

STUDIES ON REACTIVE SINTERING BEHAVIOR OF MILLED NANO Mo/Si₃N₄ POWDER MIXTURE

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Abstract. Attempts are made to fabricate Si₃N₄ - MoSi₂ *in situ* composites by reactive milling and reactive sintering of milled powders. 10 hours of milling Mo and Si₃N₄ powder mixtures shows the substantive increase in reactivity, which reaches to maximum after 30 hours of milling. The milling however even up to 104 hours does not by itself lead to the formation of MoSi₂ phase. The pyrolysis of milled powder mixture with varying amount of sintering aid in the temperature range of 1000-1400 °C indicates that MoSi₂ phase forms only at 1400 °C in argon, whereas 1350 °C in vacuum. SEM analysis of milled and pyrolysed samples shows uniform distribution of 0.5-1 micron size MoSi₂ in Si₃N₄ matrix. Longer hours of milling often leads to formation of SiC and it also played by large amount of WC contaminations.

1. INTRODUCTION

The need of advanced materials for high temperature applications has led to the development of ceramic/intermetallic matrix composites [1]. The composites based on MoSi₂ are gaining in importance for both high temperature structural and functional applications due to important combinations of their properties. Si₃N₄ possesses high wear resistant [2] characteristics whereas MoSi₂ [3] has high melting point (2030 °C), excellent oxidation resistance at high temperature, a moderate density (6.24 g/cm³) and ductile to brittle transition temperature in the vicinity of 1000 °C. Addition of MoSi₂ [4] to Si₃N₄ matrix imparts higher fracture toughness, elevated temperature oxidation resistance, improves or has no effect on wear resistance (vol. % of MoSi₂ < 20%) and facilitates machining whereas Si₃N₄ [5,6] additions to MoSi₂ matrix improves high temperature mechanical properties, intermediate temperature oxidation resistance and higher fracture toughness. The most recent applications of MoSi₂-Si₃N₄ composites [7] includes diesel engine glow plugs,

blade outer air seal (BOAS) in high temperature turbines. Most vital application of MoSi₂ is as a commercial heating-element super kanthal (1953) and Si₃N₄ [8] is widely used for cutting tool inserts, bearings, turbochargers and rotors.

Conventionally MoSi₂-Si₃N₄ composites are prepared by hot pressing and hot isostatic pressing of powders of MoSi₂ and Si₃N₄ with densification aid. Low temperature fracture toughness and high temperature strength limits abundant use of MoSi₂-Si₃N₄ composites. Within five years several works has been carried out in the field of MoSi₂-Si₃N₄ composites to develop its properties. But recently it was found that *in situ* toughened MoSi₂-βSi₃N₄ composites are observed to obtain superior property than that of MoSi₂-αSi₃N₄ [9]. The two step consolidation process of vacuum hot pressing and hot isostatic pressing at 1500 °C has significantly improved its properties and dense composites was obtained without any densification aid using powders of MoSi₂ (325 mesh) and Si₃N₄ (<2 micron). These indicate that the advantageous characteristics are not only attributable to the

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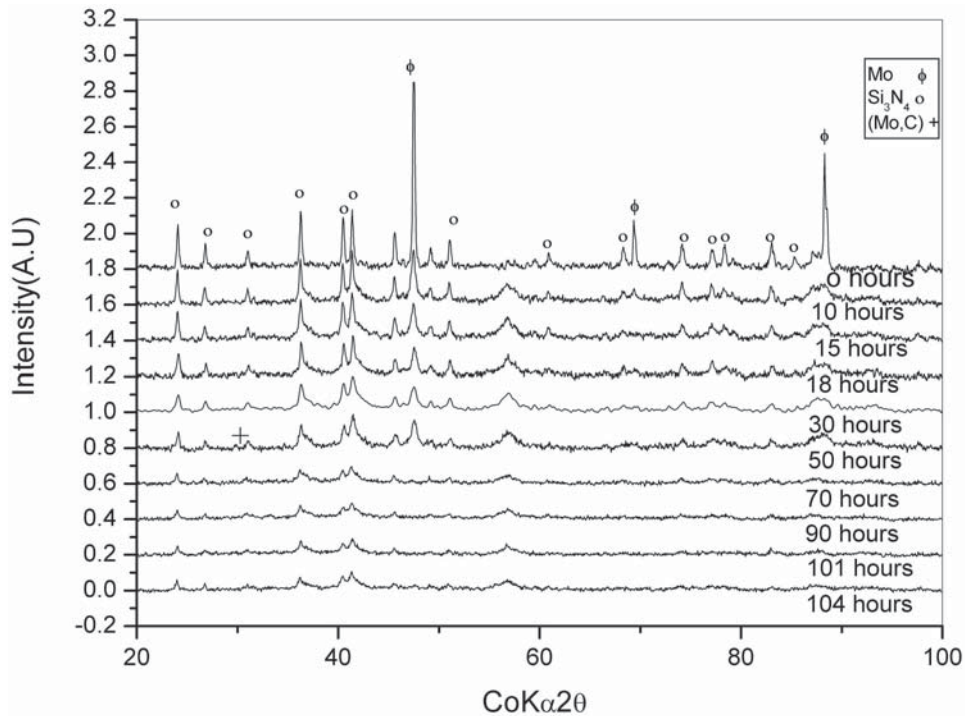


