Air Oxidation of Binary Ni-Dy Alloys at 923-1023K and Lithiation in Molten (0.62Li, 0.38K)$_2$CO$_3$ at 923K

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ABSTRACT

In order to decrease the solubility of NiO cathode of molten carbonate fuel cell (MCFC) and develop materials and coatings for separators in the cathode side of MCFC, dysprosium was introduced to modify nickel. In present paper, binary Ni-Dy alloys containing 1, 3 and 5 mass%Dy respectively were prepared. The alloys are two-phase composed of a nickel solid solution and an intermetallic phase $Ni_{17}Dy_2$. The oxidation behavior of the alloys at 923-1023K in air was evaluated by thermogravimetric tests coupled with some physical analysis techniques. The samples pre-oxidized at 923K for 100h were then immersed in molten (0.62Li, 0.38K)$_2$CO$_3$ at 923K to examine the effect of Dy on the lithiation of NiO in the melt. The results indicated that the addition of dysprosium to nickel increased its oxidation rate, except for Ni-1Dy at 1023K. The scales formed on the alloys were composed of NiO with a trace of Dy_2O_3. The lithiation of NiO in molten (Li, K)$_2$CO$_3$ could be favored by the addition of dysprosium. For comparison, binary Ni-Y alloys were also examined. The effect of yttrium on the air oxidation and molten (Li,K)$_2$CO$_3$ corrosion of nickel was similar to dysprosium, except that the Y-containing precipitates in Ni-Y alloys underwent very fast preferential corrosion while the Dy-containing intermetallic phases in Ni-Dy alloys not.

Key Words: Molten carbonate fuel cell, Ni-Dy alloys, oxidation, molten carbonates, lithiation

1. INTRODUCTION

As additives for alloys and coatings, small amounts of oxygen active elements show a positive role in improving the oxidation resistance and particularly the scale adherence on high temperature alloys. Reactive elements such as rare-earth elements, Zr, Hf etc. are usually used both as direct additions in elemental form or as oxide dispersion to alloys, and as surface coatings. A large number of publications on the effects of oxygen active elements are available. In order to obtain the beneficial effects of reactive elements by alloying, it is important that the elements are finely dispersed and present in small amounts. Over-large additions will result in grain boundary precipitates of intermetallic phases of the rare earth elements, which may be preferentially oxidized. For Ni-Cr-Al alloys, the best improvements are generally reported for additions of 0.1-0.2 mass% Y/1/. In the case of Ni-Cr-Al with additions of 0.7mass%Y, an Ni-Y phase precipitates along the grain boundaries and is selectively oxidized /2/. The present author once examined the air oxidation of Fe-2, 5at.%Y at 873-1073K, and found that the oxidation rate of the alloys was lower than that of pure iron. However, the alloys went through fast preferential oxidation along the intermetallic phase $Fe_{17}Y_2$ /3/.

Molten carbonate fuel cell is an energy converter that transforms chemical energy into electricity directly through an electrochemical reaction between hydrogen and oxygen and, therefore has high electrical efficiency. In order to decrease the dissolution of NiO in molten (Li,K)$_2$CO$_3$, attempts have been conducted to introduce reactive elements into the materials of molten carbonate fuel cell /4,5/. Daza *et al.* /4/ modified nickel oxides by impregnation with cerium as cathode materials, and found that cerium additives can retard the corrosion process of the NiO cathode and favor the lithiation process. Taking into account the possible beneficial effect of reactive elements (RE) in inhibiting the growth of NiO on Ni in molten $(Li, K)_2CO_3$, and promoting the lithiation process, the present authors proposed to introduce dysprosium into the production of cathodic materials of MCFC. In a study of corrosion of Ni-Dy containg 1, 3 and 5 mass% Dy , respectively, in eutectic $(0.62Li,0.38K)_2CO_3$ at 923K, it was found that a small amount of Dy additives could retard greatly the corrosion of Ni, and favor the lithiation of NiO /5/. Moreover, the alloys did not undergo preferential oxidation along the intermetallic phase $Ni_{17}Dy_2$, which is quite different from the alloys with large additions of other rare earth elements such as Y/2,3/. It is uncertain if this difference is related to the dopping of lithium or the special role of Dy. The results suggest that Ni-Dy alloys have potential for the production of separators in the cathode side of MCFC. In view of the fact that the cathode of MCFC is generally formed by *in situ* oxidation, it will be interesting to study the oxidation of Ni-Dy alloys in an oxidizing atmosphere. In this paper, air oxidation of Ni-Dy alloys at 923 and 1023K and subsequent lithiation in molten $(Li,K)_2CO_3$ at 923K were examined. There is limited information about the effect of the rare earth element dysprosium on the oxidation of alloys /6/.

