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Preparation of $MoSi_2$–Al_2O_3 nano-composite via MASHS route

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ABSTRACT

In this study, $MoSi_2$–Al_2O_3 nano-composite powder was prepared by mechanical alloying. Mixture of MoO_3, Si and Al powders was exposed to high energy ball milling. Phase compositions and structural evolutions during milling were investigated by X-ray diffraction (XRD) analysis. The morphology of the milled powders was evaluated by scanning electron microscope (SEM). Within short milling times [15, 25 and 60 minutes in ball to powder weight ratios (BPR) of 35:1, 20:1 and 10:1, respectively], a combustion process occurred within the milling powder and the process mechanism was characterized to be mechanically activated self-propagating high-temperature synthesis (MASHS) type. From XRD results it was found that during the combustion process, MoO_3 was completely reduced with Al and the resulting Mo reacted with Si to produce molybdenum disilicide and eventually a $MoSi_2$–Al_2O_3 nano-composite powder formed within a short period of time. Further milling resulted in reduced mean crystallite sizes and increased lattice micro strain in the product phases. After 30 hours of milling in BPR of 35:1, the mean crystallite sizes were found to be 10, 9 and 11 nm for Al_2O_3, α-$MoSi_2$ and β-$MoSi_2$, respectively. Also, effect of stearic acid addition as a Process Control Agent (PCA) was studied and the results showed that its usage postpones the reaction initiation and reduces mean crystallite sizes.

1. Introduction

Molybdenum disilicide is a promising high-temperature material, due to its unique combination of physical properties. Besides having a low density of 6.24 g/cm^3 and a high melting point of 2030 °C, it exhibits high thermal and electrical conductivities, as well as excellent corrosion and high temperature oxidation resistance [1–3].

However, like most of the intermetallics, $MoSi_2$ also exhibits extreme brittleness and poor impact strength at low temperatures, and decreased strength and creep resistance at elevated temperatures. Thus, it is essential to improve the room-temperature fracture toughness, elevated-temperature strength and creep resistance. It is well documented that an improved strengthening and toughening of $MoSi_2$ matrix is possible through the incorporation of second phase reinforcements such as ceramic particles, whiskers or continuous fibers [4,5]. $MoSi_2$ is thermodynamically stable in contact with a large number of carbide, nitride, oxide and boride ceramic reinforcements like SiC, TiC, Si_3N_4, ZrO_2, Al_2O_3, Y_2O_3, TiB_2 and ZrB_2 at elevated temperatures [1,3,6,7]. Among these compounds, Al_2O_3 has a thermal expansion coefficient similar to that of $MoSi_2$. Therefore, its use as reinforcement in $MoSi_2$ matrix can reduce the thermal tension and improve the thermal shock resistance. $MoSi_2$–Al_2O_3 composite has many industrial applications. Microlaminate $MoSi_2$–Al_2O_3 composite tubes are used as inert gas lances in molten alloys such as molten aluminum (at 725 °C) and copper alloys (at 1200 °C) [8].

$MoSi_2$ and its composites have been synthesized by various methods such as conventional arc-melting and casting, mechanical alloying, hot pressing, reaction sintering, plasma-spray processing, self propagating high-temperature synthesis, and solid-state displacement reactions [1,9–21]. Mechanical alloying (MA) is basically a dry and high energy ball milling process which has been used to synthesize alloys, oxide-dispersion-strengthened alloys, amorphous alloys, various intermetallics compounds, etc. [22]. Zakeri et al. prepared $MoSi_2$–Al_2O_3 composite by milling of MoO_3, SiO_2 and Al powders mixture [20]. In this method, the final product was contaminated because of incomplete reduction of oxides. Also, silica due to its glassy nature acts as a diluent and postpones the reduction reaction.

In this research mechanically induced self propagating reaction was used to prepare $MoSi_2$–Al_2O_3 nano-composite. MoO_3, Si and Al powders were used as staring materials and less contamination of the final product was expected in this method because of using Si instead of SiO_2. Moreover, effect of process control agent (PCA) addition on characteristics of the milling products and also on the process was studied. PCAs are generally added to reduce the effect of cold welding. They also act as surface-active agents. The PCA adsorbs on the surface of the powder particles and minimizes cold welding between powder particles and thereby inhibits agglomeration. The surface-active agents adsorbed on particle surfaces interfere with cold welding and lower the surface tension of the solid material. A reduction in surface energy results in the use of shorter milling times and/or generation of finer powders.

