Postprint: Study on Preparation Process of T2-Phase Alloys in Mo-Si-B Ternary System

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Abstract

Mo5SiB2 (T2) phase alloys were prepared by reduced-atmosphere conventional pressure sintering (TFS) and spark plasma sintering (SPS), and the microstructure of the alloys was characterized by XRD, SEM, TEM and other methods. The results indicate that a fast heating rate is the kinetic condition for synthesizing the T2 phase. Compared with conventional sintering methods, the SPS method provides a fast heating rate through its unique plasma-activated sintering mechanism, enabling rapid heating to the required temperature of 1500 ℃ in a short time. This avoids the formation of binary phases such as Mo3Si, Mo5Si3, and MoB through solid-solid reactions in the Mo, Si, and B mixed powders within the intermediate temperature range (600~1200 ℃), and instead achieves in-situ synthesis of the T2 phase through solid-liquid reactions. The alloy has an average grain size of 1.44 mm, with grain boundaries that are clear, clean, and free of transition zones, and no defects such as dislocations were observed within the crystals.

Full Text

Preamble

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Study on the Preparation Process of T2 Alloy in the Mo-Si-B System

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Abstract

Mo_5SiB_2 (T2) shows promise as an elevated-temperature structural material due to its high melting temperature (approximately 2200 °C) and excellent resistance to oxidation and creep. In this study, Mo_5SiB_2 (T2) alloys were prepared by both spark plasma sintering (SPS) and tube furnace sintering (TFS), with subsequent microstructural characterization by XRD, SEM-EDS, and TEM. The results demonstrate that a rapid heating rate is a critical dynamic condition for T2 synthesis. Compared with conventional methods, SPS provides rapid heating through its unique plasma-activated sintering mechanism, enabling the sample to reach the target temperature of 1500 °C within a short period. This allows molten Si to rapidly react with Mo and B to synthesize T2 via solid-liquid reactions before binary phases (Mo_3Si, Mo_5Si_3, MoB, etc.) can form through solid-state reactions in the 600–1200 °C range. The resulting alloy exhibits an average grain size of 1.44 m, with clear, clean grain boundaries showing no transition zones, and no defects such as dislocations observed within the crystals.

Keywords: Mo_5SiB_2 (T2), tube furnace sintering (TFS), spark plasma sintering (SPS), microstructure

Introduction

The stringent requirements for service temperature and lifespan in aerospace applications have exceeded the capabilities of conventional nickel-based superalloys. Over the past decade, numerous countries have developed structural materials for higher temperature service [1,2]. Mo-Si based alloys exhibit outstanding high-temperature strength and excellent creep resistance, but their poor high-temperature oxidation resistance has limited their application as ultra-high temperature structural materials [3]. Recent research [4] has shown that adding small amounts of boron to Mo-Si alloys significantly improves their high-temperature oxidation resistance, primarily due to the formation of the Mo_5SiB_2 (T2) phase. Consequently, the T2 phase and Mo-Si-B ternary alloys have attracted widespread attention [5–10].

Most current T2 alloy preparation methods employ arc melting or mechanical alloying. Arc melting often results in the precipitation of MoB and Mo_5Si_3 (T1) phases during solidification due to complex solidification pathways, making it difficult to prepare high-purity T2 alloys [6]. Even prolonged annealing cannot effectively remove secondary phases like MoB and instead tends to cause grain coarsening [11]. Mechanical alloying typically yields products containing substantial unreacted elemental Mo, and subsequent isothermal heat treatment more readily transforms residual Mo into binary silicides rather than the ternary

T2 phase [12,13]. Additionally, mechanical alloying lacks a necessary densification process. Therefore, systematic studies on the mechanical properties of the T2 phase remain limited compared with T1 and $MoSi_2$.

In-situ synthesis technology for composite materials, which has emerged in recent years, produces materials with clean, oxide-free, well-bonded interfaces because the reinforcement phase forms within the matrix. Moreover, the dispersed distribution and uniform microstructure benefit the improvement of mechanical properties, particularly at high temperatures [14,15]. This work leverages the advantages of in-situ synthesis to explore reasonable preparation processes and optimal parameters for T2 phase alloys, laying the foundation for subsequent systematic studies on their mechanical properties.