2. EXPERIMENTAL PROCEDURES

Binary Ni-Dy alloys containing 1, 3 and 5 mass%Dy respectively were used in the present study. For comparison, binary Ni-Y alloys containing 1, 3 and 5 mass%Y were also employed. The alloys were prepared by repeatedly arc-melting mixtures of pure nickel, dysprosium or yttrium under argon. The purity of nickel is 99.99%, and that for Dy and Y is 99.9%. Both Ni-Dy and Ni-Y alloys are two-phase composed of a Ni solid solution and an intermetallic phase $Ni_{17}Dy_2$ or $Ni_{17}Y_2$. Figure 1 shows the microstructure of Ni-Dy alloys. Sheet-shape specimens 1.4 mm thick with a surface area of 3 ~ 4.5 × 10^{-4} m^2 were cut from the original ingots by an electric spark cutting machine, ground down to 600-grit SiC paper, degreased and dried before use. The oxidation of the alloys was conducted at 923 and 1023K in air, respectively.

In order to understand the effect of Dy on the lithiation process of NiO in molten carbonates, some samples were firstly oxidized at 923K in air for 100h, and then immersed in molten $(0.62Li, 0.38K)_2CO_3$ at 923K in air. The eutectic mixtures of $(Li, K)_2CO_3$ contained in an alumina crucible were dried at 623K for 24h and then heated to the experimental temperature.

The corroded samples were analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM) coupled with energy dispersive X-ray microanalysis (EDX).

3.RESULTS AND DISCUSSION

3.1 Air oxidation

Figure 2 shows the oxidation kinetics of pure nickel and of Ni-Dy at 923 and 1023K in air. At 923K, the oxidation of pure nickel and of Ni-Dy alloys followed approximately parabolic rate law. The oxidation rates in initial stage with respect to later stage are relatively high. Pure nickel was oxidized slower than Ni-Dy alloys whose oxidation rate was increased with increasing dysprosium content of the alloys. Table 1 lists the average rate constants for pure nickel and Ni-Dy alloys. At 1023K, Ni and Ni-Dy alloys followed approximately parabolic oxidation, as observed at 923K. However, the oxidation rate of pure nickel is higher than that of Ni-1Dy, but lower than that of both Ni-3Dy and Ni-5Dy. The oxidation rate of Ni-3Dy is close to that of Ni-5Dy.

Table I

Average parabolic rate constants ($g^2m^{-4}s^{-1}$) for the oxidation of pure nickel and of Ni-Dy alloys at 923 and 1023K, respectively.

Temperature	Ni	Ni-1Dy	Ni-3Dy	Ni-5Dy
923K	2.4×10^{-4}	3.1×10^{-4}	4.5×10^{-4}	8.0×10^{-4}
1023K	1.0×10^{-3}	6.5×10^{-4}	1.5×10^{-3}	1.4×10^{-3}