Fig. 1. X-ray diffraction plot of milled powder for various length of time up to 104 hours.

materials involved but also to the methods of their production [6]. Production of composites by *in situ* synthesis method reduces costs and process steps as well as provides fine scale reinforcements and hence superior product quality.

The aim of the present investigation is to study the effect of milling on the formation of MoSi₂ in a powder mixture of elemental Mo and Si₃N₄. Efforts are also made to produce MoSi₂-Si₃N₄ composites by reaction sintering using milled nano powders of Mo and Si₃N₄ in molar ratio of 1:3 in vacuum and argon atmospheres.

Studies have been carried out also on the effect of milling on the size of the MoSi₂ formed, the rates of sintering, reaction temperature, other reaction parameters and possible effects of contaminations on the process are also investigated.

2. EXPERIMENTAL DETAILS

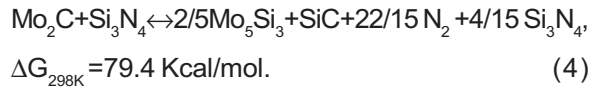
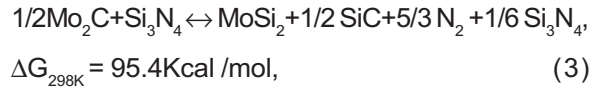
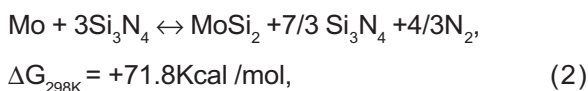
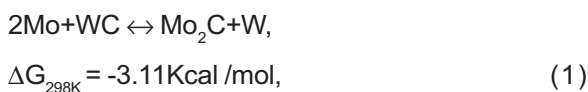
Sinterable grade molybdenum (1-3 micron) powder obtained from former Soviet Union and silicon nitride (<1 micron) powder from Permascand of Sweden were used in this study. Powders of Mo and Si₃N₄ in the molar ratio of 1:3 designated as MoSN3 were milled for various length of time up to 104 hours to produce Si₃N₄ reinforced MoSi₂ composites with

WC vial and grinding media having a charge ratio of 15:1 in a planetary type Fritsch milling machine. The samples after every 10 hours of milling were taken out and analyzed by XRD, TEM, SEM and DTA. These powders were thoroughly mixed with 5%, and 10% MgO (chemical reagent grade) as the densification aid. The powder mixture both with MgO and without MgO addition was compacted uniaxially at pressure of 108 MPa. After dimension and weight measurement pyrolysis was carried out in a horizontal tube furnace in argon (commercial grade) and vacuum (10⁻² mmHg) atmosphere, for holding times of 30, 60, and 120 minutes at a heating rate of 20 °C/min in the temperature range of 1000-1400 °C and cooled in the furnace. Samples were visually examined for sintering defects such as cracks, distortion, and blistering or inhomogeneous shrinkage. Weight changes, dimensional measurements were next carried out. The microstructural and phase changes in the composites after pyrolysis were investigated through SEM using gold coated fractured surface sample and X-ray diffraction method using CoKβ radiation. EDS analysis of carbon coated sample was used to estimate the phase composition. Densities of samples were measured by weight and dimensions measurement.