1. Experimental Methods

T2 phase alloys were prepared using both tube furnace sintering (TFS) and spark plasma sintering (SPS). The starting materials consisted of Mo and Si powders with 99.99% purity and B powder with 99.999% purity [16], with average particle sizes of 5.96 m, 6.23 m, and 3.63 m, respectively, and oxygen content below 500$×10^{-6}.The powders were mixed at a Mo : Si : B atomic ratio of 5 : 1 : 2 and ball-milled in a planetary mill at 300 r/min for 24 h (using C{2}H{5}$OH as medium), followed by vacuum drying at 50 °C for 8 h to obtain Mo-12.5Si-25B (atomic fraction, %) mixed powder according to the T2 stoichiometry.

The ball-milled Mo-12.5Si-25B powder was first pressed into cylindrical pellets (20 mm diameter, 8 mm thickness) using a tablet press, then subjected to TFS in a tube furnace with H_2 as the reducing atmosphere. The TFS parameters were: heating rate of 15 °C/min, high-purity H_2 (99.99%) flow rate of 35 L/h, sintering temperatures of 1350, 1400, 1450, 1500, and 1550 °C, and holding times of 1 and 2 h. For SPS, the same mixed powder was sintered with heating rates of 50–300 °C/min, sintering temperatures of 1300–1600 °C, holding time of 7 min, and applied pressure of 60 MPa. After sintering, samples were cooled to 500 °C at 20 °C/min, then furnace-cooled to room temperature. Pressure was maintained until 1200 °C during cooling, then gradually released, yielding T2 alloy discs 20 mm in diameter and 11 mm thick.

Phase analysis of the alloys prepared by both methods was performed using a D-Max X-ray diffractometer (XRD). Microstructural observation was conducted on a Supra 55 scanning electron microscope (SEM-EDS). The volume fractions of each phase were calculated from five SEM images using Image-Pro Plus 6.0 software. Fine microstructures were examined using a Tecnai F30 transmission electron microscope (TEM). Differential scanning calorimetry (DSC) was performed using a NETZSCH DSC 404 F3 Pegasus instrument. Sample shrinkage curves were obtained by differentiating the punch displacement data from the SPS equipment.

2. Results

2.1 T2 Phase Alloys Prepared by TFS

Figure 1 [Figure 1: see original paper] shows XRD patterns of Mo-Si-B compacts sintered by TFS at various temperatures for 1 h. At 1350 °C, strong diffraction peaks of Mo and Mo_3Si indicate substantial residual elemental Mo and Mo_3Si, suggesting incomplete reaction. As temperature increases, Mo peak intensity decreases and disappears by 1500 °C, while Mo_3Si peak intensity shows an increasing trend rather than decreasing. At 1550 °C, the Mo_3Si content exceeds that at 1500 °C and is significantly higher than at 1350 °C. This indicates that higher temperatures favor complete reaction of Mo to form Mo_3Si rather than the T2 phase, likely due to localized melting of the sample. When sintering temperature exceeds Si's melting point (1412 °C), localized melting occurs, exacerbating Si volatilization. In terms of saturated vapor pressure, Si (approximately 10^{-1} Pa at 1500 °C) is significantly higher than Mo (approximately 10^{-7} Pa at 1500 °C) and B (approximately 10^{-5} Pa at 1500 °C) [17], resulting in greater Si loss. Consequently, elevated temperatures alter the original composition, leading to formation of binary phases like Mo_3Si.

Considering T2 phase conversion rate and contents of residual Mo and Mo_3Si, 1400–1450 °C represents a relatively optimal sintering temperature range. To eliminate residual elemental Mo and obtain high-purity T2 alloys, this work extended the sintering time. Figure 2 [Figure 2: see original paper] shows XRD patterns after extending the holding time to 2 h. While Mo peak intensity decreases significantly at 1400 and 1450 °C, Mo_3Si peak intensity shows little change, indicating that extended holding time also fails to produce high-purity T2 alloys.

Figure 3 [Figure 3: see original paper] presents the relative densities of samples sintered by TFS at different temperatures, measured by the Archimedes method (with sample surfaces coated in Vaseline). The relative density shows no significant change with temperature and remains similar to the green compact density at approximately 50%, resulting in typical porous materials (Figure 4 [Figure 4: see original paper]).

2.2 T2 Phase Alloys Prepared by SPS

Figure 5 [Figure 5: see original paper] shows XRD patterns of samples sintered at 1500 °C by SPS with heating rates of 50–300 °C/min. The main phase in all samples is T2, but secondary phase contents vary significantly. At 50 °C/min, distinct peaks of Mo, MoB, and Mo_3Si indicate high contents of these phases and residual unreacted Mo. At 100 °C/min, Mo peaks disappear while Mo_3Si and MoB peak intensities decrease markedly. When the heating rate reaches 200 °C/min and above, diffraction peaks of Mo_3Si and other secondary phases vanish completely.

