Abstract

The effect of alloying element addition at the expense of Nb in combinations of 5Mo, 5Mo+20Ti, 5Mo+4Fe (compositions in at%) on microstructural evolution, mechanical and isothermal oxidation behaviour of the Nb-12Si based hypo- or Nb-19Si based hypereutectic alloys in as cast (arc-melted) or vacuum-annealed condition (1500 °C for 60 h or 100 h), has been investigated. Additionally, 3 at% Zr or Ga has been added to the Nb-19Si-5Mo-20Ti alloy, considering its promising mechanical properties and oxidation resistance. Characterization of microstructures by X-ray diffraction, scanning and transmission electron microscopy with energy dispersive spectroscopy, as well as electron probe microanalysis with wavelength dispersive spectroscopy has exhibited the presence of Nb_{ss}, ($\beta + \alpha$) 5-3 silicide [$(Nb,X)_5Si_3$ where X = alloying element] in all the examined alloys along with β-Ti_{ss} and Fe rich silicide (Nb_4FeSi) in Ti and Fe containing alloys, respectively. As an exception, the Zr containing alloys have shown a eutectic comprising the Zr rich γ-5-3 silicide phase along with absence of the β-Ti_{ss}. The morphology of the eutectic in as-cast ternary alloys is partially transformed from lamellar to non-lamellar on Fe or Zr addition, and completely on Ti or Ga addition, believed to be by the decoupled growth of Nb_{ss} and complex 5-3 silicide during solidification. Annealing has been found to alter not only the phase volume fractions, but also the eutectic morphology from lamellar to non-lamellar along with spherodization and coarsening of the Nb_{ss}.

The dynamic Young′s moduli of the examined as cast alloys have increased on annealing, probably due to $\beta \rightarrow \alpha$ transformation of 5-3 silicides, altered phase volume fractions, and partitioning of Mo to Nb_{ss}. The hardness is lowered on annealing due to coarsening of primary or eutectic Nb_{ss} and/or increase in its volume fraction, except for the annealed Fe containing alloys with deformation of Nb_{ss} being constrained by the surrounding interconnected 5-3 silicide phase. The room temperature fracture toughness values obtained by three point bend tests on single edge notch bend specimens have been found to vary from ~ 6 ± 0.3 MPa√m for the as cast ternary Nb-12Si-5Mo alloy to ~14 ± 0.37 MPa√m for the annealed hypoeutectic Nb-12Si-5Mo-20Ti alloy. Further, the post-anneal fracture toughness of the hypereutectic Nb-19Si-5Mo-20Ti alloy has increased by 35.5% to ~14.9 ± 0.2 MPa√m or by 18.2% to ~13 ± 0.1 MPa√m on addition of 3 at% Zr or Ga, respectively. In general, the fracture toughness is increased with volume fraction of Nb_{ss} along with its coarsening or spherodization, as well as change in the eutectic morphology from lamellar to non-lamellar, achieved by compositional changes and annealing. The toughening is facilitated by arrest, bridging or deflection of cracks by coarser ductile Nb_{ss} phase of the non-lamellar eutectic. The room temperature compressive strengths found as ~2200-2900 MPa for the as cast alloys are reduced after annealing with the strength reduction being higher for the hypoeutectic compositions with larger Nb_{ss} content. The fracture surfaces with cleavage facets and river patterns in the Nb_{ss} along with evidence of interfacial decohesion within the non-lamellar eutectic, indicate the predominance of brittle failure. The compressive yield strength is reduced with increase in temperature in the range of 900-1100 °C, with the hypoeutectic alloys exhibiting a higher strength retention indicating the predominant role of solid solution strengthened Nb_{ss} phase. Further, the compressive yield strengths of Nb-19Si-5Mo-20Ti alloy at both room and high temperature are found to increase on Zr and Ga addition, indicating that controlled alloying with annealing provides a strategy for simultaneous increase of strength and fracture toughness. The flow curves obtained from high temperature compression tests have shown initial work hardening, followed by a steady state regime indicating dynamic recovery with formation of low angle grain boundaries in the Nb_{ss}, as confirmed by electron backscattered diffraction.

On isothermal exposure for 24 h, the ternary alloys have exhibited lower mass gain at 900 °C than the quaternary and quinary alloys, but the trend is reversed at 1100 °C and 1200 °C. Annealed samples with coarser microstructure has exhibited higher mass gain than that in as cast condition. The identified oxidation products are Nb_2O_5 and SiO_2, with TiO_2, $TiNb_2O_7$ and $Ti_2Nb_{10}O_{29}$ being formed in the oxide scales of the Ti containing alloys, as well as ZrO_2 and Ga_2O_3 formed additionally in Zr and Ga added alloys, respectively. Analysis of the oxidation kinetics suggests the occurrence of an initial interface-reaction controlled rapid increase of mass, followed by a stage of parabolic behaviour, where diffusion of species through the oxide scale could be the rate-controlling. The as cast and annealed Nb-19Si-5Mo-20Ti alloy along with the Zr containing alloy has exhibited lower parabolic rate constant at ≥1100 °C, which is considered as signature of a compact oxide scale. Reduced oxygen solubility and diffusivity due to solid solubility of Mo, Ti and Zr in the Nb_{ss}, along with formation of SiO_2-rich oxide scale at the surface or sub-surface locations appears to have contributed to the oxidation resistance.

Keywords: Nb–Si–Mo alloys; Intermetallics (silicides); alloying, arc-melting; annealing; microstructure; x-ray diffraction; scanning electron microscopy, transmission electron microscopy; elastic properties; hardness; fracture toughness; compressive deformation; isothermal oxidation; oxide scale, oxidation kinetics.