

Abstract

A comparative study has been carried out on densification, microstructural evolution, as well as, high temperature oxidation behavior of the W–Cr alloys with or without addition of Nb or Y₂O₃. The processing of W_{1-x}Cr_x ($x = 0.3, 0.5$ or 0.6) alloys, (W_{1-x}Cr_x)_{0.9}Nb₁₀ ($x = 0.3, 0.5$ or 0.6) alloys and W_{1-x}Cr_x–3 wt.% Y₂O₃ ($x = 0.3$ or 0.5) composites have involved the formation of nanostructured powders through mechanical milling route, followed by conventional pressure-less sintering. This work has been aimed particularly at optimization of composition and process parameters to achieve maximum densification, as well as to acquire superior oxidation protection.

Investigation has been carried out initially on the binary W–Cr alloys. The optimized process parameters, i.e., milling time of 5 h and sintering temperature of > 1500 °C, have been adopted to consolidate both W–Cr–Nb alloys and W–Cr–Y₂O₃ composites with different compositions. Results of this study have shown that sintering of W–based alloys/composites using nanostructured powders as raw materials to obtain products with relative density between 96 and 98% is possible at relatively lower temperatures (e.g. 1790 °C) compared to that required for densification of coarser powders, even without using sintering activators. X–ray diffraction, scanning electron microscopy and energy dispersive spectroscopy have confirmed the presence of W–rich (β_1) and Cr–rich (β_2) phases in the W–Cr alloys sintered at 1700 °C. However, the microstructures of the W–Cr–Nb alloys sintered at 1790 °C have shown the presence of Cr₂Nb phase at W rich solid solution (α) grain boundaries. The microstructures of the W–Cr–Y₂O₃ composite samples sintered at 1700 °C are characterized by the presence of W–rich (β_1) + Cr–rich (β_2) regions and more or less uniformly distributed Y₂O₃ particles. Unlike, the W–Cr alloys, sintering of W–Cr–Nb alloys at 1790 °C is promoted by the presence of liquid phase comprising the molten Cr₂Nb phase (melting point ≈ 1730 °C). On the other hand, densification of W–Cr–Y₂O₃ composites at 1700 °C is promoted by incipient melting of the eutectic comprising W and Y₂O₃ at 1560 °C.

All three W–Cr alloys have shown sound oxidation resistance at 800 °C. On increasing the temperature of exposure to ≥ 1000 °C, the alloys with 50 and 60 at.% Cr have shown superior oxidation resistance following more or less parabolic–rate kinetics. The oxidation resistance of the alloy with lower Cr content (W with 30 at.% Cr) is found to be poor in the range of 1000–1200 °C, indicating that 30 at.% of Cr in the W–Cr alloy would be insufficient to form and maintain a stable and protective oxide scale at temperatures up to 1200 °C. Major challenge with the W–Cr system is spallation of the oxide scale during thermal cycling, due to pores formed on vaporization of WO_3 and Cr_2O_3 and also due to thermal expansion mismatch between oxide scale and base alloy. However, formation of Cr_2WO_6 through reaction between Cr_2O_3 and WO_3 significantly lower the environmental degradation rate of W–Cr alloys with higher Cr content. In the W–Cr–Nb alloys, consumption of Cr_2O_3 and WO_3 in formation of more complex oxides of Cr_2WO_6 and $\text{Nb}_2\text{O}_5 \cdot 3\text{WO}_3$ enhances oxidation resistance. However, Y_2O_3 appears to be more promising candidate for improving the high temperature capabilities of the W–Cr based alloys. The $\text{W}_{0.5}\text{Cr}_{0.5}$ alloy containing 3 wt.% Y_2O_3 has exhibited excellent oxidation resistance up to 1200 °C for 100 h. Protection against high temperature oxidation is possible if a stable mixed oxide scale containing both Cr_2WO_6 and $\text{Y}_2\text{W}_3\text{O}_{12}$ is formed at the oxide–air interface. Melting of the eutectic composition of $\text{Y}_2\text{W}_3\text{O}_{12}$ and WO_3 leads to the formation of a liquid phase, which helps in closure in pores by sintering and viscoplastic flow of the oxide scale, thereby enhancing its resistance to spallation and further oxidation.

Keywords: Tungsten–Chromium; Tungsten–Chromium–Niobium; Tungsten–Chromium–Yttria; Mechanical milling; Sintering; High temperature oxidation;