3. RESULTS AND DISCUSSION

3.1. Milling

3.1.1. X-ray diffraction. The powder mixture after every 10 hours of milling was analyzed through X-ray diffraction. Fig. 1 compares the X-ray diffraction pattern of powders milled for various lengths of time up to 104 hours. It was observed that with increase in milling period broadening as well decrease in intensity of Mo and Si₃N₄ peaks take place. Molybdenum peak intensities decrease extensively up to 30 hours (and the peak intensity remains same for 40 hours milled samples). But an increase in peak height was observed for 50 and 60 hours samples. The particle coarsening of Mo may be due to reactions taking place between Mo and WC (Eq. (1)) forming (Mo,C) molybdenum carbide and tungsten solubility in molybdenum. One peak of (Mo,C) appears in 50 hours milled samples. Further verification of molybdenum carbide formation using powders of Mo and WC was carried out by reacting particles of Mo and WC within the temperature range of 400-900 °C in commercial argon atmosphere. Peaks of Molybdenum carbide (Mo₂C) and MoO₂ were observed at 900 °C after 12 minutes holding in argon atmosphere and which vanishes with increase in holding time. Molybdenum carbide being very unstable compound could react with oxygen of the atmosphere and dissociates into CO and MoO₂. MoO₂ has a high vapour pressure sublimates. The Mo peak was found to become amorphous after milling for more than 70 hours. The lower intensity peaks of silicon nitride get diminished and more intense peaks get merged during milling process indicating that some deformation has occurred in Si₃N₄. No peaks of MoSi₂, Mo₅Si₃ or Mo₃Si could be observed. The *in situ* formation of silicides during reaction milling could not be achieved possibly due to the stable covalent bond of Si₃N₄ which limits the molybdenum diffusivity into it and also the formation of MoSi₂ using Mo and Si₃N₄ as the starting material has a high positive free energy of formation at the room temperature as indicated by reaction 2. The free energy of formation for the reaction 2 becomes negative above 1355K in vacuum (10⁻² mm Hg) for materials in standard state. The possible reactions and their free energy of formation at ambient temperature are as follows:



The level of mixing of insoluble constituents during milling is due to enthalpy change of the possible chemical reactions in the system under consideration. For Si₃N₄ and molybdenum system the mixing of Si₃N₄ and Mo at atomic level increases the free energy (reaction 2) whereas for Mo and WC decreases free energy of system (reaction 4). So it is probable that Mo particle is intimately mixed with WC or even dissolved in the matrix during the whole milling process.

3.1.2. SEM & EDS. Morphology and energy dispersive spectroscopic analysis of different hours of milled powders both before and after pyrolysis were studied by SEM with an attached EDS. The SEM microphotograph of milled powders shows the agglomerate of fine powders. The EDS spot analysis for various milled samples shows the presence of W, Si, Mo, & Co as shown. With increase in milling hours the percentage of WC contamination has increased and it reached to as high as 9-10 wt. %.

3.1.3. TEM. TEM analysis of samples after every 10 of hours milling was carried out. It was observed that with increase in milling period the particle size has reduced to nano level. Calculation of crystal size from St.-cry software shows that Mo particle has reduced to nano size after 30 hours of milling, and the same is confirmed by electron diffraction analysis of 30 hours samples which shows spot on the ring as shown. For every hour of milling, sample particles were observed to be atomically segregated in the form of dark gray and black particles. Due to difference in their reflectivity Si₃N₄ were appears to be dark grey particles and Mo as black particles. Few big particles of Mo are observed in all milled samples. But with increase in milling time the volume fraction of big particles decreases.

3.1.4. DTA & TGA. The milled samples after different hours of milling were analysed by DTA-TGA to study its behaviour under the influence of increasing temperature (Fig.2). In the given figure zero hours, 10 hours, 30 hours, 50 hours, and 104 hours milled samples are designated as Ho, H10, H30, H50, and H104, respectively. The TGA of zero hours milled samples shows weight gain due to molybdenum oxidation. After 1100 °C weight loss was observed due to molybdenum sublimation and also due N₂ gas evolution due to reaction between Mo and Si₃N₄.

