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High Temperature Steam Oxidation

of Fe-Cr-Ni-Nb Austenitic Steels at 1073 K

In A-USC power plants, piping materials must meet requirements of creep rupture strength and steam oxidation resistance. Newly developed Fe-20Cr-30Ni-2Nb (at. %) austenitic steel is one of the candidates because of its superior creep rupture strength provided by formation of Fe_2Nb Laves. In this study, steam oxidation of these steels was conducted in Ar-15%H_2O at 1073 K for up to 1209.6 ks. Duplex scale consisted of outer scale of magnetite and inner scale of spinel formed in the initial stage in which oxidation rate was high. The longer exposure offered the protective Cr_2O_3 scale at the steel/scale interface, which suppressed the growth of oxide scale. Steam oxidation mechanism of the developed steels at 1073 K was proposed. The in-situ measurement of the oxygen potential at the surface of the scale clarified the steam oxidation mechanism. Boron doped steel with higher creep resistance exhibited better resistance to steam oxidation. The results obtained the estimated scale thickness after 10^5 hours exposure at 1073 K to be less than 100 μm. In conclusion, these steels are expected to be applicable in power plants operated at 1073 K.

In this thesis, the high temperature steam oxidation of Fe-Cr-Ni-Nb austenitic steels at 1073 K was investigated systematically. The structure of the thesis is summarized below:

Chapter 1: "Introduction"

The background of this thesis is explained in relation to the global energy problem and the issue to be solved in fossil fuel power plants. The improvement of efficiency in power plants is going on progress by operation at higher temperature in which the steam oxidation of steels is an issue to overcome. The objective of this thesis is to evaluate the availability of newly developed Fe-Cr-Ni-Nb austenitic steels to A-USC power plants

operated at 1073 K in the view point of high temperature steam oxidation.

Chapter 2: "Steam Oxidation Behavior of Fe-20Cr-30Ni-2Nb (at. %) at 1073 K"

Steam oxidation of Fe-20Cr-30Ni-2Nb (at. %) austenitic steel with various heat treatments and polishing treatments was conducted at 1073 K in Ar-15%H_2O flow. In the initial stage of steam oxidation, Fe_3O_4 is formed as the continuous scale and $(Fe,Cr)_3O_4$ and Cr_2O_3 are formed as internal oxides. After about 20 ks, Cr_2O_3 become a continuous layer at the steel/scale interface. The continuous layer suppresses the growth rate of oxide scale as same as that of Fe-25Cr alloy. Therefore this steel is expected to be applicable in A-USC power plant operated at 1073 K. And the formation of continuous Cr_2O_3 layer is independent on the heat treatments, but dependent on the polishing treatments.

Chapter 3: "Surface Oxygen Potential Measurement in Steam Oxidation of Fe-20Cr-30Ni-2Nb (at. %) at 1073 K"

In-situ monitoring of the surface oxygen chemical potential was conducted by an oxygen concentration cell using CaO stabilized ZrO_2 electrolyte touching at the Fe-20Cr-30Ni-2Nb steel. At the initial stage, the oxygen potential at the surface of the scale (-550 kJ・mol^{-1}) was lower than that in the atmosphere (-500 kJ・mol^{-1}). According to the formation of continuous Cr_2O_3 layer, after 200 ks, the oxygen potential at the surface of the scale increased to be -510 kJ・mol^{-1}. Continuous monitoring of surface oxygen potential was applied to clarify steam oxidation mechanism.

Chapter 4: "Effect of Addition of Boron on Oxidation Behavior of Fe-20Cr-30Ni-2Nb (at. %) at 1073 K"

Steam oxidation of Fe-20Cr-30Ni-2Nb-0.03B (at. %) austenitic steel with various

heat treatments has been conducted. The oxidation behavior was basically as same as that of the steel without boron. However the addition of boron decreased slightly the growth rate of the oxide scale but the mechanism has not been clarified yet. This boron-added steel is potentially applicable in A-USC power plant operated at 1073 K.

Chapter 5: “Conclusion”

The results obtained in the present study are summarized as conclusion.