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Synthesis of α-Mo–Mo_5SiB_2–Mo_3Si nanocomposite powders by two-step mechanical alloying and subsequent heat treatment

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ABSTRACT

A two-step mechanical alloying process followed by heat treatment was developed as a novel approach for fabrication of Mo–12.5 mol%Si–25 mol%B nanocomposite powders. In this regard, a Si–43.62 wt.% B powder mixture was milled for 20 h. Then, Mo was added to the mechanically alloyed Si–B powders in order to achieve Mo–12.5 mol%Si–25 mol%B powder. This powder mixture was further milled for 2,5,10 and 20 h. All of the milled powders were annealed at 1100 °C for 1 h. After first step of milling, a nanocomposite structure composed of boron particles embedded in Si matrix was formed. On the other hand, an α-Mo/$MoSi_2$ nanocomposite was produced after second step while no ternary phases between Mo, Si and B were formed. At this stage, the subsequent annealing led to formation of α-Mo and Mo_5SiB_2 as major phases. The phase evolutions during heat treatment of powders can be affected by milling conditions. It should be mentioned that the desirable intermetallic phases were not formed during heat treatment of unmilled powders. On the other hand, α-Mo–Mo_5SiB_2–Mo_3Si nanocomposites were formed after annealing of powders milled for 22 h. With increasing milling time (at the second step), the formation of Mo_3Si during subsequent heat treatment was disturbed. Here, an α-Mo–Mo_5SiB_2–$MoSi_2$ nanocomposite was formed after annealing of 30 and 40 h milled powders.

1. Introduction

The increasing demands for materials which can withstand prolonged exposure to extremely high operating temperatures have led to the design and development of high temperature materials in recent decades [1,2]. In this regard, conventional Ni-based superalloys are currently used for manufacturing of many hot sections such as gas turbine components [3]. Ni-based superalloys show adequate oxidation and mechanical properties at elevated temperatures, but their service temperature is limited to 1000 °C.

In many industries such as aerospace or power plants, the service temperature exceeds 1000 °C [3–6]. The oxidation resistant intermetallics such as iron, nickel and titanium aluminides are of considerable interest for these applications. These intermetallics have densities lower than superalloys, but their melting temperatures (1400–1600 °C) limit their maximum service temperature to approximately 1200 °C [7,8].

Here, molybdenum desilicides with good oxidation and creep resistance can be considered as an alternative. $MoSi_2$ has a high melting point (2030 °C), a moderate density (6.24 g/cm^3) and good oxidation resistance due to the formation of a protective silica scale at high temperatures. $MoSi_2$ is widely used in heating elements of resistance furnaces because it shows good oxidation resistance during long-term exposure in air at high temperatures. However, $MoSi_2$ is very brittle at room temperature and exhibits poor creep resistance at high temperatures. On the other hand, it shows pest oxidation at moderated temperatures (500–800 °C) [9–11]. Therefore, the structural applications of $MoSi_2$ have encountered some issues.

Other Mo–Si compounds such as Mo_5Si_3, Mo_3Si, and α-Mo (Mo-rich solid solution) show low oxidation resistance, but they may show greater fracture toughness in comparison to $MoSi_2$, especially in the case of α-Mo. On the other hand, Mo_5Si_3 has superior creep resistance when compared to $MoSi_2$, but, the oxidation resistance of this compound is poor [12]. However, Meyer et al. [12–15] found that small additions (2 wt.%) of boron to Mo_5Si_3 can noticeably improve the isothermal oxidation behavior of this compound at high temperatures and can eliminate the pest oxidation at moderate temperatures. Therefore, Mo–Si–B ternary system has been of considerable interest in recent years.

A main point of the microstructural designs in Mo–Si–B system is the ternary intermetallic Mo_5SiB_2 (T2) phase. T2 shows high melting temperature and outstanding creep resistance at high temperatures due to its complex tetragonal structure. On the other hand, it shows better high temperature strength than $MoSi_2$ and Mo_5Si_3. The excellent oxidation resistance of T2 phase is due to the

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formation of the boron-added silica glass scale at high temperatures [16,17].