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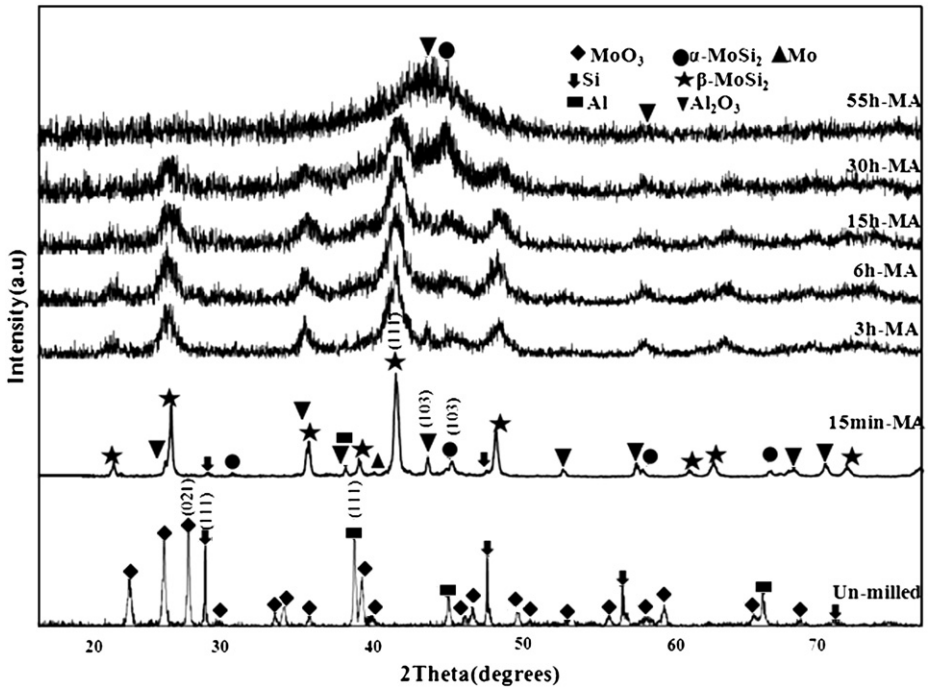

Fig. 1. XRD patterns of the un-milled powder mixture together with samples milled with a BPR of 35:1 for different milling times.

2. Experimental procedure

Commercially pure MoO_3 (99.5%, 1–15 μm), Al (99.8%, <100 μm) and Si (99.999%, <60 mesh) powders were used as starting materials. They were accurately weighed according to Reaction (1) and mixed together.

$$MoO_3 + 2Si + 2Al \rightarrow MoSi_2 + Al_2O_3 \left(\Delta G^o{}_{25} = -1045.81 \text{ kJ mol}^{-1} \text{ and } \Delta H^o{}_{25} = -1061.5 \text{ kJ mol}^{-1}\right) \quad (1)$$

In a number of experiments, 1 wt.% of stearic acid was also added to the powder mixture as a process control agent (PCA) before milling operation.

The powder mixture was milled in a Fritch P6 type planetary ball mill. The vial and balls were made of hardened chromium steel. The BPRs were 35:1, 20:1 and 10:1 and the rotation speed (cup speed) was 600 rpm during the milling. The milling operation was pursued in argon atmosphere to avoid the oxidation of materials. The morphology and phase identification of the samples were examined by SEM (CamScan MV2300) equipped with an energy dispersive spectrometer (EDS, Oxford Instrument) and XRD (Philips PW-1730) using CuKα

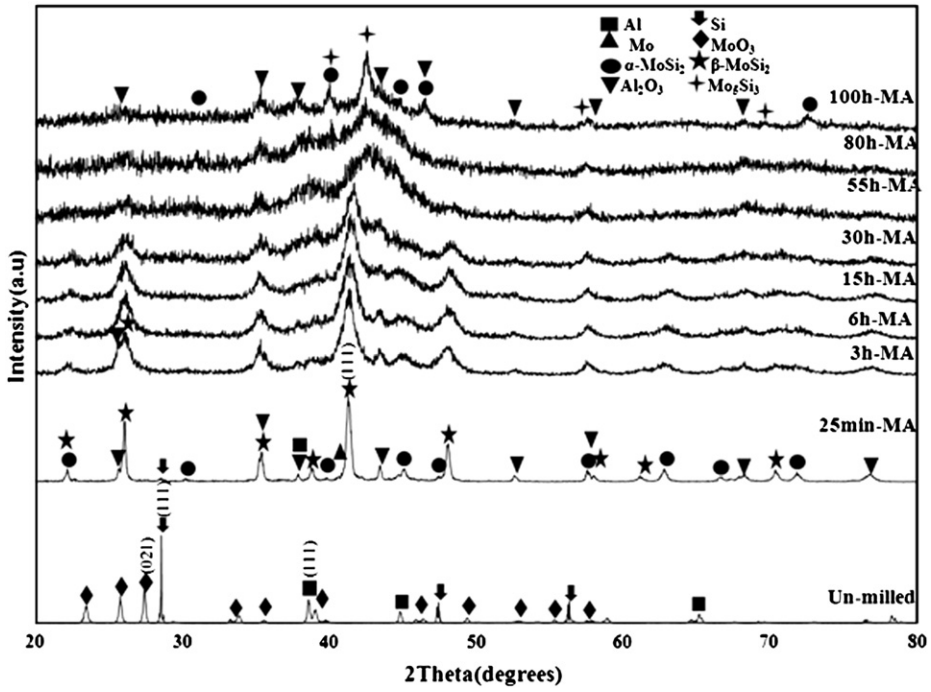

Fig. 2. XRD patterns of the un-milled powder together with the samples milled for different periods of time in a BPR of 20:1.