Abstract

The present thesis attempt to investigate the production of Si_3N_4-$MoSi_2$ in-situ composites through varying the relative proportion of Mo and Si_3N_4 in the powder mixtures. Various processing routes such as a) reaction synthesis b) mechanical activated synthesis and c) reactive hot pressing have been tried. The effect of process parameters on the properties and morphology of the product composite has been investigated.

The dissertation is divided into six chapters. The first chapter deals with the introduction and definition of the problem and the scope and limitations of the present work. The second chapter contains the detailed literature review, which has been focused on six different areas. The first two sections are regarding the basic properties, applications, limitations and synthesis of Si_3N_4 and $MoSi_2$. The third section is concerned with the formation of dense Si_3N_4-$MoSi_2$ composites, its properties with varying $MoSi_2$ phase size and its content, different production routes, advantages associated with the insitu synthesis and thermodynamics of reaction for the Mo+Si_3N_4 system. The fourth section deals with mechanical activation and milling energy calculation. The fifth section regarding composite consolidation parameter such as temperature, pressure, atmosphere and densification aid etc. The sixth and the last section is related to high temperature oxidation and wears behaviour of Si_3N_4-$MoSi_2$ composites. The experimental procedures include scheme of experiment, materials characterization. Experimental details used during different processing routes and also for properties evaluation are explained in chapter three. The experimental results obtained during the three processing routes (reaction synthesis, mechanical activated synthesis and reactive hot pressing) have been

discussed in chapter 4. The relevant conclusions are drawn in chapter five. The present study indicates that

1) High temperature reaction in $Mo+Si_3N_4$ powder mixtures in the molar ratio of 1:1, 1:2 and 1:3 (MoSN1, MoSN2 and MoSN3) without any sintering additive leads to the formation of $MoSi_2$ at 1600°C for 1h holding in argon atmosphere. In the absence of sintering additive (MgO) the complete $MoSi_2$ formation was observed for the sample of all compositions at 1600°C for 1h holding. Excess Si_3N_4 in the powder mixture and the glassy phase of magnesium silicate formed from sintering aid MgO were found to delay the formation of $MoSi_2$. Reaction diffusion leading to formation of $MoSi_2$ was first observed for MoSN2 samples (Mo: Si_3N_4 : 1: 2) (fig 4.3). Complete conversion to $MoSi_2$ was observed in case of MoSN1 after 2h holding and in MoSN2 after 3h holding at 1600°C in argon atmosphere In vacuum complete formation of $MoSi_2$ was not observed at 1600°C. The density of the reaction product obtained during pyrolysis under argon atmosphere is higher than the samples pyrolised in vacuum and is approximately in the range of 70-85%T.D.

2) For mechanical activation the powder mixtures were subjected to high energy ball milling with steel, ZrO_2 and WC grinding media with a ball to powder ratio (BPR) of 10:1 and 15:1 for 0-70h. $MoSi_2$ formation was not observed during milling of $Mo+Si_3N_4$ powder mixtures of any composition. Mechanical activation of powder mixtures increases $MoSi_2$ conversion during subsequent reaction and produces composites having ultrafine reinforcement phase, uniform distribution, and

reduction in reaction temperature. The optimum impact energy of ball required for mechanical activation of powder mixtures by WC grinding media was found to be in the range of 0.145-0.173J. A reduction in temperature of 100-200°C for the formation of $MoSi_2$ was observed for the samples milled for 10h in the optimum impact energy range. Additional milling beyond 10 hours does not lead to further reduction in the pyrolysis temperature. Samples milled with higher impact energy than the optimum range led to the formation of undesirable phases, which dilutes the effect of mechanical activation. Mechanical activation was not observed in the samples milled with steel or ZrO_2 grinding media (impact energy/ball <0.10 J/ball). The intensities of peaks of $MoSi_2$ in the pyrolised samples increased with increase in milling time. The density of composites and size of insitu formed silicides from mechanical activated ($Mo+Si_3N_4$) are lower than that formed from unmilled ($Mo+Si_3N_4$).

3) Reactive hot pressing of unmilled powder mixtures led to the formation of dense Si_3N_4-$MoSi_2$ composites. In the mechanically activated samples, composites of Si_3N_4-Mo_5Si_3C/Mo_2C were formed. Loss of molybdenum and silicon as MoO_3 and SiO during high temperature consolidation affect the final product composition during various high temperature processes. Minimum loss of molybdenum and silicon is observed during reactive hot pressing in argon atmosphere. Si_3N_4-Mo_5Si_3C and Si_3N_4-Mo_2C *in-situ* composites produced through hot pressing of milled powders possess higher hardness, lower specific wear rate, lower fracture toughness and poorer oxidation resistance in comparison to Si_3N_4-$MoSi_2$ composites produced by reactive hot

pressing of unmilled powder mixtures. However, oxygen pick up in mechanically activated samples was observed to degrade the properties such as fracture toughness and elastic modulus values of Si_3N_4-Mo_5Si_3C composites. Si_3N_4-$MoSi_2$ composites exhibited very good resistance to isothermal, cyclic and non-isothermal oxidation at all temperatures studied. Presence of additional Mo_5Si_3 phase obtained in some of the composites deteriorates oxidation behaviour of the composite. On the other hand presence of Mo_2C in composites show very good oxidation resistance due to the formation of Si_2ON_2 at low temperature (500°C-900°C), but it disintegrates with increase in temperature to 1250°C.The density of reactive hot pressed and mechanical activated hot pressing composites lies in the range of (91-99.5%T.D). Significant improvements in the mechanical properties were observed for Si_3N_4-$MoSi_2$ composites produced by *in-situ* synthesis of $MoSi_2$ from $Mo+Si_3N_4$ powder mixtures over those of composites produced by conventional hot pressing of $MoSi_2$-Si_3N_4.