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Dense $MoSi_2$ produced by reactive flash sintering: Control of Mo/Si agglomerates prepared by high-energy ball milling

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ABSTRACT

The objective of this work is to determine the influence of the agglomeration state of the MA mixture on the microstructure and the chemical composition of SPS end-products. In order to produce $MoSi_2$ with a microstructure and a density perfectly controlled via reactive sintering implying an SHS reaction, the characteristics of Mo/Si mechanically activated (MA) powder mixtures were investigated. Indeed, the MA powders have been characterized in terms of their surface specific area, size, phase composition and microstructure. The high-energy milling allows the formation of agglomerates (0.8 to 800 μm) composed of nanometric crystallites of molybdenum and silicon, as a consequence of a continuous fracture-welding process. This enhances the reactivity of powder mixtures due to an increase of interface number. The simultaneous synthesis–consolidation in one step could be performed using the spark plasma sintering (SPS) process. This study was performed on three agglomerate sizes: ∅<125 μm, ≤125 μm<250 μm and ≥250 μm.

1. Introduction

Molybdenum disilicide ($MoSi_2$) is a promising material for high-temperature applications. It has a high melting point (2303 K), a high hardness (1–1.3 GPa) and a good oxidation resistance compared to other refractory intermetallic compounds [1]. Thus, this material is mainly used for furnace heating elements and coatings on molybdenum or other refractory metals. Moreover, with additions of Mo_5Si_3 as a second phase, $MoSi_2$ is designed to satisfy the demands of high-temperature applications in an aggressive atmosphere [2]. The high melting point of $MoSi_2$ makes difficult its synthesis by conventional processing methods, such as solid-state reactions [3], spray forming [4] or hot pressing [5–8]. Prior works on a consolidation of nanopowders obtained by mechanical alloying aimed at accomplishing this challenge [9]. The consolidation techniques to produce materials with a density close to the theoretical one while preserving a nano-organization can be hot-pressing [10], hot electric discharge sintering [11], plasma activated sintering (PAS) [12] and spark plasma sintering (SPS) [13,14]. Prior works reported that SPS was an effective method for the fabrication of monolithic $MoSi_2$ using powders prepared by SHS [15]. Few years ago, nano-organized materials were simultaneously synthesized and consolidated from MA powder mixtures [16] by the combined application of an electrical field (AC current, 60 Hz) and a mechanical pressure during combustion synthesis. High-energy milling allows the formation of agglomerates (0.8 to 800 μm) composed of nanometric crystallites of molybdenum and silicon, as a consequence of a continuous fracture-welding process. It allows the control of the formation of nano-organized materials [14]. Gras et al. [17] showed that mechanically activated mixture powders are mainly composed of Mo and Si elements, but also with the C11b-type α-$MoSi_2$ phase. Mechanical treatment of powder mixtures before a combustion synthesis enhanced their reactivity due to a fracture-welding process which increased the number of interfaces. Indeed, mechanical activation of Mo and Si powders increases the heat rates and the combustion wave velocity by a factor up to three [17]. Consequently, we were able to perform simultaneous synthesis–consolidation in one step using the SPS process. It was possible to master the microstructure (grain size, defects) of the end-product by controlling the SPS processing parameters [18,19]. The objective of this work is to investigate the influence of the agglomeration state of the Mo/Si mixture prepared by ball milling on the chemical composition and on the microstructure of SPS end-products in terms of crystallite size and density for producing dense $MoSi_2$ exhibiting a well defined microstructure.

2. Experimental procedure

The synthesis process to produce dense nanostructured $MoSi_2$ from elemental powders consists in two steps [16]: (i) mechanical activation of the elemental powder mixture by a short treatment in a planetary mill, and (ii) synthesis and densification of $MoSi_2$ in one step by SPS.

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The Si and Mo reactants are taken in stoichiometric ratio 2:1. 10 g mixture of elemental powders of Mo (Sigma-Aldrich, −100 mesh and 99.9% purity) and Si (Sigma-Aldrich, −325 mesh and 99% purity) was co-milled in a planetary ball vario-mill Fritsch Pulverisette [20,21]. Based on previous works [22,23], a specific ball-milling condition was established at 350 rpm (rotation per minute) for the disk rotation speed, −250 rpm for the absolute vial rotation speed and the milling time was selected to be 2 h uninterrupted. The powders being constituted of quite abrasive materials, a short duration of milling has been selected to avoid the contamination of the product by the milling tools. Indeed, for the selected milling condition, no contamination from the vials or the stainless steel balls was detected (Fig. 1). In fact, in order to limit or to control the powder contamination by the milling tools but, also to increase simultaneously the yield of MA powder mixtures, three millings without cleaning milling tools have been carried out. Indeed, under these conditions, the ductile character of powders induced the formation of Mo/2Si coating on the vial surface aging as a protective coating against the abrasion on the surface of tempered iron tools. In addition, the milling parameters were selected to be short to avoid the formation of mechanically-induced product phases, but still sufficiently long for producing mechanically activated agglomerates (Fig. 2). In fact, fracture and welding are the two basic events which cause a permanent exchange of material between particles and ensure a mixing of components at a nanometer scale level [22,23].