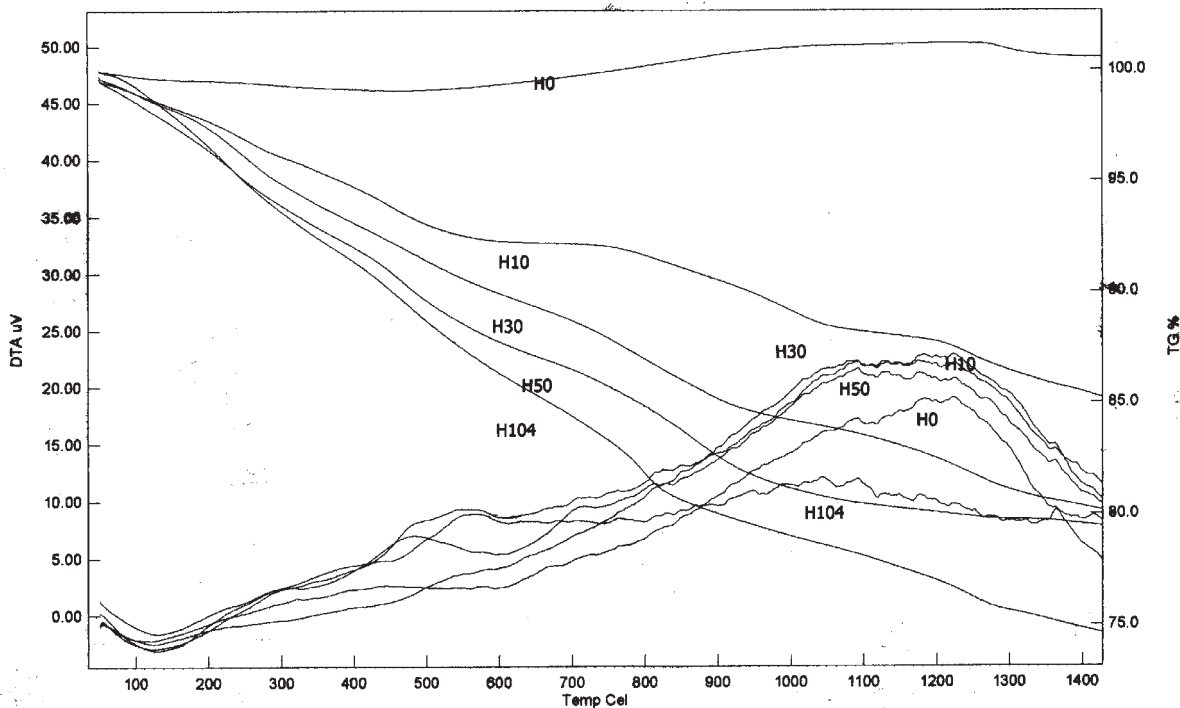


Fig. 2. Comparison of DTA-TGA curve of different hours of milled samples with unmilled samples.

In H10 sample also some weight gain was observed within the temperature range of 600-1000 °C but with increased hours of milling weight gain for the H30, H50, and H104 samples was not detected which may be due to intimate mixing of molybdenum with Si_3N_4 and WC. The weight loss in the samples increases with increase in milling hours and is found to be 15%, 19.55%, 20.3% and 25.4% for H10, H30, H50, and H104, whereas 0.8 wt.% gain was observed for H0 sample. The DTA analysis of milled sample shows recovery and recrystallisation of Si_3N_4 in the temperature ranges of 262-352 °C and 355-600 °C followed by recovery and recrystallisation of WC in the temperature ranges of 643-753 °C and 782-831 °C which has been confirmed by X-ray diffraction analysis of milled samples heated in the above given temperature ranges. Along with these peaks a major reaction peak due to reaction of Mo and Si_3N_4 was observed for all samples at higher temperature. The amount of heat of reaction released (Area under DTA curve) for all samples are different and is $-1349 \mu\text{V/gm}$, $-1525 \mu\text{V/gm}$, $-2599 \mu\text{V/gm}$, $-1451 \mu\text{V/gm}$, and $-548 \mu\text{V/gm}$ for H0, H10, H30, H50, and H104 samples. The smaller is the particle size, the larger is the exothermic area of the DTA curve. The heat of reaction for 30 hours milled (nano)

samples is maximum. Increase in milling hours does not further enhance the reactivity probably due to increased contamination and thus amount of heat generated for 104 hours milled sample appears less than that of unmilled samples.

3.2. Sintering and pyrolysis

3.2.1. X-ray diffraction analysis. The pyrolysed samples were analyzed by X-ray diffraction pattern and it was found that the behaviour of all milled samples is similar. The conversion of Mo completely to MoSi_2 phase occurs at 1400 °C after 60 minutes of holding in all cases. The X-ray diffraction plot of 104 hours milled samples pyrolysed within the temperature range of 1000-1400 °C. The peaks of Mo, WC and Si_3N_4 are observed at 1000 °C. At 1200 °C some peaks of Mo_2C and Mo_5Si_3 were also seen. With further increase in temperature to 1350 °C major phase is of Mo_5Si_3 along with SiC and minor MoSi_2 peaks. Conversion to MoSi_2 is observed after Mo_5Si_3 formation this is because the free energy of formation reaction 4 is less positive than that of reaction 3. The presence of high percentage of WC in samples seems to facilitate Mo_2C and hence SiC formation. At 1400 °C the reaction reaches comple-

