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Effects of oxide precursors on fabrication of Mo_5Si_3–Al_2O_3 composites via thermite-based combustion synthesis

C.L. Yeh*, J.A. Peng

Department of Aerospace and Systems Engineering, Feng Chia University, 100 Wenhwa Rd., Seatwen, Taichung, 40724, Taiwan

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ABSTRACT

Fabrication of the Mo_5Si_3–Al_2O_3 composite with a broad composition range was studied by thermite-based combustion synthesis. The addition of two thermite mixtures composed of $0.6MoO_3 + 0.6SiO_2 + 2Al$ and $MoO_3 + 2Al$ into the Mo–Si reaction system was thermally beneficial for the self-sustaining combustion process. The former thermite reagent is less exothermic than the latter. Moreover, experimental results showed that the combustion temperature and flame-front velocity decreased with increasing molar ratio of Mo_5Si_3 to Al_2O_3 formed in the composite. As a consequence, the MoO_3/SiO_2/Al-based reaction scheme was adopted to synthesize composites with Mo_5Si_3/Al_2O_3 from 0.4 to 0.7, and MoO_3/Al-based system was for the products with Mo_5Si_3/Al_2O_3 from 0.8 to 1.6. The XRD pattern indicated Mo_5Si_3 as the dominant silicide. Mo_3Si was formed as the minor phase, because a small amount of Si dissolved in Al_2O_3. This was confirmed by the presence of both Al_2O_3 and aluminum silicate, a solid solution of Al_2O_3 and SiO_2, in the final products.

1. Introduction

Refractory metal silicides have received considerable attention for high-temperature structural applications, owing to their favorable properties such as high melting point, high strength, good oxidation resistance, and excellent creep behavior at elevated temperatures [1,2]. Compared to other refractory metals like Ta, W, and Re, molybdenum silicides are more attractive because of a lower density for Mo [3]. The Mo–Si binary system has three silicides, $MoSi_2$, Mo_5Si_3, and Mo_3Si. Of these, $MoSi_2$ is the most extensively studied phase [4–7]. Besides, Mo_5Si_3 has been recently considered for ultra-high temperature use due to its high melting temperature of 2180 °C, reasonable density of 8.19 g/cm^3, and creep strength higher than $MoSi_2$ [8]. Mo_3Si is also promising because Mo_3Si with Al additions exhibits excellent oxidation resistance [9].

Among various fabrication techniques, combustion synthesis in the self-propagating high-temperature synthesis (SHS) mode takes advantage of the highly exothermic reaction, and hence, has the merits of low energy requirement, short processing time, simplicity, and a structural and functional diversity of final products [10–12]. Preparation of transition metal silicides of the Ti–Si, Zr–Si, Nb–Si, Ta–Si, and Mo–Si systems has been widely investigated by the conventional SHS process using elemental powder compacts of their corresponding stoichiometries [13–16]. In contrast to the processing of $MoSi_2$, weak reaction exothermicity hinders formation of Mo_5Si_3 from the elemental sample via the classical SHS process. As a result, Zhang and Munir [17] reported that a preheating temperature of 500 °C (thermal activation) was required for the 5Mo + 3Si sample to achieve self-propagating combustion and a multiphasic product composed of $MoSi_2$ and Mo_5Si_3 was obtained. Subrahmanyam [18] produced pure Mo_5Si_3 through volumetric reaction (thermal explosion of combustion synthesis) of a reactant pellet initially heated in an induction furnace at a rate of 600–700 °C/min to the ignition temperature of 1200 °C. Another modification known as microwave activated combustion synthesis (MACS) was utilized by Jokisaari et al. [19]. Their results pointed out that an off-stoichiometric mixture containing 16 wt% Si and 84 wt% Mo favored the formation of Mo_5Si_3 [19].