The second step is the field-activated synthesis using the SPS device. The mechanically activated powders were first cold compacted into a green body in a cylindrical graphite die lined with graphite foil using a uniaxial pressure of 80 MPa during 1 min. The relative density of the green sample resulting from the cold compaction was about 60%, determined by geometrical measurements. The graphite die containing the cold-compacted sample was set inside the SPS chamber. Dr Sinter 515 S SPS was used [24]. SPS process is a pressure-assisted pulse-current sintering using direct current (DC). By repeated application of DC pulses, spark point discharges and Joule heating points result in efficient sintering with low power consumption. The experimental procedure is well-detailed elsewhere [22]. A uniaxial pressure of 70 MPa was applied both during the reaction and during the cooling. A high DC current was generated, increasing from 0 to 1750 A in 20 s then held at a maximum value for 160 s. Thus, the total duration for applying DC pulse current from the beginning of the heating to the beginning of the cooling down is equal to 3 min. Temperatures were measured by means of a K-type thermocouple. A heating rate up to 453 K/min and a holding time of 10 min at 1414 °C were performed for reducing the formation of Mo_5Si_3 [22,23]. The products were typically disks of 18.8 mm in diameter and 2.2 mm in height. Before characterization, the samples were first polished with 180-grit silicon carbide and up to 1 μm with diamond paste and, finally cleaned in an ultrasonic ethanol bath in order to remove surface contamination from graphite foil. The density of the products was evaluated by Archimede's method.

X-ray powder diffraction (XRD) measurements were performed with a Bruker-AXS D8 Advance diffractometer (CuK_α radiation, $\lambda = 0.154051$ nm) using a super speed VANTEC-1 detector. Pattern decomposition was carried out with the profile-fitting program TOPAS© using Le Bail's method [25]. The particle size distribution was calculated from a laser granulometer Coulter LS 130. A JEOL 6400F Scanning Electron Microscope (SEM) with a field emission gun (FEG) and coupled with a LINK OXFORD Energy Dispersive X-ray Spectrometry (EDXS) were used to analyze respectively the grain morphology and the local chemical composition of MA-agglomerates and SPS end-products. Consequently, MA powders were embedded and polished whereas dense materials were cut along the axial direction and were embedded in carbon charged resin (Konductomet®). A back scattered electron (BSE) technique was also used to determine the elemental chemical distribution. To estimate the global chemical composition of each granulometry class, EDXS measurements were also performed on $MoSi_2$ products annealed at 1000 °C in vacuum during 24 h in order to get a reference material, these analyses were performed on square surfaces (100×100 μm²). The chemical composition was determined from 50 measurements.

3. Experimental results

The particle size distribution in the powder mixture is very large (0.4 to 150 μm, Fig. 3a). Coupled with SEM observations (Fig. 3b), it has been found that the ball milling induces the formation of aggregates by a fracture-welding process [26]. The composition inside aggregates is not homogeneous, especially when the aggregate size is larger than 250 μm. As observed in Fig. 4, the mechanically activated mixture is composed of Mo and Si. The crystallite size of this powder was found, via the method described by Le bail [25] from XRD patterns, to be equal to 50 nm and to 20 nm for Mo and Si, respectively. A quantitative Rietveld analysis shows that the chemical

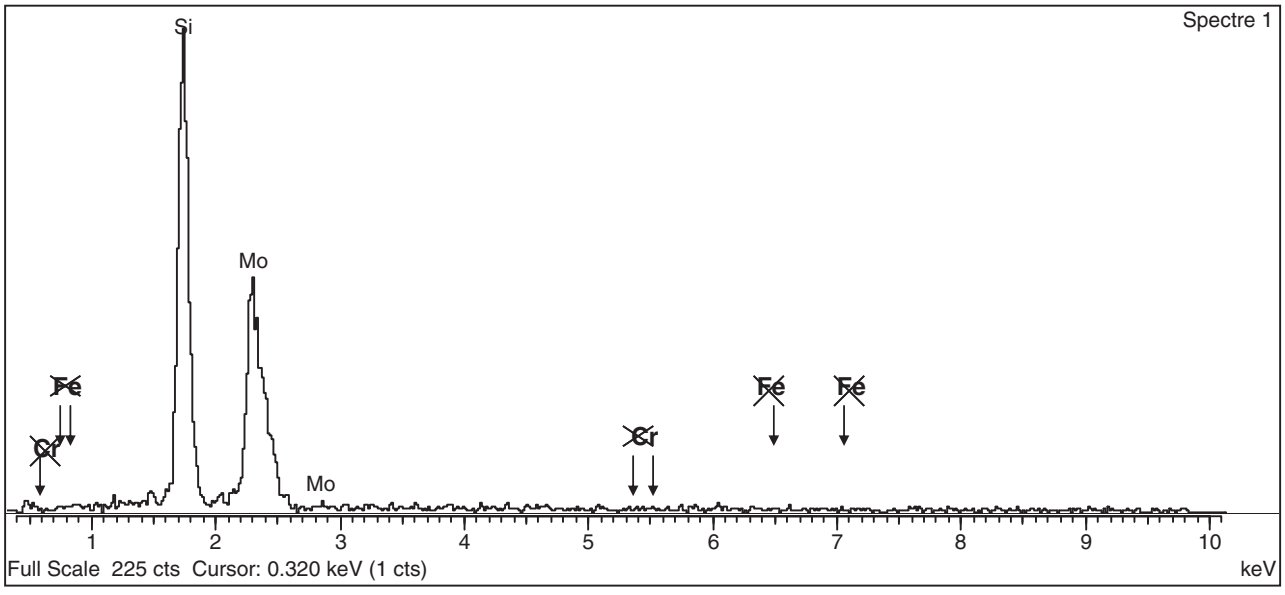

Fig. 1. EDXS spectrum of Mo/Si mechanically activated mixture from the following ball milling condition P4 (350 r.p.m./−250 r.p.m./2 h)].