

Synopsis

The present thesis deals with Nb-Si alloy composites in both bulk and multilayer forms. The work has been divided into two parts. First part (chapter 4-6) deals with Nb based silicides binary and ternary alloys with alloying additions like Ga and Al. These alloys are synthesized by vacuum arc melting and suction casting (non-equilibrium processing techniques). The studies on intermetallic coatings of Nb-Si alloys and Nb/Si multilayer synthesized by pulsed laser deposition technique have been presented in the second part (chapter 7-8).

Nb-Si alloys are one of the candidate materials for the advanced structural and microelectronic applications. There are few issues with these materials like poor oxidation resistance, low fracture toughness and brittleness which need to be solved. Microstructure plays a crucial role to control these properties. The main focus of this work is to understand the process of phase transformation and thereby control the microstructure in both bulk alloys and thin films. We have also investigated in a limited manner mechanical and environmental properties of bulk alloys.

This thesis is subdivided into nine chapters. After a brief introduction in the first chapter, a brief overview on Nb-Si phase diagram and literature reviews on Nb-Si based alloys are presented with emphasis on the current work in the second chapter. Literature reviews on the phase formations sequence and stability in Nb-Si alloys thin films and Nb/Si multilayers are also discussed in the same chapter.

In the third chapter different experimental techniques, processing parameters and characterization tools like XRD, SEM, TEM etc. are briefly discussed. Special emphasis is given on two non-equilibrium techniques: laser deposition technique to deposit the thin film/multilayer and vacuum suction casting to produce the 3 mm diameter rods of different Nb-Si alloys.

The fourth chapter discusses the microstructural aspects of Nb-Si alloys prepared by suction casting and its mechanical behavior. The samples have the compositions hypoeutectic (Nb-10at.%Si and Nb-14at.%Si), eutectic (Nb-18.7at.%Si) and hypereutectic (Nb-22at.% Si and Nb-25at.% Si). SEM microstructural analyses of all the samples clearly show the enhancement in the volume fraction of eutectic and decrease in the eutectic spacings in microstructure due to large undercooling. Rod eutectic is observed in most of places with irregular eutectic a few places in all samples. First check of phases has been done by XRD in all samples. Phase confirmation using TEM showed the eutectic between Nb_{ss} and Nb_3Si phases in all samples. The primary phase for hypoeutectic alloys is Nb_{ss} (dendritic structure), Nb_3Si phase for eutectic composition and $\beta-Nb_5Si_3$ phase for hypereutectic alloys. Compositional analysis using EDS and EPMA also supported the above results. No signature of eutectoid reaction ($Nb_3Si \rightarrow Nb + \alpha-Nb_5Si_3$) is observed. Mechanical properties like hardness, strength, ductility and indentation fracture toughness have been determined for above mention alloy compositions. SEM micrographs showed that silicides fractured by cleavage and Nb phase in a ductile manner during the compression tests carried out at room temperature. We attempt to explain how the above mention mechanical properties change with alloy compositions and processing.

Chapter five deals with the effect of Ga addition on the microstructure and mechanical properties of the Nb-Si alloy. The composition selected for this study is Nb-20.2at.%Si-2.7at.%Ga. The results of ternary alloy have been compared with the binary alloy composition Nb-18.7at.%Si. Phase analysis has been carried out using TEM and XRD. Ga addition has suppressed the formation of Nb_3Si phase and promoted the formation of $\beta-Nb_5Si_3$ phase. Ga addition also established the eutectic between Nb_{ss} and $\beta-Nb_5Si_3$, which is a metastable eutectic. Ga added ternary alloy, on suction casting, yields ultrafine eutectic with nanometer length scale (50-100nm). From the compression tests, it is concluded that the combination of ultrafine eutectic ($Nb_{ss}-\beta-Nb_5Si_3$) and primary $\beta-Nb_5Si_3$ in ternary alloy results in a high compressive strength $\sim 2.8 \pm 0.1$ GPa with 4.3% plasticity. In contrast binary alloy under identical conditions shows the compressive strength $\sim 1.35 \pm 0.1$ GPa and 0.2% plasticity. Ga addition also enhances the indentation fracture toughness from

9.2±0.05 MPa√m (binary) to 24.11±0.5 MPa√m (ternary). Composite hardness values of the ternary and binary alloys are 1064±20 Hv and 1031±20 Hv respectively.