Like most of the transition metal silicides, molybdenum silicides suffer from brittleness and poor impact strength at low temperatures. The addition of a ceramic compound, such as ZrO_2, Al_2O_3, SiC, Si_3N_4, and ZrB_2, to the silicide matrix in a form of composites has been proven to be effective in improving the low-temperature fracture toughness, high-temperature strength, and oxidation resistance [5,20–22]. Al_2O_3 is a particularly suitable reinforcement for Mo_5Si_3 due to its thermal expansion coefficient similar to that of

* Corresponding author.
E-mail address: clyeh@fcu.edu.tw (C.L. Yeh).

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Mo_5Si_3. The Mo_5Si_3–Al_2O_3 composite with a dense microstructure was fabricated from MoO_3, Mo, Si, and Al powders through ball milling followed by a hot-pressing sintering method [22]. It was reported that the high-energy milling induced an energetic thermite reaction between MoO_3 and Al, and then a self-propagating synthesis reaction of the powder mixture. Evaluation of mechanical properties and oxidation resistance of the Mo_5Si_3–Al_2O_3 composite confirmed the role of Al_2O_3 in reinforcement [22]. Besides the thermite reagent of MoO_3 and Al, some highly exothermic additives such as the Ti/C, Ti/B, and Mo/B mixtures have recently been incorporated into the Mo-Si reaction system to enable the SHS process and prepare various composites based upon molybdenum silicides or borosilicides [23,24].

Because there are relatively few studies available on the production of Mo_5Si_3-based composites, this study aims at fabricating the Mo_5Si_3–Al_2O_3 composite by self-propagating combustion synthesis involving thermite reduction of oxide precursors. When incorporated with the thermite reaction based on Al as the reducing agent, the SHS process represents an in situ manufacturing route capable of producing Al_2O_3-reinforced composites with uniform phase distribution [25,26]. Two thermite mixtures, Al–MoO_3–SiO_2 and Al–MoO_3, were adopted to broaden the composition range of the Mo_5Si_3–Al_2O_3 composite. Their influence on sustainability of the SHS process was explored. Effects of sample stoichiometry were studied on the flame-front velocity, combustion temperature, and phase constituents of the final products.

2. Experimental methods of approach

The starting materials of this study included Mo (Strem Chemicals, < 45 μm, 99.9%), Si (Strem Chemicals, <45 μm, 99.5%), Al (Showa Chemical Co., <45 μm, 99.9%), MoO_3 (Acros Organics, 99.5%), and SiO_2 (Strem Chemicals, 99%). Two thermite reagents were prepared to mix with Mo and Si powders. One comprises two oxide precursors (MoO_3 and SiO_2) and Al at a molar ratio of MoO_3:SiO_2:Al = 0.6:0.6:2. The other is a MoO_3/Al-based reaction scheme adopting a single oxide at MoO_3:Al = 1:2. Reactions (1) and (2) represent two combustion systems with different thermite mixtures for the production of Mo_5Si_3–Al_2O_3 composites.

$$(5x-0.6)Mo+(3x-0.6)Si+0.6MoO_3+0.6SiO_2+2Al\rightarrow xMo_5Si_3+Al_2O_3 \quad (1)$$

$$(5y-1)Mo+(3y)Si+MoO_3+2Al\rightarrow yMo_5Si_3+Al_2O_3 \quad (2)$$

where the stoichiometric coefficients, x and y, signify the number of mole of Mo_5Si_3 formed in the composite per unit mole of Al_2O_3 from Reactions (1) and (2), respectively. It should be noted that the thermite reagent adopted in Reaction (2) is the same as that used by Chen at al. [22]. In their study, the starting composition of the reactant mixture was equivalent to the stoichiometry of Reaction (2) with $y = 1$.