Two main alloy systems have been developed in Mo–Si–B system so far [18–24]. Ternary alloys consisting of Mo_5Si_3, Mo_5SiB_2, and Mo_3Si exhibit excellent oxidation resistance at elevated temperatures (e.g., 1300 °C) [18–21]. However, because of their brittleness, three phase alloys including α-Mo, T2 and Mo_3S have been earlier developed [22–24]. These alloys contain a ductile phase (α-Mo). They exhibit lower oxidation resistant than Mo_5Si_3-T2–Mo_3Si alloys, but, the presence of α-Mo can improve the fracture toughness at ambient and/or elevated temperatures [18–24].

The industrial manufacturing of the Mo–Si–B alloys has encountered some limitations due to high melting point of these materials. So, the application of conventional casting and forming processes has been limited. Several techniques including mixing and pressing of elemental powders followed by sintering and hot isostatic pressing (HIP) [8], reaction hot pressing [25,26], arc melting and remelting [27,28], siliciding of molybdenum and boronizing of $MoSi_2$ using molten salt systems [29], plasma rotating electrode process followed by consolidation by HIP [30,31], and induction plasma spraying [32,33] have been developed to synthesis the Mo–Si–B alloys.

Mechanical alloying (MA) is a solid state technique used for fabrication of nanocrystalline alloys and intermetallic compounds. MA allows materials scientists to overcome material limitations and to manufacture alloys that are difficult or impossible to be produced by conventional melting and casting techniques. Through this technique, the fine-grained powders can be formed [34–38]. During the last decade, many equilibrium and/or non-equilibrium materials have been successfully synthesized through this technique. These materials include amorphous, nanocrystalline and quasicrystals materials, rare earth magnets and intermetallics [39–43]. The milling of binary Mo–Si system has been reported in the many literatures [44–53], however, the literatures describing the mechanical alloying of ternary Mo–Si–B system are a few [54,55].

Yamauchi et al. [54] attempted to produce Mo–Si–B in situ composites (Mo_5SiB_2 and Mo/Mo_5SiB_2) by MA, combination of MA and heat treatment, and combination of MA and spark plasma sintering. They reported that the direct synthesis of Mo–Si–B in situ composite powder (Mo and Mo_5SiB_2) is unsuccessful by MA and heat treatment. They pointed up that Mo–Si compounds formation could be suppressed in MA process due to preferred reaction between Mo and B. But, they obtained Mo_5SiB_2 by combination of MA and spark plasma sintering. Since mechanical alloying is a step-by-step process, the formation of phases during mechanical alloying can be influenced by milling conditions such as addition sequence of powders during mechanical alloying. Sadeghian et al. [56] studied the synthesis of Al–TiB_2 composite by mechanical alloying of pure Al, Ti and B. They reported that direct mechanical alloying leads to the formation of undesirable Al_3Ti intermetallic compound, but double stage addition of aluminum can prevent the formation of undesirable compounds even after annealing at high temperatures.

In this study, a two step mechanical alloying process was used to produce Mo–Si–B nanocomposite powders. The main concern was to hinder the formation of undesirable phases like molybdenum borides during mechanical alloying and heat treatment. The phase transformations and the structural and morphological evolutions of powders during mechanical alloying and subsequent heat treatment were also investigated.

2. Experimental procedure

The elemental powders of Mo (99.7 wt.% purity), Si (99.8 wt.% purity), and B (99 wt.% purity) were used as starting materials. A two step mechanical alloying process was designed to obtain Mo–Si–B alloy powders. In the first step, a mixture of Si–43.62 wt.%B was milled for 20 h. In the second step, Mo was added to the mechanically alloyed B–Si powders in order to achieve Mo–12.5 mol%Si–25 mol%B powders. At this stage, the powders were milled for 2,5,10 and 20 h. Finally, all of the milled powders were annealed under argon atmosphere at 1373 K for 1 h. Details of process parameters and abbreviated name of products are given in Table 1.

