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A study on microstructure development and oxidation phenomenon of arc consolidated Mo-Nb-Si-(Y) alloys

Sanjib Majumdar*

High Temperature Materials Development Section, Materials Processing and Corrosion Engineering Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

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ABSTRACT

Two alloys of compositions Mo-26Nb-19Si and Mo-26Nb-19Si-0.5Y (at.%) were prepared by non-consumable arc melting. The alloys characterized using BSE, EDS and EBSD techniques confirmed the formation of two phase $(Mo, Nb)_{SS}$-$(Mo, Nb)_5Si_3$ microstructures. Y-rich (Y_2O_3) particles were mainly found to be present at the inter-phase boundaries creating different phase morphologies in Mo-26Nb-19Si-0.5Y alloy. Both the phases showed a preferred orientation indicating a directional growth during solidification. Oxidation tests conducted in air at 1000 and 1300 °C showed a porous oxide scale formation on the alloy surface and loss of material due to evaporation of MoO_3. The detailed SEM-EDS analysis of the oxide scale formed on these alloys in argon environment at 1000 °C, indicated the presence of Nb_2O_5 particles in the silica (SiO_2) matrix.

1. Introduction

Molybdenum silicide (Mo-Si-X) based alloys or composites are the most promising candidates to replace nickel based superalloys to meet the increasing temperature requirement of gas turbines and jet engine turbines [1–5]. A great amount of research work has been focused on developing Mo-Si-B alloy [6–8], which showed the optimum combination of mechanical and oxidation properties at high-temperatures. Mo-Si-B alloy comprises with three phases namely molybdenum solid solution (Mo_{ss}), Mo_3Si (A15) and Mo_5SiB_2 (T2). While T2 phase is mainly responsible for the superior oxidation resistance of the alloy, Mo_3Si (A15) phase possesses inferior linear oxidation behaviour [9]. Detailed studies were conducted to improve the oxidation behaviour of the alloy by addition of reactive and rare earth elements [10,11]. T1 type Mo_5Si_3 silicide shows superior oxidation and creep properties. Boron added T1 forming T2 phase creates the distinctive advantage in Mo-Si-B alloy for deriving superior high-temperature properties [12]. Investigations are carried out to avoid the formation of Mo_3Si phase in the Mo—Si system containing about 10–15 at.% Si. Niobium is another refractory metal, which stabilizes Mo_5Si_3 phase. Fig. 1 represents the equilibrium Mo-Nb-Si ternary phase diagram at 800 °C indicating the stability of Mo_5Si_3 and Nb_5Si_3 phases in a wide composition range. The Nb_5Si_3 exists in two crystallographic variants, of which only one is isostructural (D8m) with Mo_5Si_3 and hence there exists mutual solid solubility. Therefore, the addition of Nb in Mo-Si-B type system would be beneficial in stabilizing T1 and T2 phases in the microstructure [4]. Increase in fracture toughness of Mo-Si-B with addition of Nb was also reported [13]. Nb rich silicide composites are also being studied for high-temperature applications. Development of Nb-based composites such as Nb-Ti-Si, Nb-Ti-Cr-Si, Nb-Ti-Hf-Si with other alloying additions such as Al, Sn etc. are in progress [14–16]. Nb addition in Mo-Si system will be beneficial with respect to lowering of density, superior fracture toughness, strengthening of the solid solution phase and stabilization of Mo_5Si_3 phase.

High-temperature oxidation phenomenon of these Mo and Nb silicide based composites is complex in nature. Mo-Si-B alloys are mainly protected in 1100–1250 °C regimes by formation of a glassy borosilica scale [12] in oxidizing environment. Mo-silicides develop a protective silica scale beyond 1250 °C, however, they suffer from 'pesting' or catastrophic oxidation [12] at intermediate temperatures. The effect of Nb addition on the oxidation behaviour of Mo-silicides is not studied in detail. Presence of boron in structural materials for high temperature nuclear reactor applications might change the reactor chemistry; hence, the studies on Mo-Nb-Si systems will be useful for such applications.

The current work mainly focused on the microstructural characterization of two alloys of Mo-Nb-Si and Mo-Nb-Si-Y. Phase formation behaviour of as cast and heat treated alloys were identified using SEM, EDS and EBSD techniques. Oxidation tests of the alloys were carried out at high temperatures in static air and argon environments. Detailed microstructural characterization of the oxide scale was conducted to

* Corresponding author.
E-mail address: sanjib@barc.gov.in.

