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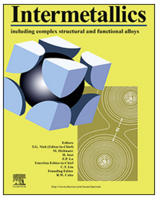

Effect of Si content on microstructure, mechanical and oxidation properties of hot pressed Mo-Ti-Si alloys

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ABSTRACT

Mo-Ti-Si based materials are promising candidates for high-temperature applications beyond the capability limits of nickel based superalloys. In the present investigation, two alloy compositions with different Si content namely Mo-40Ti-30Si (in at.%) (alloy 1) and Mo-40Ti-10Si (alloy 2) were prepared in the form of plates by adopting mechanical alloying and subsequent reactive hot pressing at 1600 °C. The densities of the alloys were found to be much lower than the conventional alloys used for high-temperature applications. The detailed microstructural characterization using scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and electron back-scattered diffraction (EBSD) analysis indicated that alloy 1 was composed with Ti(Mo)$_5$Si$_3$ matrix and Ti(Mo)$_3$Si precipitates. Alloy 2 consisted with three phase microstructure containing α-Mo(Ti)$_{ss}$, β-Ti(Mo)$_{ss}$ and Mo(Ti)$_3$Si. Micro-hardness values of 1400 H V and 850 H V respectively for alloy 1 and alloy 2 were noticed, however, alloy 1 showed the tendencies of micro-crack formation from the corners of the Vickers indentations. Alloy 1 showed a superior isothermal oxidation resistance at 900 °C, 1000 °C, and 1300 °C for prolonged duration due to formation of a thin duplex SiO$_2$ (TiO$_2$) oxide scale. However, the formation of a porous oxide layer led to evaporation of MoO$_3$, showing drastic weight loss of alloy 2 at all three tested temperatures. Enrichment of Si was done using pack siliconizing process forming a (Mo, Ti)Si$_2$ layer of thickness 10 μm and 30 μm on the surfaces of alloys 1 and 2 respectively at 900 °C. The silicide coated alloy 1 showed further improvement in the oxidation behaviour, and enrichment of Si on alloy 2 surface imparted a drastic improvement in the resistance against oxidation in air at 1300 °C for the prolonged exposure times of 70 h.

1. Introduction

Mo-Si-B based materials are being investigated for replacing nickel based superalloys to improve the efficiency of the turbine engines operated at very high temperatures [1,2]. These materials comprised with three phase Mo$_{ss}$-Mo$_3$Si-Mo$_5$SiB$_2$ microstructure are studied extensively [1–7]. These materials exhibit superior high-temperature strength and creep properties, and moderate oxidation resistance. Mo$_5$Si$_3$ (T1) type Mo$_5$SiB$_2$ (T2) phase is actually responsible for superior oxidation properties of the alloy which contributes towards formation of a protective borosilica scale in 1000–1250 °C. These alloys show a transient weight loss during initial period of oxidation due to vaporization loss of MoO$_3$ followed by SiO$_2$(B$_2$O$_3$) scale formation [3,6]. The borosilica scale possesses sufficient viscosity to flow over the entire surface of the substrate providing a protective cover on the Mo-Si-B alloys. Addition of reactive metals Ti, Zr, Hf etc on phase formation and oxidation behaviour of these alloy systems were studied in detail [8–10]. It was reported that macro-alloying of Ti in Mo$_5$Si$_3$ forms (Mo, Ti)$_5$Si$_3$ phase possessing superior oxidation resistance in 750–1300 °C [11]. Subsequently, the high-temperature oxidation behaviour of macro-alloyed Ti in Mo-Si-B system was reported [12–14] indicating the beneficial effect of Ti on oxidation resistance at a wide temperature regime. Addition of Ti in the form of TiC was reported to impart lower density ($\sim$7 g/cm^3) and superior fracture toughness in MoSiBTiC systems [15,16]. Therefore, Ti-addition in Mo-Si-X system may be beneficial in deriving superior oxidation resistance property and imparting a reduction in density of the material thereby the specific strength of the alloy could be enhanced. Presence of boron in structural materials for high temperature nuclear reactor applications might change the reactor chemistry; hence, the studies on Mo-Si-Ti systems will be useful for such applications. The detailed thermodynamic phase stabilities of the ternary Mo-Si-Ti system are reported earlier [17,18].

The amount of Si present in the Mo-Si-Ti systems plays a very important role in influencing the oxidation and mechanical properties of

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these materials. Si-rich $MoSi_2$ shows superior oxidation resistance at high temperatures, however, it possesses poor mechanical properties. Therefore, the strategies are adopted to form the Si-rich coating on the surfaces of the Mo-Si-X alloys.

In the current investigation, the effect of Si-content on the microstructure, micro-hardness, and high-temperature oxidation properties of Mo-Ti-Si alloys were studied. Two alloy composition of Mo-Ti-Si system comprised; (1) with close to single phase $(Mo, Ti)_5Si_3$ or $(Ti, Mo)_5Si_3$ and (2) composite structure having solid solution phase as matrix reinforced with silicide phases, were selected. The alloys were synthesised using mechanical alloying followed by reactive hot pressing. Detailed microstructures and oxidation behaviour of both the alloy systems were analysed. Further, enrichment of Si on the surfaces of the alloys was carried out using pack siliconizing technique. The silicide coated specimens were further tested under oxidizing environment and characterized in detail.

