

Quantitative Evaluation of the Effect of the Al Addition on the Internal-External Oxidation in Ni-Cr Alloys

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INTRODUCTION

The formation of a protective oxide scale offers highly oxidation-resistant alloys. The alloy composition affects its oxidation behavior of internal or external oxidation. Transition from internal oxidation to external oxidation is a great importance in material design. In a binary A-B alloy, Wagner¹⁾ derived a quantitative equation describing the minimum content of B at which the transition from internal oxidation to external oxidation occurs,

$$N_B \geq \left(\frac{\pi g^* N_O^s D_O V_M}{2 \nu D_B V_{OX}} \right)^{\frac{1}{2}} \dots (1)$$

where ν is the atomic ratio of B and oxygen in oxide (BO_ν), N_O^s is the concentration of oxygen at the surface of the alloy, D_O and D_B are diffusivity of oxygen and B in the alloy, V_M and V_{OX} are molar volumes of alloy and oxide (BO_ν), g^* is the volume fraction of oxide in the internal oxidation zone at which the internal-external transition occurs. Rapp²⁾ proposed g^* to be around 0.3.

The addition of the third element is sometime beneficial to form the external scale. The effect of Al in Ni-Cr alloys on oxide scale has qualitatively reported as an oxide map³⁾. Less than 4 mass% Al enhances the formation of Cr_2O_3 scale and more Al gives Al_2O_3 scale. This study is for the quantitative understanding of the effect of Al on high temperature oxidation of Ni-Cr

EXPERIMENTAL

Internal oxidation experiment was conducted on the alloy of Ni-5.49mol%Cr-4.16Al mol% (Ni-5.0mass%-2.0mass%Al). The samples were cut into 10 x 10 x 2 mm³ and annealed at 1473 K, for 43.2 ks in vacuum to assure the homogeneity. After that, samples were polished with 4 micron diamond paste.

A sample was placed in an evacuated apparatus, which contained Cr/ Cr_2O_3 mixed powders as oxygen supplier. An R-type thermocouple placed about 1 mm from the top of sample for monitoring the temperature. The oxidation was carried out at 1273 K.

After oxidation, samples were cut and analyzed with optical microscopes, SEM and EPMA.

RESULT AND DISCUSSION

The morphology and concentration of Cr and Al in metallic phase both in bulk and internal oxidation zone (IOZ) are shown in Fig. 1. At the oxygen pressure of Cr/ Cr_2O_3 equilibrium, Al was selectively oxidized and there are no continuous external scale formed. Alloy nodules are observed at the surface due to creep deformation by the stress arises from the volume increase of oxidation of Al.

The concentration of Al deplete from bulk to oxidation front. As a result of Al consumption in IOZ, the

Al concentration in alloy of IOZ is almost zero. Conversely, the concentration of Cr increases towards oxidation front and enriches in IOZ.

The alloy in IOZ is a binary Ni-Cr alloy. Suppose the bulk ternary alloy and IOZ binary alloy are in equilibrium, the activities of Cr in both alloys are identical.

$$a_3^{Cr} = \gamma_3 N_3^{Cr} = \gamma_2 N_2^{Cr} = a_2^{Cr} \dots (2)$$

Therefore, the enrichment of Cr arises from the difference in activity coefficients between binary and ternary alloys.

In equation (1), one oxide is assumed to be form. But in case of ternary alloys internally oxidized in sufficiently high oxygen potential, more than one oxide may form. At oxygen potential high enough to form Cr_2O_3 , Al_2O_3 has already been formed. Thus, to estimate minimum concentration which required to form external Cr_2O_3 scale, one should deduce the volume fraction of Al_2O_3 , $g_{Al_2O_3}$. The value of $g_{Al_2O_3}$ measured from the microstructure observation was ≈ 0.25 , which was independent of time.

As described above, the minimum Cr concentration for the transition from internal to external scale in ternary Ni-Cr-Al alloys is expressed with Cr activity coefficient ratio and volume fraction of Al_2O_3 in IOZ.

$$N_{Cr}^{(3)} \geq \frac{V_2}{V_3} \left(\frac{\pi (g^* - g_{Al_2O_3}) N_O^s D_O V_M}{2 \nu D_{Cr} V_{Cr_2O_3}} \right)^{\frac{1}{2}} \dots (3)$$

Using equation (3), we estimated the minimum concentration of Cr in ternary Ni-Cr-Al alloys to perform external scale is lower than in binary Ni-Cr alloys.

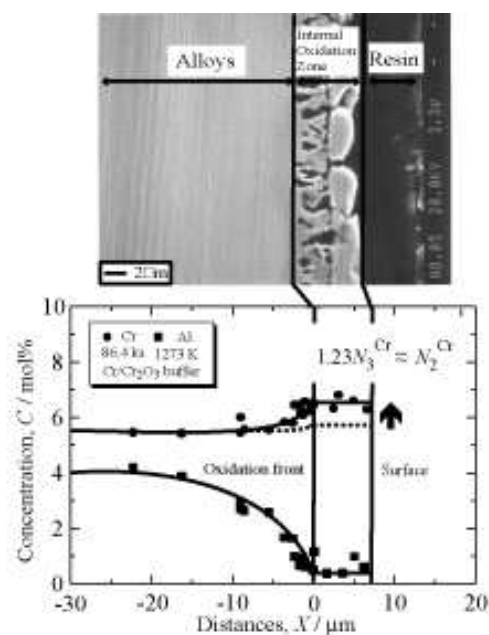


Figure 1 : Morphology and concentration of Cr and Al in bulk and IOZ. Dotted line shows the calculated Cr concentration without Al.

REFERENCES

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