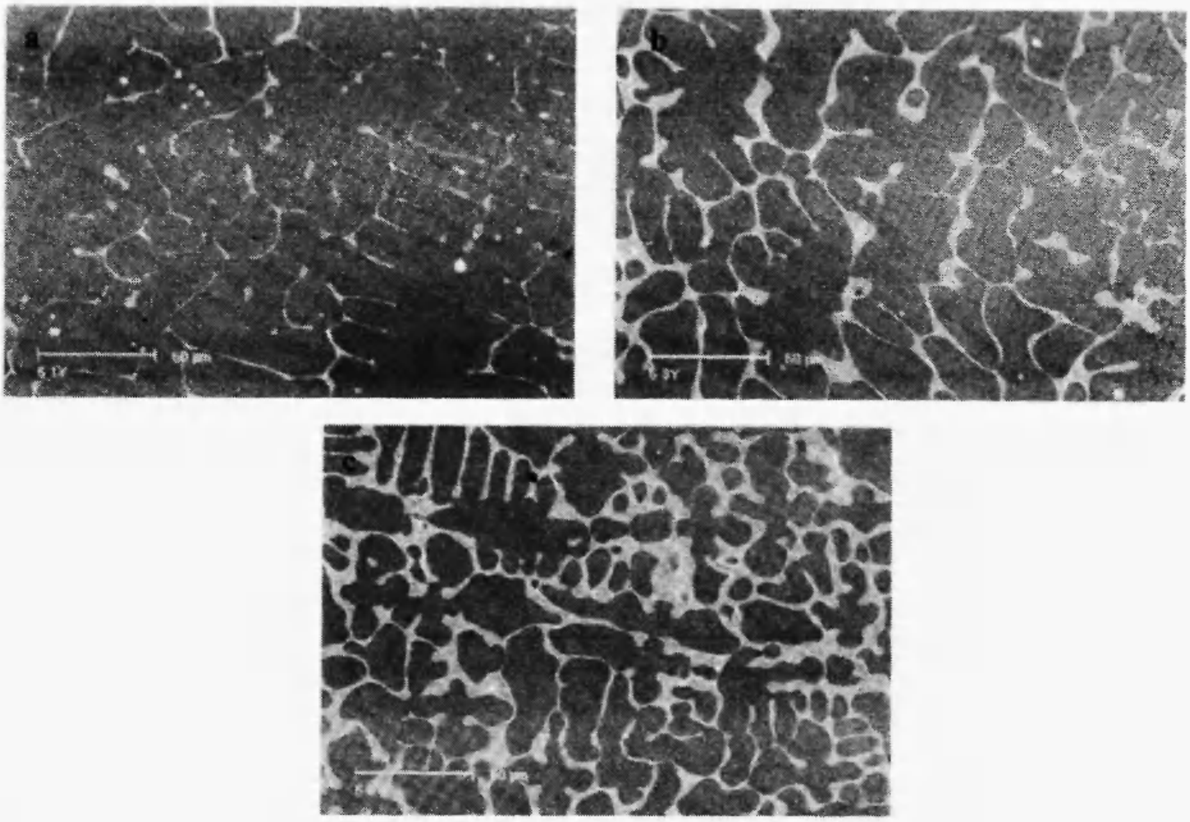

Fig. 1: Microstructure of binary Ni-Dy alloys:(1a)Ni-1Dy; (1b)Ni-3Dy; (1c)Ni-5Dy; grey phase: Ni solid solution; bright phase: $Ni_{17}Dy_2$.

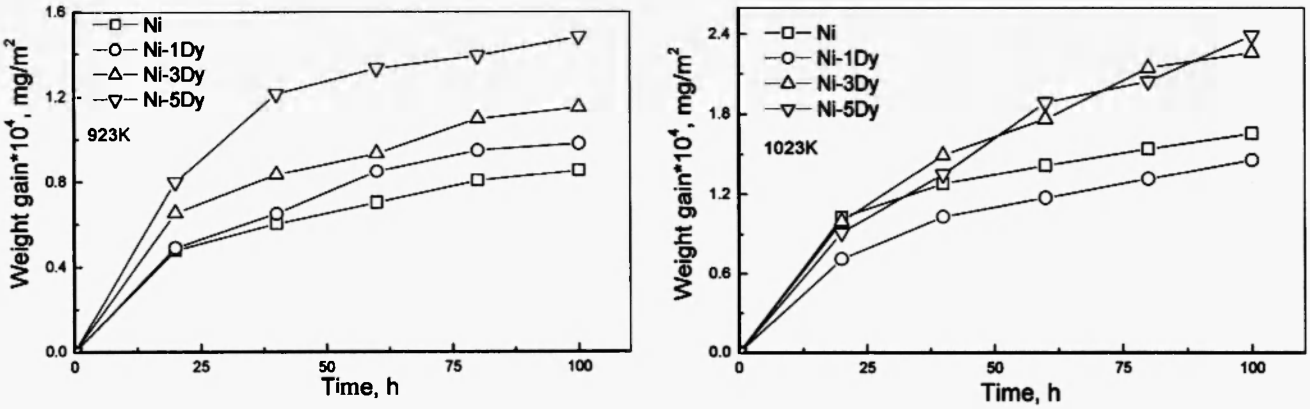

Fig. 2: Air-oxidation kinetics of pure nickel and Ni-Dy alloys at 923-1023K.

