. Milling energies (1.6 kJ/g and 3.2 kJ/g after milling for 15 h and 30 h respectively) were found to enhance the reactivity of chromium carbide powders with Al, and lowered the activation energy of reaction significantly. The enthalpy of reaction was found to be changed from −53 kJ/mol to −66 kJ/mol and the change in Gibbs free energy of reaction was decreased from −107 kJ/mol to −139 kJ/mol, when milling duration was increased from 15 h to 30 h. Thus the mechanical activation provides more favorable condition for the conversion and nearly pure Cr_2AlC powder with ultrafine (<400 nm) size were produced at relatively lower temperature (at 800 °C).

1. Introduction

MAX phase ternary carbides feature a hexagonal structure, which is represented by a general formula of $M_{n+1}AX_n$ (MAX), where n = 1, 2, or 3. Where M is an early transition metal, A is an A-group element and X is either carbon or nitrogen. Strong M—X bonds and weaker M—A bonds associated with nano-layered structure endow these solids with a unique combination of metallic and ceramic properties. For example, like metals, they are readily machinable, damage tolerant, thermally and electrically conductive, at the same time it has good resistant to thermal shock and plastically deformable at elevated temperature [1–3]. Cr_2AlC is one of the MAX phase compounds, has excellent oxidation and corrosion resistance [4,5] and promising candidate for high temperature applications. In addition, the thermal expansion of Cr_2AlC is close to the superalloys; it has potential applications in protective coatings on the superalloys and steels, etc. [6,7].

The production of phase pure MAX powders at low temperatures is challenging and the identification of low temperature formation pathways is an active research area for bulk processing. There are several methods including hot pressing, hot iso-static pressing and pulse discharge sintering (SPS), etc. [8–13] to produce Cr_2AlC bulk ceramics using reactants such as Cr/Al/C, $Cr/Al_4C_3/C$, and $AlCr_2/C$ or $CrC_{0.5}/Al$. However, the problems such as high impurities (Cr_7C_3 and Cr_2Al) and the volatilization of Al still exist. Moreover, production of MAX phase compound through the pressure assisted sintering methods leads to increase the cost and limits the applications. There are few reports on synthesis of Cr_2AlC powders. Panigrahi et al. [14] produced Cr_2AlC powders of about 9 μm using chromium carbides (CrC_x) and aluminum powders at about 1100 °C. Excess of about 10 at.% Al than the stoichiometric requirement was used to increase the conversion. Su et al. [15] produced Cr_2AlC powders with very large size range through pressureless heating of Cr—Al—C powders at high temperatures about 1350 °C. Molten salt method was used to refine the particle size by Tian et al. [9], where particles were mostly in the range of 2–8 μm. In this method NaCl and KCl salts were used to provide liquid and inert media to inhibit the coarsening of newly formed grains. Hendaoui et al. [16] studied the synthesis of MAX phase in Ti—Al—C ternary system through mechanically activated self-propagating high temperature synthesis. The presence of considerable amounts of impurity phases were observed in most of the above reports.

Generally in the solid state reaction of ternary and higher order compounds, there are different stages: (i) diffusion begins at inter-particle contacts, (ii) formation of solid solutions or intermediate phases depending on the solid solubility limits. If this phase is stable, it acts as a diffusion barrier around the unreacted core. (iii) Finally, the intermediate phases react with each other to form

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http://dx.doi.org/10.1016/j.apt.2016.11.020
0921-8831/

Please cite this article in press as: Y. Rajkumar, B.B. Panigrahi, Thermodynamic assessments and mechanically activated synthesis of ultrafine Cr_2AlC MAX phase powders, Advanced Powder Technology (2016), http://dx.doi.org/10.1016/j.apt.2016.11.020

a ternary phase. The last stage is normally very slow as the activation energy for the dissolution of intermediate phase is very high. To overcome those diffusion barriers, it usually needs higher temperatures, which have a side effect, ranging from economic penalties to evaporation loss of constituent phases, such as Al in Ti_3AlC_2 and Cr_2AlC compounds. There have been many strategies to overcome these difficulties, mostly at the pre-processing stage that allows rapid short range diffusion. Mechanically activated process is a convenient and effective method to produce fine and pure material [17–20]. It is well known that the fine particles improve the sinterability and properties.

Though a lot of efforts have been put on the production of MAX phase bulk materials and powders; understanding the underlying thermodynamic characteristics and phase formation sequences in MAX phase, is also extremely essential. However, experimentally reported information is very limited in this direction; although few attempts were made through Calphad and ab initio calculations. Schuster et al. [21] investigated isothermal sections at 1073 K and 1273 K of Cr—Al—C system to understand the phase relations, where Cr_2AlC phase was found to be in stoichiometric at extremely narrow zone. There was no appreciable solubility of third element in any of the binary compounds. Hallstedt et al. [22] employed the ab initio calculations to evaluate some thermodynamic parameters of Cr_2AlC while using the reaction characteristics and parameters of the binary Al—Cr, Al—C and Cr—C systems. The condition for formation of Cr_2AlC phase was proposed in terms of Gibb's free energy of formation (ΔG_f), which was estimated to be about −86 kJ/mol. The current investigation attempts to address some of the issues in this area.