In Reaction (1), the thermite reaction of $0.6MoO_3 + 0.6SiO_2 + 2Al$ is highly exothermic with $\Delta H = -683.7$ kJ and $T_{ad} = 3150$ K [27]. In spite of the heat of formation $\Delta H_f = -307.84$ kJ/mol for Mo_5Si_3, the 5Mo + 3Si reaction has a low adiabatic temperature of 1672 K due to the large heat capacity of Mo_5Si_3 [19]. This means that the addition of Mo and Si into the thermite mixture for the production of Mo_5Si_3 has a dilution effect on combustion. In this study, Reaction (1) was conducted with x varying from 0.4 to 0.7, within which self-sustaining combustion was achieved and products in a composite form were retained. Massive melting of the product was observed in the samples of Reaction (1) with $x < 0.3$ because of violent combustion, which resulted in the separation of intermetallic silicides from alumina in the recovered product. On the contrary, combustion ceased to proceed in Reaction (1) with $x > 0.7$ due to insufficient reaction exothermicity.

The thermite mixture of MoO_3 + 2Al is more energetic ($\Delta H = -930.7$ kJ and $T_{ad} = 4280$ K) than the $0.6MoO_3 + 0.6SiO_2 + 2Al$ reagent [27]. Consequently, Reaction (2) was anticipated to be capable of producing the composite with a larger proportion of Mo_5Si_3 to Al_2O_3. The performance regime of Reaction (2) was found in the range of $0.8 \le y \le 1.6$, within which combustion was self-sustaining and composite products were obtained. However, for the MoO_3/Al-based reaction scheme phase separation often occurred when the value of y less than 0.8 and combustion was quenched when y larger than 1.6.

Reactant powders were dry mixed in a ball mill and compressed into cylindrical samples with 7 mm in diameter, 12 mm in length, and 60% in relative density. The SHS experiments were performed under high-purity (99.99%) argon of 0.15 MPa. The combustion temperature of the powder compact was measured by a fine-wire (125 μm) Pt/Pt-13%Rh thermocouple (Omega Inc.) attached on the sample surface at the position about 8 mm below the ignition point. The propagation rate of combustion wave was deduced from the sequence of combustion images recorded by a color CCD video camera (Pulnix TMC-7). To facilitate the accurate measurement of instantaneous locations of the combustion front, a beam splitter (Rolyn Optics), with a mirror characteristic of 75% transmission and 25% reflection, was used to optically superimpose a scale onto the image of the test sample. Phase constituents of the synthesized product were identified by an X-ray diffractometer (XRD) (Bruker, D8 SSS) and the microstructure was examined under a scanning electron microscope (SEM) (Hitachi, S3000N). Details of the experimental methods were previously reported [28].

3. Results and discussion

3.1. Combustion front velocity and reaction temperature

Fig. 1 illustrates a typical sequence of combustion images associated with Reaction (1) with $x = 0.6$. Experimental observations revealed that, as shown in Fig. 1, combustion propagated in a self-sustaining manner and usually accompanied a collapsed sample, confirming the synthesis reaction of strong exothermicity. Deformation of the sample pellet was attributed to formation of molten compounds during the SHS process. It is believed that MoO_3 and Al with relatively low melting points of 795 °C and 660 °C, respectively, are responsible for the presence of liquid phases. In order to provide better images with a distinct combustion front, the time intervals between selected pictures in Fig. 1 are not consistent. It should be noted that the time intervals ($\Delta t = 0.20$, 0.23, or 0.24 s) are very close during the flame propagation period ($t = 0.04$–2.30 s). Although the time intervals between images are not exactly the same, there is a scale optically superimposed on the left-hand side of the sample. This facilitates the analysis of the sequence of combustion images. It is useful to note that for Reaction (1) with $x < 0.3$ and Reaction (2) with $y < 0.8$, the melting of the sample became too massive to preserve the products in a composite form. The silicide phase and Al_2O_3 were separated from each other due to the difference in their densities.

Formation of porous products is inherent in the SHS process. The pores or crevices could be produced by unbalanced diffusion between the reactant particles or by vaporization and expulsion of the volatile impurities due to high temperatures. However, self-densification of the end product occurred in this study with the aid of molten phases formed during the SHS process. Therefore, the final products obtained in this study were much denser than the