3.2 Oxidation products

Surface analysis by XRD indicated that the scales formed on the Ni-Dy alloys were mainly composed of NiO with a trace of Dy_2O_3. Figure 3 shows the cross-sectional morphologies of Ni-5Dy oxidized at 923 and 1023K for 100h. The scale formed on Ni-5Dy oxidized at 923K was composed of gray NiO incorporated with a little bright Dy_2O_3-rich oxide. The thickness of the external scale is not uniform. The thick part mainly

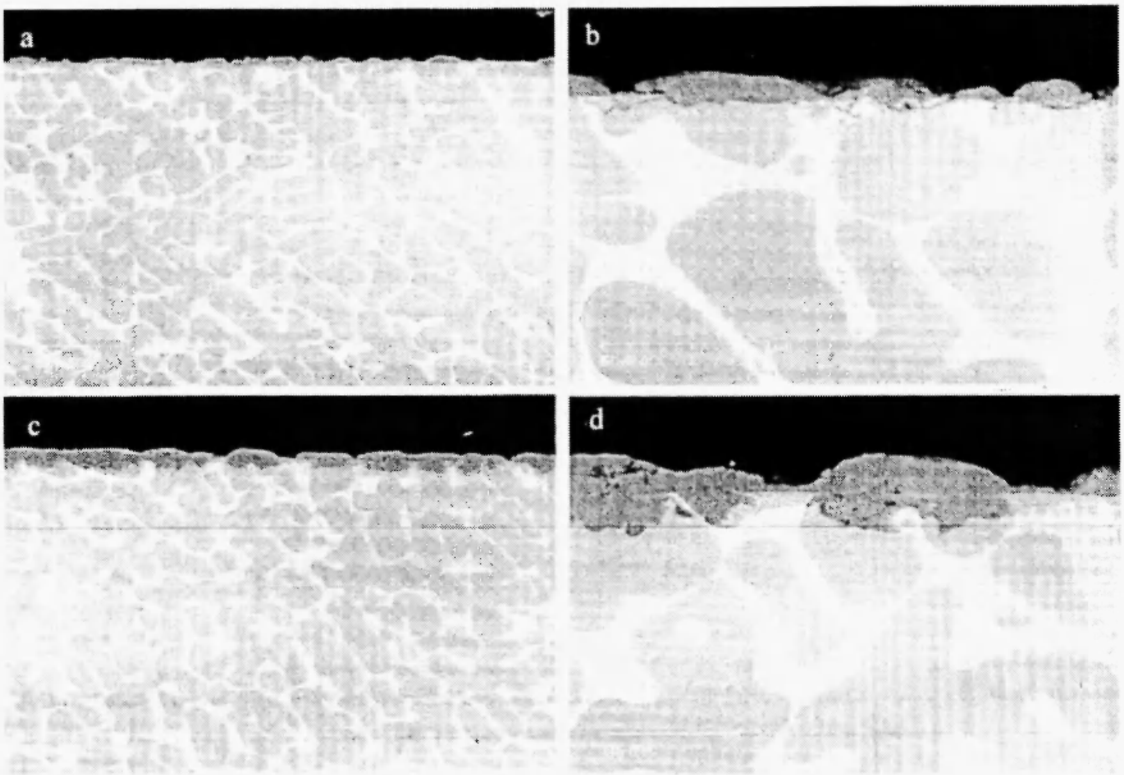

Fig. 3: Cross-sectional morphologies of Ni-5Dy oxidized at 923-1023K for 100h: (3a)923K; (3b) amplified image of (3a); (3c)1023K; (3d)amplified image of (3c).