tion and phases obtained are MoSi₂ and SiC along with Si₃N₄. Tungsten having large solubility in Mo may be present as a Mo(W)Si₂. The contamination pick up in the sample increases the process step and thereby the energy requirement of the process ($\Delta G_{\text{equation3}} > \Delta G_{\text{equation2}}$) for a mole of MoSi₂ formed. Addition of densification aid does not effect the reaction temperature. MgSiO₃ was observed at lower temperature and less holding time. In vacuum conversion occurs at 1350 °C for 60 minutes holding. The X-ray diffraction plot of 104 hour milled sample after sintering at 1400 °C for different holding time. It shows that after 30 minutes of holding Mo₅Si₃ and SiC form as major phases and peaks of MoSi₂ also appear but the intensity of peak is small. With increase in holding time the intensity of MoSi₂ peak intensity is increases and that of Si₃N₄ decreases. The XRD plot of different milled powders pyrolised at 1400 °C for 60 minutes with those of unmilled powder. In unmilled samples the peaks Mo₅Si₃ are present along with MoSi₂ peaks, where as in milled samples after sintering Mo₅Si₃ peaks are absent. 10 hours milled & pyrolised samples show the presence of MoSi₂ and Si₃N₄. With increase in hours of milling the silicon nitride peak is getting diminished and presence of SiC peaks are observed after 30 hours of milling. In 104 hour milled samples the peaks found are of MoSi₂ and SiC. Milling beyond 10 hours does not further improve the reactivity of powder may be due to presence of large volume fraction of WC contaminants which during the process of milling get intimately mixed with Mo and facilitates Mo₂C formation.

3.2.2. SEM & EDS. Pyrolysis at 1350 °C in vacuum and at 1400 °C in argon gives complete conversion to MoSi₂ after 60 minutes of holding. The morphology of samples pyrolised in vacuum shows the combination of interconnected lamellar particles in the matrix whereas those sintered in argon atmosphere consists of MoSi₂ particles size of 0.5–1 micron uniformly distributed through out matrix for every hour of milled samples. With increase in milling hours the MoSi₂ phase obtained appear more equiaxed. Minor microscopic cracks was found in every hours of milled samples sintered without densification aid. Among all samples, dense packing was observed for 30 hours of milled and pyrolised samples (Fig. 3). With increase in milling hours, weight loss during the process increases either because of gas evolution due to contaminants or by nitrogen loss, thereby facilitates cracks in the samples and decreases the density of packing. Increase in holding

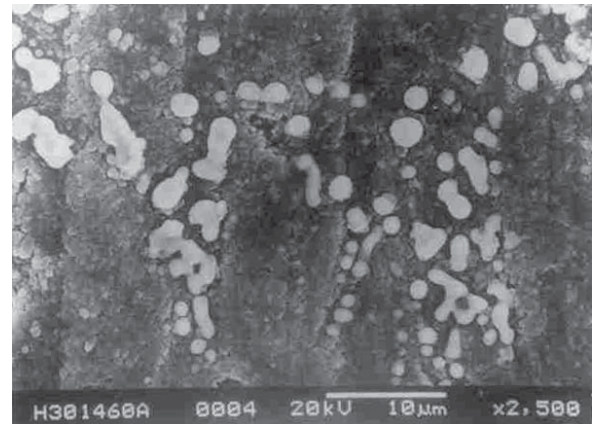


Fig. 3. SEM microphotograph of 30 hours milled sample after Pyrolysis at 1400 °C for 60 minutes in argon.

time, temperature and densification aid leads to coarsening of particles.

3.2.3. Density and porosity. The density of samples was calculated through dimensions and weight measurement for both green and sintered compact. It was observed that the density of compact after sintering remains unchanged irrespective of time of milling, whereas the SEM study shows difference in packing. Image analyzer was used for porosity measurement and cracks were observed in samples though particles were densely packed. Due to this crack formation, densification could not be accurately evaluated.

4. CONCLUSIONS

Reactive sintering of milled nano powders of Mo and Si₃N₄ led to the formation of (Mo,W)Si₂-Si₃N₄/SiC composites. The present investigation indicates that even 104 hours of milling alone does not lead to the formation of MoSi₂ phase. SEM – EDS spot analysis of samples showed the presence of WC contamination as high as 10%. DTA analysis of samples shows that milling of powders to 10 hours itself has increased the reactivity but maximum amount of heat released is observed for 30 hours milled samples. Extended milling up to 104 hours does not lead to any additional increase in reactivity. Presence of WC contaminations seems to inhibit the reaction. The various phases observed during reactions for milled nano powders are Mo₂C-Mo₅Si₃-SiC-MoSi₂/Si₃N₄ whereas for unmilled powders it is Mo₅Si₃-MoSi₂/Si₃N₄. SEM analysis of milled and pyrolised samples shows uniform distribution of 0.5-1 micron size MoSi₂ and Si₃N₄.

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