MA process was carried out in a high energy planetary ball mill under Ar atmosphere. The milling media consisted of nine 20 mm diameter balls confined in a 250 ml volume vial. In this regard, hardened steel vials and balls were used for ball milling. The ball-to-powder weight ratio and milling speed were 15:1 and 300 rpm, respectively. The total powder mass was 20 g. The phase composition of powders were investigated using X-ray diffraction (Philips X'PERT MPD) using Cu Kα radiation (λ = 0.1542 nm) generated at 40 kV. During X-ray diffractometery, the step size was 0.05°. Microstructural studies of samples were performed by using a scanning electron microscope (SEM, Philips XL30) operated at 30 kV. In this regard, powder particles were mounted and their surfaces were polished using abrasive papers followed by a series of diamond pastes. The polished cross-section of powders was studied by SEM.

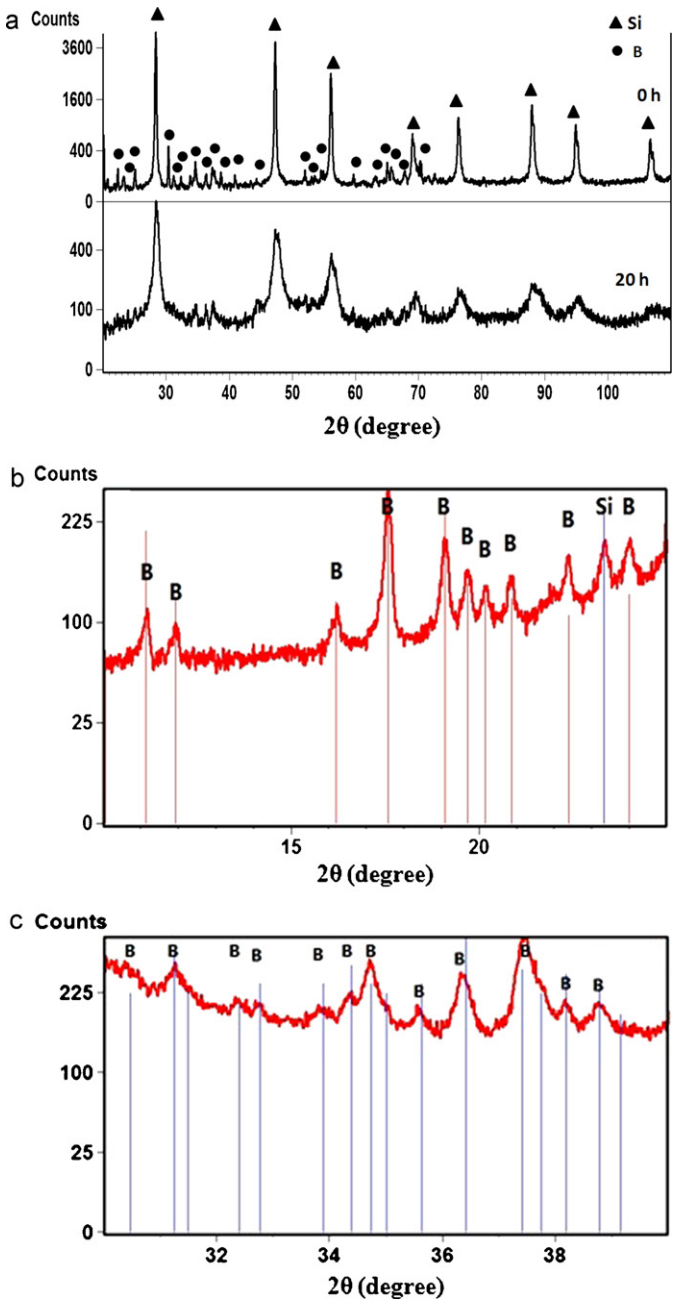

Fig. 1. (a) X-ray diffractograms of Si–43.62 wt.%B powder mixture before and after 20 h mechanical alloying. (b,c) X-ray diffractograms of 20 h mechanically alloyed Si–43.62 wt.%B powder mixture in 2θ angles between 10–25° (b) and 30–40° (c) at test condition of very low step size (0.005), high maintenance time per each steps (2.5 s) and more extent of powders.