2. Experimental

Elemental powder of Mo, Si and Ti with an average size of 10 µm and 99.9% purity were mixed in the desired composition ratio of Mo-40Ti-30Si (alloy-1) and Mo-40Ti-10Si (alloy-2) (at.%), and subjected to mechanical alloying in a high energy planetary ball mill for a duration of 35 h. The mechanical alloying was carried out using ball to charge ratio of 10:1 with milling speed of 200 rpm in inert (Ar) atmosphere. The mechanically alloyed powder was characterized using XRD and SEM. The alloy powder was subsequently consolidated into plate like shapes of dimensions 60 mm diameter and 6 mm thickness (Fig. 1) by vacuum hot pressing. The parameters of hot pressing were optimized to 1600 °C, 2 h and applied load of 25 ton (~10 MPa pressure). Fig. 1a shows the top view of the hot pressed plate and Fig. 1b represents the cross-section (along thickness) of the broken plate showing the lustre of brittle failure. The consolidated alloy plates were subsequently ground from all sides to remove the traces of carbon came from the graphite mould and dies used in hot pressing. The densities of the hot pressed alloys were measured through the immersion method based on the Archimedean principle using water as the liquid medium. Small samples were cut from the plates by EDM and subsequently ground and polished for microstructural characterization. The microstructure and compositional analysis of the alloys were carried out using a Camscan make SEM attached with Oxford EDS (Model: X-max 80). The as-pressed alloys were also characterized in EBSD (Oxford Model: NordlysNano) for analysing texture and phases. The samples for EBSD analysis were prepared by grinding up to 1 µm diamond finish and subsequent polishing with colloidal silica solution.

The micro hardness of the alloys was determined through Vickers micro-hardness tester applying the load of 500 g and maintaining load residence time of 10 s. The indentations were further characterized using SEM.

For oxidation studies, small specimens of dimensions 10 mm × 5 mm × 5 mm were cut from the hot pressed plates using EDM cutting. All the sides of the specimens were ground and metallographically polished with SiC paper up to 1200 grit and ultrasonically cleaned in acetone. For isothermal oxidation studies, the samples were introduced into the muffle type furnace using alumina crucible, when the furnace temperature reached the set value. The isothermal tests were conducted at three temperatures of 900 °C, 1000 °C and 1300 °C for different time intervals up to 100 h. Each sample was carefully weighed before and after exposure to determine the weight changes during the oxidation. The surface of the oxidized samples was characterized using XRD. The morphology and nature of oxide layer was investigated by observing the surface as well as the cross-section in SEM and EDS.

For improving the oxidation resistance, pack siliconizing experiments were carried out to form silicide coatings on the outer surfaces of alloys. Details of the pack siliconizing procedure followed are presented elsewhere [19]. Coatings were formed on both the alloys using a pack mixture of $15Si\text{-}2.5NH_4F\text{-}82.5Al_2O_3$ (wt.%) at 900 °C held for 8 h. The cross-section of the coating layers were characterized using SEM and EDS. The as-coated alloy samples were further oxidation tested isothermally at 1300 °C in air. The oxidation performance of the bare and coated alloys was compared systematically.

3. Results and discussion

3.1. Microstructure

3.1.1. Alloy 1 (Mo-40Ti-30Si)

Fig. 2 represents a back scattered electron image of as polished hot pressed alloy 1. The alloy is mainly composed with single (bright) phase with non-uniformly distributed fine size dark phases. The detailed compositional analysis obtained from these phases using EDS technique is presented in Table 1. The EBSD maps obtained from alloy 1 is presented in Fig. 3. Comparing the EDS data and EBSD analysis (Fig. 3b), it was confirmed that the matrix phase of alloy 1 is composed with $Ti(Mo)_5Si_3$ phase. The dark coloured precipitates are identified as $Ti(Mo)_3Si$ phase having hexagonal crystal structure. The density of the hot pressed alloy 1 was found to be about 5.8 g/cm^3. No porosity was detected in the microstructure of the hot pressed alloy. Although, XRD analysis (not presented here) of the alloyed powder showed the presence of peaks from Ti_5Si_3 type phase, the consolidation during hot pressing proceeds through reaction and diffusion processes. Self-propagating high-temperature synthesis (SHS) process is another technique adopted for producing silicide (e.g. Nb-Si, Mo-Si [20–22]) compounds. Exothermic heat produced during reaction causes localized melting and formation of these intermediate compounds. Similar reactive sintering mechanisms are expected to operate during hot pressing of alloy 1 at about 1600 °C. It is noteworthy here that the major phase produced in

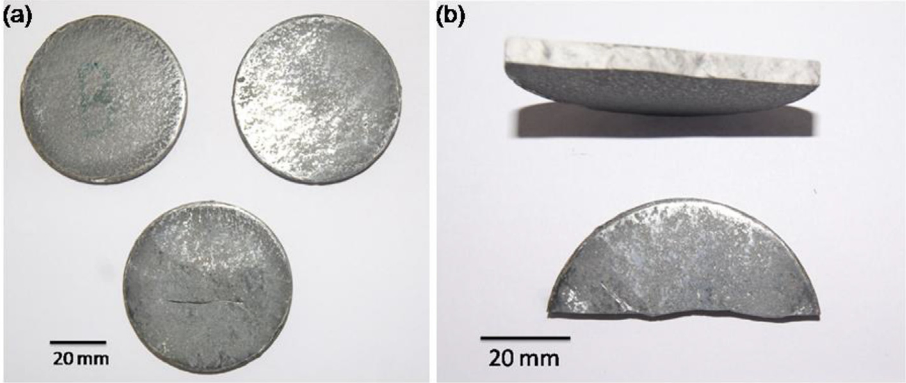

Fig. 1. Outlook of hot pressed Mo-Ti-Si alloy plates of 60 mm diameter and 6 mm thickness; (a) top view and (b) view along the thickness.