Role of Minor Alloying Elements on the Oxidation Behavior of Ni-base Alloys in a High Temperature Steam Environment

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1. Introduction

The High Temperature Gas-cooled Reactor (HTGR) is one of the Generation IV nuclear reactor designs being developed with the aims of high efficiency and industrial applications such as mass hydrogen production. The HTGR is expected to operate at temperatures around 900 °C and 7 MPa for a 60-year design lifetime. The structural materials for the HTGR will be exposed to various environments at high temperatures such as helium, steam, and hydrogenated steam. Such conditions limit the material selection to Ni-base alloys for high temperature strength and superior corrosion resistance. Alloy 617 and Haynes 230 are primary candidate materials considered for key components in the HTGR such as the intermediate heat exchanger (IHX) and hot gas duct (HGD).

In terms of creep behavior, it has been reported that Alloy 617 exhibits superior creep resistance compared to Haynes 230 [1]. On the other hand, oxidation resistance must be considered, as it is another important factor for structural material integrity, especially for components like the IHX having thin thicknesses. In this perspective, previous investigations have stated that Haynes 230 would exhibit slower oxidation kinetics compared to Alloy 617 [2, 3]. This behavior was ascribed to the formation of a continuous Cr-Mn-rich spinel layer on 230, as opposed to nodular Ti-rich oxides on 617. Such behavior is thought to stem from the differences in chemical composition between 230 and 617, mainly for minor elements that partake in oxide formation.

In this study, to elucidate the effect of each minor alloying element on oxidation behavior and improve the high temperature oxidation resistance, model alloys based on Alloy 617 were fabricated with varying Mn, Ti and Al contents. Then, model alloys were exposed to steam environment at 900 °C for up to 1000 h. The oxidation behavior was evaluated and compared in view of the differences in chemical composition.

2. Experimental Procedure and Results

2.1 Material Fabrication and Analysis Methods

Eight model alloys were fabricated by vacuum arc remelting (VAR) method based on the chemical composition of Alloy 617. The cast alloys were subsequently subjected to thermomechanical processes applied to Alloy 617. These alloys were machined into coupon-type specimens of 12 mm diameter and 1 mm thickness. The coupon specimens were mechanically polished on both sides with 1200 grit SiC paper and ultrasonically cleaned in ethanol prior to the oxidation test.

Various analysis techniques such as weight change measurement, X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM) equipped with energy dispersive spectroscope (EDS) was utilized to analyze the specimens.

2.2 High temperature steam oxidation

For the steam oxidation test, distilled water with a dissolved oxygen content below 100 ppb was supplied at a flow rate of 20 sccm to the test chamber maintained at 900 °C. The coupon specimens were hung on a Pt wire and separated by alumina spacers, then installed on an alumina rack which was lowered into the test chamber for the test. In order to attain the oxidation kinetics of the alloys, two specimens for each alloy were removed from the test at certain intervals for analysis.

The weight gain results attained from this procedure are shown in Fig. 1. It should be noted that the two commercial alloys, Haynes 230 and Alloy 617, show oxidation behaviors that are consistent with previously reported results [3, 4]. In the case of the model alloys, it can be seen that there are two distinct trends. Alloys 1-4, which do not contain any Ti or Al, show similar weight gain trends as Haynes 230, while alloys 5-8, containing Ti and Al follow weight gains of Alloy 617.

Microstructural analysis via SEM showed different oxide morphologies in accordance with the weight gain trends. It was found that alloys 5-8 formed distinctive oxide ridges observed also on 617, which is indicative of accelerated element transport along the grain boundaries during oxidation (Fig. 2.). This is thought to have contributed to the greater weight gains of these alloys. Alloys 1-4 showed varying behaviors according to the differences in their Mn content. Alloy 1 initially formed a continuous Cr-rich oxide layer, but suffered severe spallation at longer times which is also reflected in its weight loss. In the case of alloy 2, a continuous Mn-Cr-rich spinel oxide formed, which seemed to be more resistant to spallation than the oxide formed on alloy 1. For alloys 3 and 4, large nodular oxides rich mainly in Mn formed on the surface, owing to the comparatively high Mn contents (Fig. 3.). However, the exact effect of Mn on the oxidation behavior is not clear and further analysis is underway.

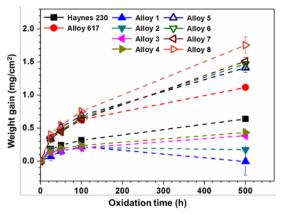


Fig. 1. Weight gain measurements of the model alloys after exposure to steam at 900 $^{\circ}$ C for up to 500 h.

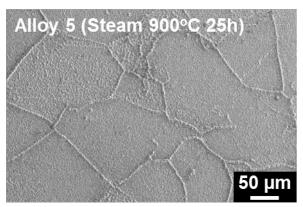


Fig. 2. Surface SEM micrograph of alloy 5 exhibiting oxide ridges along grain boundaries after exposure to steam at 900 $^{\circ}$ C for 25 h.

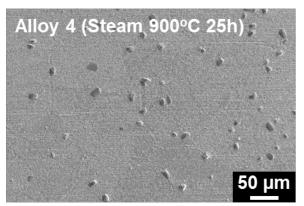


Fig. 3. Surface SEM micrograph of alloy 4 exhibiting nodular oxide formation after exposure to steam at 900 °C for 25 h.

3. Conclusion

Model Ni-base alloys were developed and tested in high temperature steam environment to investigate the role of minor alloying elements on oxidation behavior. Results indicate that alloys containing Ti exhibit comparatively greater weight gains owing to faster oxide growth at the grain boundaries, while alloys containing Mn showed varying behaviors according to its content. Further testing to 1000 h and detailed analyses will be conducted to obtain a clearer understanding of the role of each alloying element in high temperature oxidation behavior.

Acknowledgements

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