Chapter six deals with Al added Nb-Si ternary alloy. Here we have discussed microstructural and mechanical properties like in chapter 5 along with oxidation behavior for the alloy composition Nb-12.7at.%Si-9at.%Al. SEM micrograph shows the presence of primary dendrites structure with ultra fine lamellar eutectic (50-100nm). Detailed TEM studies confirm the Nb_{ss} as primary phase present in form of dendrites. These dendrites contain the plate shape precipitates of δ-Nb₁₁Si₄ (body centered orthorhombic structure) phase in Nb matrix (primary dendrites). Eutectic phases are Nb_{ss} and β-Nb₅Si₃. The analysis of the results indicates that Al addition promote the formation of β-Nb₅Si₃ phase in the eutectic. The results of this ternary composition were also compared with the binary alloy composition Nb-18.7at.%Si. Compression tests have been carried out at room and elevated temperatures to measure the strength of the material. Al added ternary alloy yields the compressive strength value 1.6±0.01 GPa whereas binary alloy yields the compressive strength value 1.1±0.01 GPa. Enhancement in indentation fractured toughness is observed in Al added ternary alloy (20.4±0.5MPa√m) compare to binary alloy (9.2±0.05 MPa√m). Thermal analysis by TGA and DTA were used to see the oxidation behavior of Al added ternary alloy.

Chapter seven deals with the deposition characteristics and the TEM studies on the laser deposited Nb-Si thin films. Films were deposited on the NaCl crystals and Si single crystal substrates. The compositions chosen in this case are Nb-25at.%Si, Nb-37.5at.%Si and Nb-66.7at.%Si. These compositions correspond to the equilibrium intermetallic compounds Nb₃Si, Nb₅Si₃ and NbSi₂ respectively. In this chapter we have briefly discussed the microstructural and phase evolutions in the intermetallic coatings. The smooth films quenched from the vapor and/or plasma state show amorphous structure. The sequence of crystallization was studied by hot stage TEM experiments as well as by cross sectional TEM in the films deposited at the elevated temperatures (600°C and 700°C) on Si substrates. During the hot stage experiment, crystallization is observed in Nb-25at.%Si film around 850°C with nucleation of metastable cubic Nb₃Si phase. Occasionally

metastable hexagonal Nb₃Si₃ phase has also been observed (close to Si substrate) along with cubic Nb₃Si phase in the films at elevated temperatures. For Nb-37.5at.%Si film, crystallization is observed at 800°C with the nucleation of grains of metastable hexagonal Nb₅Si₃ phase. Cross-sectional TEM shows the presence of hexagonal Nb₅Si₃ phase along with few grains of NbSi₃ (equilibrium) phase in the films deposited at elevated temperatures. Hot stage experiment of Nb-66.3at.%Si film showed the onset of crystallization much earlier at 400°C and complete crystallization at 600°C. This crystallization leads to the nucleation of grains of NbSi₂ phase. Films of this composition deposited at elevated temperatures showed the presence of NbSi₂ and metastable hexagonal Nb₅Si₃ phases (occasionally). The laser ablated films, besides the film matrix also contain the micron and submicron sized spherical droplets of different sizes. These droplets travel at very high velocities and impinge on the substrate resulting in a very high rate of heat transfer during solidification from liquid state. Therefore in this work we have also studied the microstructural evolution in the droplets for each composition. The phases observed in the droplets embedded in the matrix of Nb-25 at% Si alloy film are the bcc Nb and the cubic Nb₃Si (metastable phase). The droplets in the matrix of Nb-37.5 at% Si alloy showed the bcc Nb and tetragonal β-Nb₅Si₃ phases. The phases observed in the droplets of in the Nb-66.3at.%Si alloy are the bcc Nb, tetragonal β-Nb₅Si₃ and the hexagonal NbSi₂ (metastable phase).

Chapter eight describes the synthesis and microstructural characterization using TEM of Nb/Si multilayers. The aim of this work is to check the stability and phase formation sequence in Nb/Si multilayer. Nb/Si multilayers were first annealed at different time intervals at 600°C and at different temperatures (for 2 hours) and then characterized by the cross-sectional transmission electron microscopy. As-deposited Nb layer is crystalline while Si layer is amorphous. Microstructural and compositional evidences suggest the intermixing between the Nb and Si layers at the interfaces. Nb/Si multilayer annealed at 600°C for 1 hour, NbSi₂ was identified as the first crystalline nucleating phase. However amorphous silicide layers were also observed between Nb and NbSi₂ layers. Metastable hexagonal Nb₅Si₃ was identified as the next crystalline phase that nucleated from the amorphous silicide layers at the interfaces of Nb and NbSi₂ layers. Occasionally few grains

of cubic Nb₃Si phase were also observed after 8 hours of annealing at 600°C. In the chapter we have compared the results to the other reported works in Nb-Si bulk diffusion couples and also thin film couples.

The final chapter summarizes the major conclusions of the present work and scope of future work.