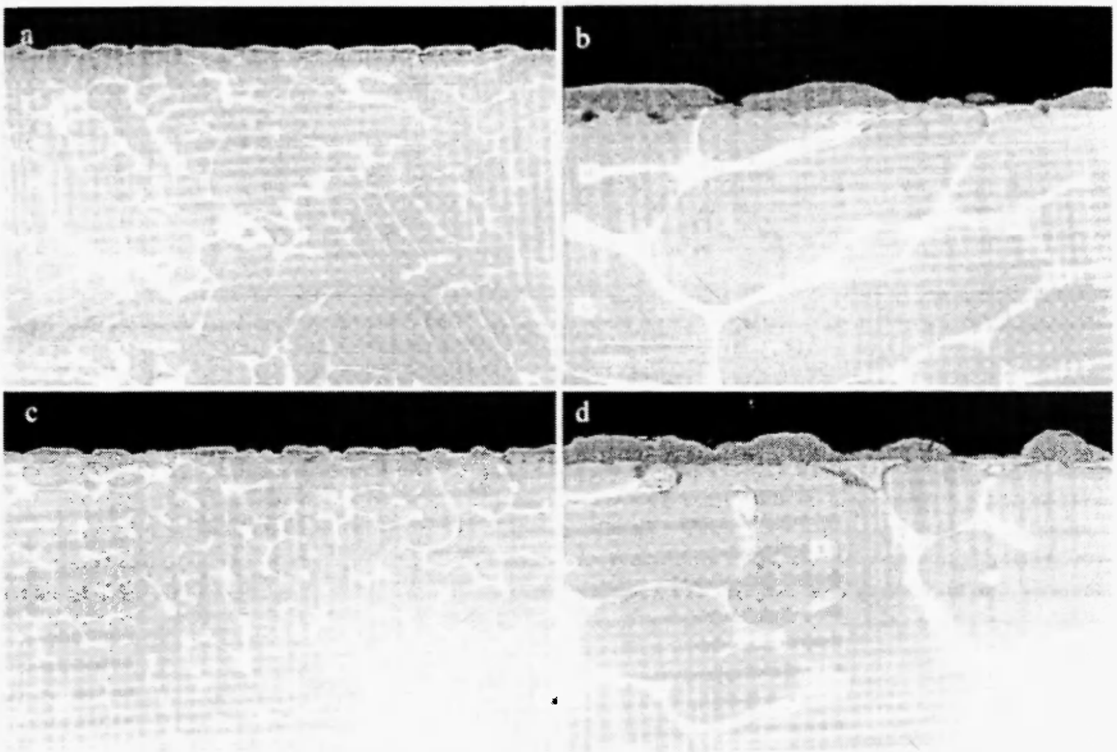

Fig. 4: Cross-sectional morphologies of Ni-3Dy oxidized at 923-1023K for 100h: (4a)923K; (4b) amplified image of (4a); (4c)1023K; (4d)amplified image of (4c).