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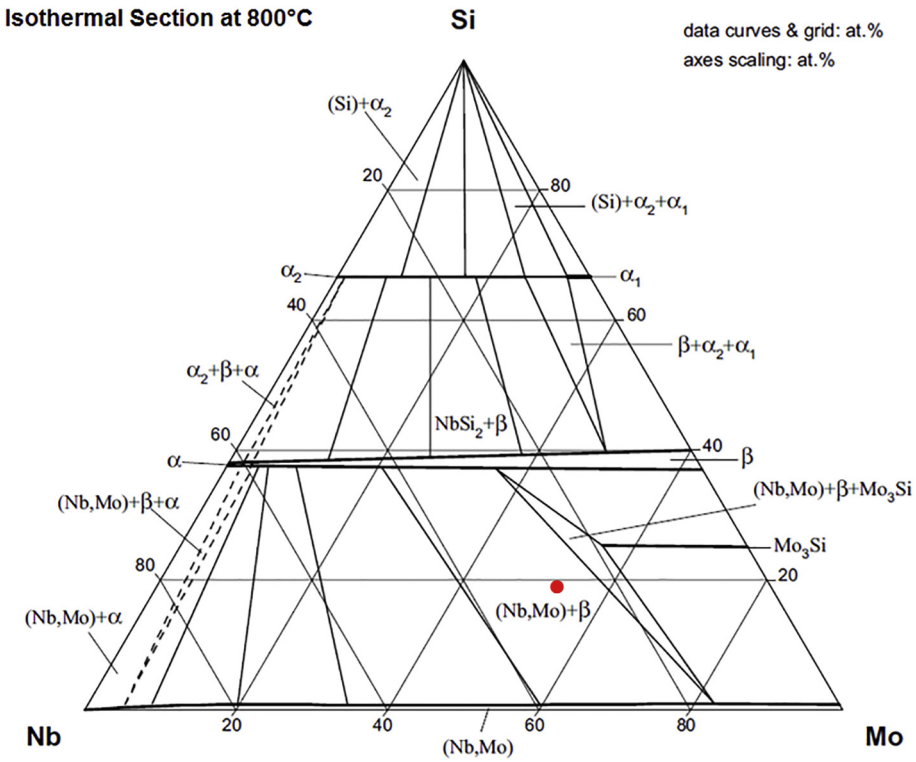

Fig. 1. Isothermal section of Mo-Nb-Si ternary phase diagram at 800 °C [17].

understand the operative oxidation mechanisms.

2. Experimental

Pure constituents of Mo, Nb, Si and Y of about 99.9% purity were used as starting material. Alloys were prepared by non-consumable arc melting using a tungsten electrode under a positive argon pressure of 500–600 mbar. Melting was done on a water-cooled copper hearth containing finger type slots for keeping the metal pieces before carrying out the melting trials. For attaining homogeneity, the melting operations were carried out for 5–6 times. Two alloys of compositions Mo-26Nb-19Si (at.%) and Mo-26Nb-19Si-0.5Y (at.%) mentioned in the text as Alloy 1 and Alloy 2, respectively, were prepared. The alloy compositions were chosen as indicated by the dotted point in the ternary phase diagram (Fig. 1) [17]. About 150 g of each alloy was prepared in finger like shape by following multiple arc melting procedure. Small pieces of dimensions 15 mm × 15 mm × 15 mm were cut using electro discharge machining (EDM) for metallographic observations. The samples were ground up to 1200 size SiC embedded emery paper and subsequently polished up to 0.5 μ diamond finish. Polished samples were observed under a scanning electron microscope (SEM) of Model-Camscan MV 100. Both secondary and back scattered electron microstructures were observed simultaneously. Energy dispersive spectroscopic (EDS) analysis using Oxford X-max 80 of the individual phases identified in BSE imaging was carried out. Some of the samples were analysed using the SEM of type Helios Nanolab 600 FE-SEM (FEI make). The polished surfaces were also characterized using XRD and electron back scattered diffraction (EBSD) to evaluate the phase formations and texture. For the EBSD measurements, the samples were prepared by metallographic polishing followed by electro-polishing using the electrolyte comprised of 12.5 vol% methanol and 87.5 vol% H_2SO_4. Electro-polishing was carried out using LectroPol 5 (Struers make) maintaining a bath temperature of 1 °C with the applied potential of 20 V for 20 s. EBSD mapping was done using Oxford make detector (Model: NordlysNano) and the data was analysed using Aztec Channel 5 software. As cast alloy samples were further heat treated at 1500 and 1700 °C for 5 h in a tungsten mesh heater furnace at a vacuum level of 1×10^{-5} mbar. Heat treated samples were further characterized using the above mentioned techniques.

For oxidation analysis, the specimens of dimensions 5 mm × 4 mm × 4 mm were prepared using diamond wheel cutting. The specimens were ground up to 500-grit size SiC embedded paper, and cleaned in ethanol. The oxidation behaviour was studied under isothermal conditions applying continuous thermogravimetric analysis (TGA). TGA was carried out in static laboratory air at 1000 and 1300 °C using a Setaram make (Setsys evolution 24) thermo-balance. The specimens were placed on a platinum crucible at the centre of the furnace chamber of the TGA unit using platinum suspension wires. For confirming the weight change data of TGA and characterizing the oxide scale at intermediate exposure times, the separate oxidation experiments were also conducted using the resistance heating muffle type furnaces in static air at selected temperatures. Both the alloys showed a drastic loss of weight in air at the tested temperatures. Therefore, for understanding the mechanisms of oxidation a separate test was conducted by heating the alloy coupons under argon atmosphere at 1000 °C for about 24 h in a resistance heating furnace. The surface of the oxidized specimens was characterized using XRD, SEM and EDS. The cross-section of the oxide scale was studied using SE and BSE imaging coupled with EDS analysis. Before observing the cross-section of the oxide layers, the samples were coated with pure nickel using electrolytic technique. The nickel coating was provided to avoid the possible damage of the outer oxide layers during metallographic grinding and polishing stages.

3. Results

3.1. Microstructures

Back-scattered electron (BSE) microstructures of Alloy 1 (Mo-Nb-Si) are presented in Fig. 2(a) and (b). While Fig. 2(a) is indicating the overall microstructure at a lower magnification, Fig. 2(b) shows a magnified image exhibiting the morphological characteristics of the