The objectives of the present investigation are to produce ultrafine Cr_2AlC powders with high phase purity and to lower the synthesis temperatures through the mechanically activated reactants. Effect of milling and particle size reduction of chromium carbides on the reaction with aluminum and conversion to yield Cr_2AlC phase have been studied. Effect of Al concentration on Cr_2AlC conversion has been studied. Efforts have been made to understand the reaction kinetics and to reveal some of the thermodynamic parameters, such as changes in enthalpies and Gibbs free energy, etc. through the help of differential scanning calorimetry (DSC).

2. Experimental

Chromium powder of 99.5% purity having a particle size of <45 μm was obtained from Sigma Aldrich Pvt. Ltd. The graphite powder of <10 μm size and aluminum powder (99% purity) of <45 μm were procured from Alfa Aesar. Cr_2AlC synthesis was carried out in three stages: (i) synthesis of CrC_x powder, (ii) mechanical activation of carbides (CrC_x), and (iii) reaction of activated carbides with aluminum.

In the first stage, Cr and graphite powders were mixed in a molar ratio of 2:1 using a planetary ball mill (Pulverisette-5, Fritsch, GmbH, Germany) for about one hour. Powders were charged (with a ball to powder weight ratio of 10:1) and milled at a speed of about 300 rpm using tungsten carbide (WC) vial (250 ml capacity) and the balls (10 mm diameter). The mixed powder was taken into an alumina crucible and heated at a rate of 15 °C/min up to 1100 °C for 2 h under flowing argon. Synthesized CrC_x was pulverized using agate mortar and pestle and sieved using −325 mesh screens.

In the second stage the synthesized CrC_x powders was milled for 15 h and 30 h on the same mill and media. The balls to powder weight ratio was 15:1 and rotated at a speed of 300 rpm with regular intervals of pause time to avoid the heat generated during milling. Toluene (ACS grade, >99.5% pure) was used as a process control dispersion media. After milling, the powder was dried at 60 °C for 4 h on a petri-disc while stirring continuously to avoid the settling of the particles.

In the third stage, the milled carbide powders (obtained after milling for different length of time) were mixed (separately) with Al powder in a molar ratio of 1:1.4, using agate mortar and pestle. The reactant mixture of CrC_x/Al was compacted uniaxially at a low pressure using pre-compaction press and placed into a tubular furnace (High Vacuum Technologies). After charging the sample, the furnace chamber was flushed with Ar about 30 min prior to heating. The furnace was heated at a rate of 15 °C/min to a temperature range of 700–1100 °C and kept at an isothermal condition for 2 h. The pyrolised product was fragile; it was ground easily into the fine size with the help of agate mortar/pestle and sieved (using −325 mesh).

Powders at every stage of processing were characterized for the phase analysis using X-ray diffraction (PANalytical, model:X'pert PRO) with Cu k_α radiation using 40 kV of applied voltage and scanning speed of 0.03°/s. The microstructures were characterized using a field emission scanning electron microscope (FESEM; Carl-Zeiss, Model: Supra 40). Formation reaction was characterized through the differential scanning calorimetry (Netzsch DSC 404 F_3) up to 1400 °C in high purity Ar atmosphere.

3. Results and discussion

3.1. Synthesis and mechanical activation of CrC_x

The XRD patterns of, as synthesized and mechanically activated CrC_x powders have been shown in Fig. 1. Chromium carbide was found to be contain two major phases, Cr_3C_2 and Cr_7C_3. The fractions of above two phases were found to be about 33.4 and 66.6 wt% respectively [14]. Thus the reactants to prepare Cr_2AlC were above two carbides and Al metal. When the synthesized carbide powder was milled for 15 h and 30 h, there was no significant change in the stability of the carbide; i.e. phase transformation or formation of any new phase did not happen (Fig. 1). However the intensities of the peaks were found to be reduced slightly after milling, along with some broadening of peaks, indicates the reduction in crystallite size and straining. The measured FWHM values (full width half maximum) and crystallite size for 15 h

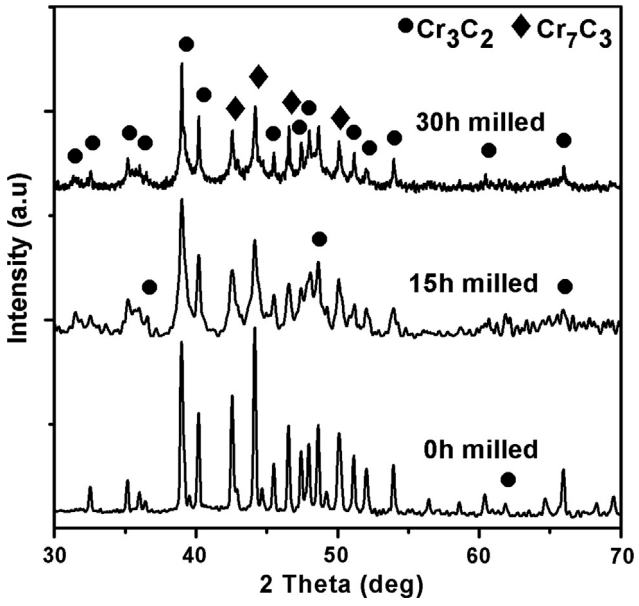

Fig. 1. X-ray diffraction patterns of CrC_x powders milled at various time durations of 0 h (as-synthesized), 15 h and 30 h.

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