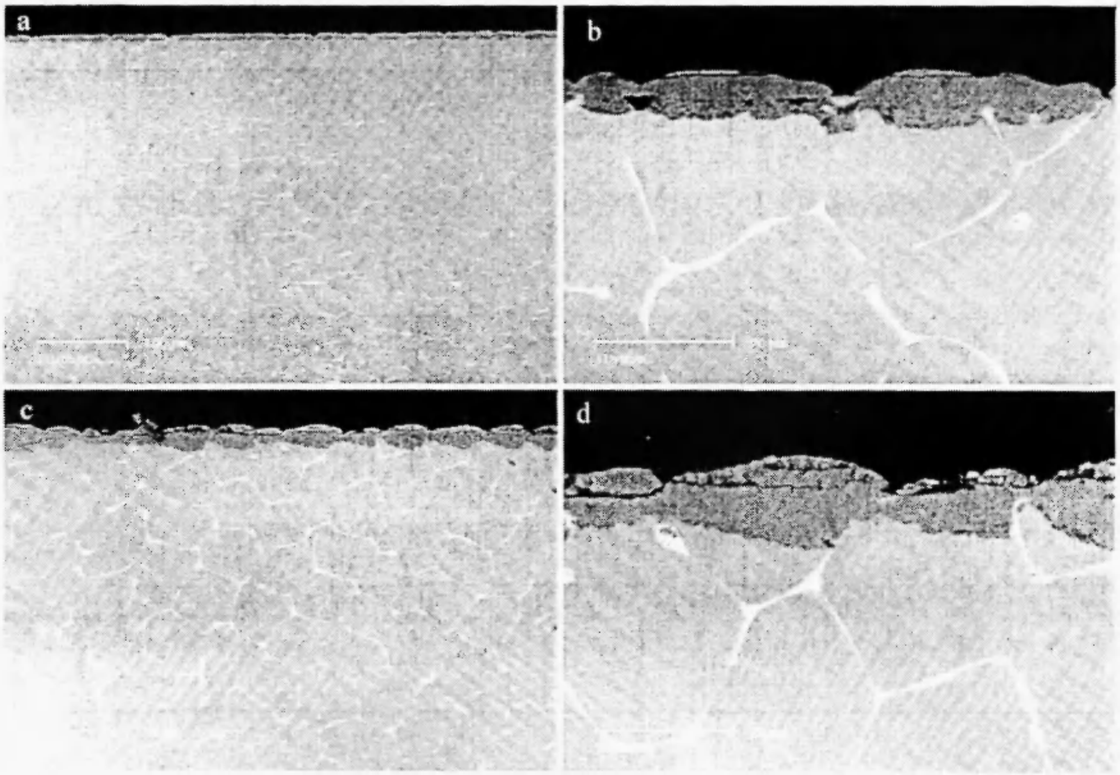

Fig. 5: Cross-sectional morphologies of Ni-1Dy oxidized at 923-1023K for 100h: (5a)923K; (5b) amplified image of (5a); (5c)1023K; (5d)amplified image of (5c).

developed over the nickel solid solution phase, while the thin part over the intermetallic phase Ni_{17} Dy_2. The scale formed on Ni-5Dy at 1023K is similar to that at 923K. However, it can be observed clearly from Fig. 3d that very slight preferential oxidation of Dy along the Dy-containing intermetallic phase occurred at 1023K. The intermetallic phase Ni_{17} Dy_2 has been converted into a mixture of metallic nickel particles (gray) with Dy_2O_3 (bright).

Both Ni-3Dy and Ni-1Dy oxidized at 923 and 1023K produced a similar scale to Ni-5Dy, as shown in Figure 4 and Figure 5, respectively.

3.3 Oxidation mechanism

The oxidation rates of the three Ni-Dy alloys are higher than that of pure nickel, except for Ni-1Dy at 1023K. The oxidation gain of the alloys mainly comes from the contribution of external scale mainly consisting of NiO. Very slight preferential oxidation of Dy along the intermetallic phase $Ni_{17}Dy_2$ occurred, obviously for Ni-5Dy at 1023K.

The effect of reactive elements on high temperature oxidation resistance of alloys has been studied extensively. It is widely known that the improvement of oxidation resistance and scale adhesion can be realized by small additions of oxygen active elements. Too large additions may give rise to the precipitation of RE-containing phase oxidized preferentially /2/. In the present study, however, the intermetallic phase $Ni_{17}Dy_2$ of the two-phase Ni-Dy alloys did not go through fast preferential attack involving the oxidation of dysprosium, just as the corrosion in molten $(Li,K)_2CO_3$/5/. In order to understand the preferential oxidation of the Y-containing phases, binary Ni-Y alloys containing 1, 3 and 5 mass%Y, respectively, were also oxidized at 923 and 1023K. Figure 6 shows the cross-sectional morphologies of Ni-3Y. Differing from Ni-Dy alloys, Ni-Y alloys underwent very fast preferential oxidation of yttrium along the intermetallic phase $Ni_{17}Y_2$ at both temperatures, forming an external layer of NiO and a sub-layer composed of a mixture of