Heating rate substantially affects relative density (Figure 6 [Figure 6: see orig-

inal paper]). After sintering at 1500 °C, samples exhibit relative densities of 98.91% and 99.47% at heating rates of 50 and 200 °C/min, respectively. However, at 300 °C/min, relative density decreases to 97.83%. Higher heating rates create steeper temperature gradients that induce intense local reactions, releasing substantial reaction heat and accelerating atomic diffusion and synthesis rates, thereby promoting densification under axial pressure. However, excessively high heating rates (300 °C/min) prevent trapped gases (adsorbed moisture, air, MoO_3 and B_2O_3 volatiles [18]) from escaping [19], leaving pores in the microstructure and reducing density. Similarly, Shen et al. [20] found that heating rates exceeding 350 °C/min produced porous Al_2O_3 ceramics rather than dense bodies. Therefore, considering both T2 phase conversion and relative density, the optimal heating rate is 200 °C/min.

Figure 7 [Figure 7: see original paper] shows XRD patterns of samples sintered at various temperatures with a heating rate of 200 °C/min. All samples consist primarily of T2 phase but contain varying volume fractions of SiO_2, MoB, and Mo_3Si as secondary phases. At 1350 °C, unreacted Mo and substantial Mo_3Si and MoB indicate incomplete reaction due to low sintering temperature, slow atomic diffusion, and short diffusion distances, making it difficult for Mo, Si, and B powders to fully form T2 phase through solid-state reactions. As temperature increases, T2 diffraction peaks intensify and Mo peaks disappear. At 1500 °C, low-melting-point Si melts and rapidly diffuses to Mo and B particle surfaces (liquid Si diffusivity is 10^3–10^5 times higher than solid Si) [21], forming T2 phase through solid-liquid interfacial reactions and yielding high-purity T2 alloys. However, further temperature increases raise secondary phase contents; MoB and SiO_2 peaks intensify at 1550 and 1600 °C. Excessive sintering temperature reduces T2 content because localized discharge during SPS generates extremely high temperatures, causing particle melting. High temperatures reduce melt viscosity, allowing material to be extruded onto the die walls under pressure, altering local composition and decreasing T2 conversion. In this work, overflow material observed on graphite die walls after sintering at 1600 °C was found to be primarily Si, consistent with Si's low melting point. Additionally, increased SiO_2 content at higher temperatures (Figure 8 [Figure 8: see original paper]) indicates greater oxidation probability. Therefore, the optimal sintering temperature is 1500 °C.

Figure 9a [Figure 9: see original paper] shows an SEM image of the sample sintered at 1500 °C with a heating rate of 200 °C/min and an optical micrograph of T2 alloy grains after oxalic acid etching. Using Image-Pro Plus 6.0 software, the volume fractions were calculated as 99.15% T2, 0.25% MoB, and 0.60% SiO_2, with an average T2 grain size of 1.44 m (Figure 9b). Figure 10 [Figure 10: see original paper] presents a bright-field TEM image and corresponding SAED patterns for the sample prepared by SPS (200 °C/min, 1500 °C). The grain boundaries are clear, clean, and free of transition zones or other substances, with no defects such as dislocations observed within the crystals. SAED identification confirms these grains as single-phase T2, demonstrating that SPS is superior to argon arc melting, mechanical alloying, and TFS for producing high-purity,

dense T2 alloys with fine grains.

3. Analysis and Discussion

The TFS method was conducted in a tube furnace and, besides lacking necessary external densification pressure, produced samples containing substantial Mo_3Si and other secondary phases, primarily due to its heating mechanism. Resistance-heated furnaces have heating rates below 20 °C/min. In contrast, SPS achieves rapid sample heating through its unique spark plasma sintering mechanism, providing the essential kinetic conditions for T2 phase formation.

Investigating the phase evolution during heating of Mo-12.5Si-25B mixed powder helps explain why SPS produces high-purity T2 alloys. DSC and XRD were used to characterize this process. Figure 11a [Figure 11: see original paper] shows the DSC curve at a heating rate of 10 °C/min. The endothermic peak at 466.2 °C likely results from volume expansion or gas evolution, while the exothermic peak at 786.2 °C indicates phase transformations. Based on the XRD pattern of powder heated to 850 °C and quenched (Figure 11b), the reaction at 786.2 °C is inferred to be: $2Mo + B \rightarrow Mo_2B$. A prominent exothermic peak at 1093.5 °C corresponds to possible reactions based on the XRD pattern after heating to 1200 °C (showing Mo, T2, Mo_5Si_3, Mo_2B, Mo_3Si, and MoB peaks): $3Mo + Si \rightarrow Mo_3Si$; $5Mo + 3Si \rightarrow Mo_5Si_3$; $Mo + B \rightarrow MoB$; $5Mo + Si + 2B \rightarrow Mo_5SiB_2$.