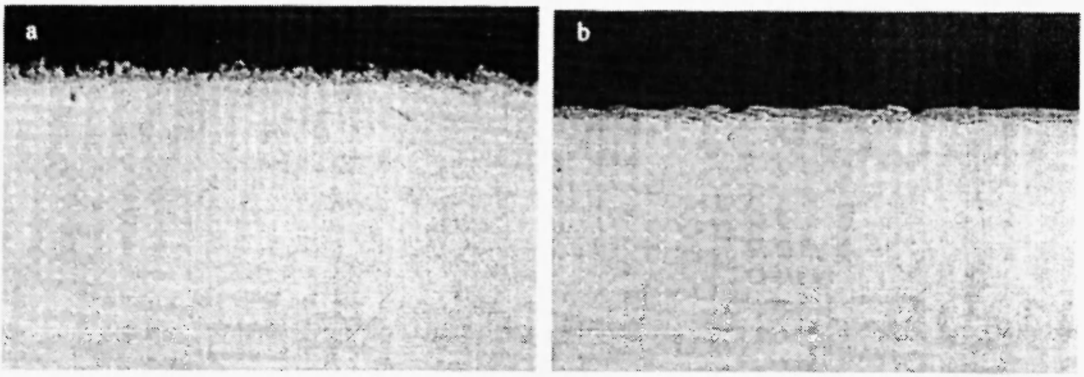

Fig. 6: Cross-sectional morphologies of Ni-3Y oxidized in air for 100h: (6a)923K; (6b)1023K.

metallic nickel with some Y_2O_3.

Fernandes and Ramanathan /6/ examined the influence of Dy_2O_3 coating on oxidation behavior of Fe-20Cr, and confirmed its positive roles in decreasing the oxidation rate of Fe-20Cr alloys. It is clear that dysprosium can show the same beneficial effects on the oxidation resistance of alloys as some other oxygen active elements except that the Dy-containing precipitates are not preferentially oxidized significantly under the present environments.

Except for Ni-1Dy at 1023K, the addition of dysprosium to nickel gives rise to a higher oxidation rate, especially with higher Dy content, which may be ascribed to the following aspects. On the one hand, NiO is a P-type oxide with a low level of defects, which may be increased by doping cations with higher valence such as present Dy^{3+}. Thus, the dissolution of Dy in NiO may increase its defect concentration, producing an elevated oxidation rate. Meanwhile, the oxidation of oxygen reactive element Dy may give rise to an enhanced oxidation, which can be confirmed by the higher oxidation of the alloys with higher content of Dy. On the other hand, Dy ions may act as barriers to block the diffusion of nickel along grain boundaries, as reported in some studies on other reactive elements /7,8/. The formation of Dy-rich oxides may block the diffusion of nickel, and thus reduce the formation of nickel oxide.

3.4 Corrosion and lithiation of the preoxidized Ni-Dy alloys in molten carbonates

In order to examine the effect of Dy on the lithiation process of NiO, pure nickel and Ni-Dy alloys preoxidized at 923K in air for 100h were totally immersed in molten $(0.62Li,0.38K)_2CO_3$ at 923K and then analyzed by XRD. Figure 7 shows the partial XRD patterns of NiO on pure nickel and Ni-Dy alloys. It can be seen clearly that the addition of a small amount of Dy caused the diffraction peaks of NiO at about $2\theta=37^0$ to shift positively. The incorporation of lithium ions into NiO can cause the displacement of the diffraction peaks of NiO at about $2\theta=37^0$ to a higher angle. As a result, Ni^{2+} ions are partly transferred into Ni^{3+}, therefore decreasing the lattice parameter and producing a more conductive oxide. Obviously, the lithiation process of NiO in molten $(Li,K)_2CO_3$ was favored by the Dy additives, among which the content of 3 mass% showed the best effect.

Besides the increase in electric conductivity, the incorporation of lithium ions with lower valence than Ni^{2+} may decrease the defect concentration of NiO and thus probably reduce the corrosion rate of nickel. Therefore, the presence of Dy can offer further improvement in the protection of the NiO scale by the promotion of the lithiation process, which was responsible for the lower corrosion rate of Ni-Dy alloys than pure nickel in molten $(Li,K)_2CO_3$/5/.

A previous study indicated that the Dy-containing precipitates of Ni-Dy alloys did not suffer from selective attack in molten $(Li,K)_2CO_3$ at 923K /5/. In order to understand the chemical stability of $Ni_{17}Y_2$ in molten $(Li,K)_2CO_3$, the corrosion of Ni-Y alloys in the melt at 923K was also conducted. Figure 8 shows the cross-sectional morphologies of Ni-1Y, Ni-3Y and Ni-5Y corroded in molten $(0.62Li,0.38K)_2CO_3$ for 100h. Just as oxidation in air, the intermetallic phase $Ni_{17}Y_2$ in