Si melts at 1412 °C. When powder is heated to 1500 °C at 10 °C/min, Si melting occurs (under rapid heating conditions, reactions between Si and other elements may not complete entirely below 1412 °C; at 10 °C/min, there is no evidence that reaction temperatures exceed 1412 °C). Combining DSC and XRD data at 1500 °C suggests the exothermic peak between 1200–1500 °C corresponds to: $5Mo + Si(l) + 2B \rightarrow Mo_5SiB_2$; $2Mo_2B + Si(l) + Mo \rightarrow Mo_5SiB_2$; $2MoB + Mo_3Si \rightarrow Mo_5SiB_2$. Due to rapid liquid Si diffusion, reactions (6) and (7) proceed to form T2 from Mo_2B, Mo, Si, and B, while some Mo_3Si and MoB remain. Reactions between Mo_3Si and MoB are solid-state processes controlled by atomic diffusion. Since Mo_3Si and MoB crystal structures have relatively few vacancies and slow diffusion [23,24], complete transformation to T2 within short times is difficult [24]. Additionally, Mo_5Si_3 (T1) has large solid solubility, and B diffuses rapidly in T1 as a small atom; when B content in T1 exceeds its solubility limit, T1 can transform to T2 [25–27]. Compared with sintering at 1200 °C, residual Mo, MoB, and Mo_3Si do not decrease significantly, indicating that increasing sintering temperature is unrealistic for converting MoB and Mo_3Si to T2. To obtain single-phase T2 alloys, formation of binary phases like MoB and Mo_3Si must be avoided.

This analysis shows that binary phases (T1, Mo_2B, Mo_3Si, and MoB) form in the temperature range of 600–1200 °C. Nucleation and growth of these binary phases are controlled by atomic diffusion, which dominates at low and medium temperatures. SPS provides rapid heating rates that reduce the time spent in

the 600–1200 °C range, shortening atomic diffusion distances and suppressing binary phase formation. Conversely, rapid heating to the target temperature enables T2 formation through solid-liquid reactions (equation (6)) at solid-liquid interfaces, thereby increasing T2 conversion.

SPS not only produces higher-purity T2 alloys than TFS but also achieves simultaneous in-situ reaction and hot pressing in a single step. Figure 12 [Figure 12: see original paper] shows the shrinkage curve during SPS sintering. With increasing pressure and temperature, samples undergo densification. In the 1000–1200 °C range, axial pressure significantly promotes densification (first stage). Subsequently, at 1300–1500 °C, face diffusion, volume diffusion, and grain boundary migration occur under axial pressure [28]—the critical densification stage. The high temperature gradient created by rapid heating also accelerates this process, achieving relative densities around 99% and reaching a maximum of 99.47% at 1500 °C. In contrast, TFS samples show low relative density (Figures 3 and 4). This is because T2 has a narrow composition range (approximately a line compound) with limited ability to dissolve small atoms, low vacancy concentration, and small interdiffusion coefficients. Without pressure, extensive volume diffusion and grain boundary migration are difficult, resulting in porous materials (Figure 4). Additionally, at high sintering temperatures, localized melts tend to connect, hindering gas escape and forming connected pores under pressureless conditions, contributing to high porosity.

Conclusions

(1) A rapid heating rate is a necessary kinetic condition for synthesizing T2 phase alloys.

(2) Compared with pressureless sintering (tube furnace sintering), SPS provides sufficiently high heating rates to produce high-purity, uniformly fine-grained, dense T2 alloys. The method also offers the advantages of in-situ synthesis, producing materials with extremely clean, clear interfaces free of transition zones and linear in appearance, indicating no other substances at the interfaces, and no defects such as dislocations within crystals.

(3) Excessively high heating rates can trap adsorbed gases, resulting in high porosity, while excessively low heating rates increase time in the intermediate temperature range (600–1200 °C), promoting formation of substantial binary phases (Mo_3Si, T1, and MoB). A heating rate of 200 °C/min is optimal, avoiding high porosity while suppressing binary phase formation.

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Note: Figure translations are in progress. See original paper for figures.