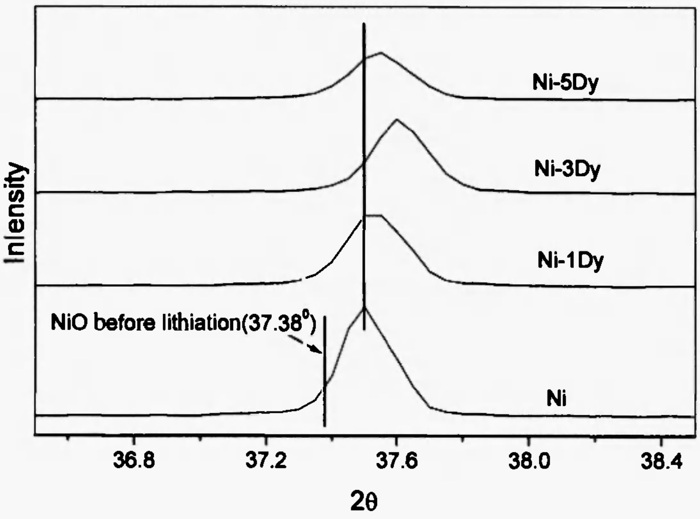

Fig. 7: Partial XRD patterns for NiO on the pre-oxidized nickel and Ni-Dy alloys after immersion in $(0.62Li, 0.38K)_2CO_3$ for 20h.

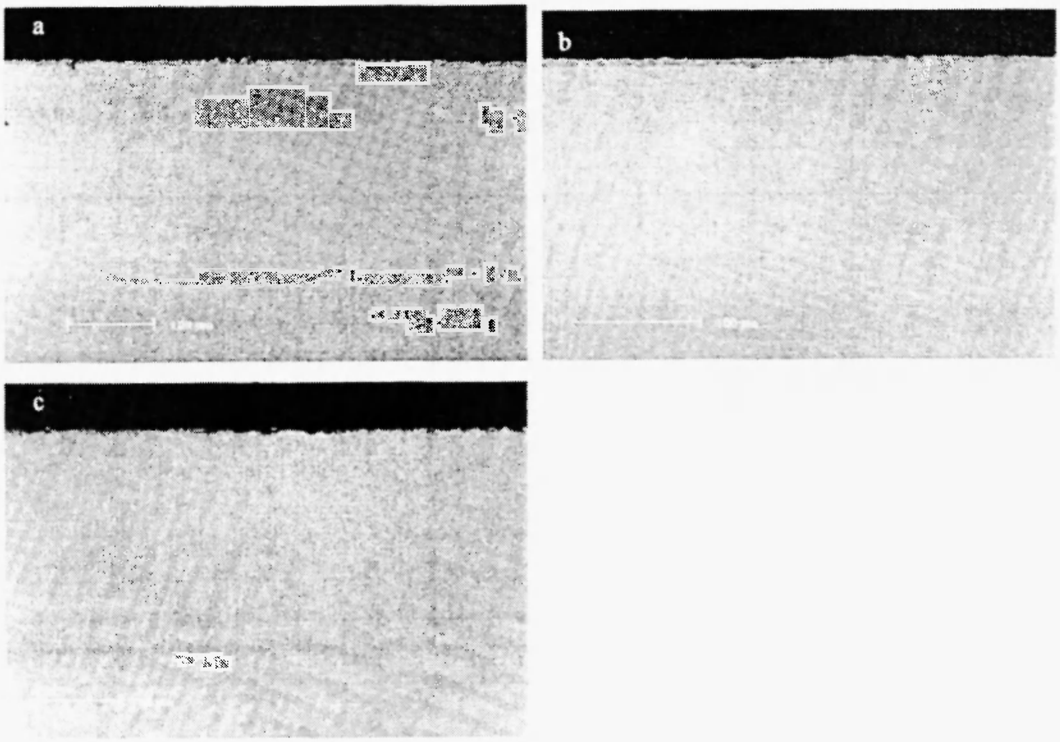

Fig. 8: Cross-sectional morphologies of Ni-1Y(8a), Ni-3Y(8b) and Ni-5Y(8c) corroded in $(0.62Li,0.38K)_2CO_3$ at 923K in air for 100h.

the alloys was preferentially oxidized deep into the substrate alloy. However, the growth of NiO was inhibited with increasing the content of yttrium. The analysis of the corrosion products by XRD also indicated that the addition of yttrium to the alloys could favor the lithiation of NiO in molten $(Li,K)_2CO_3$. The results imply that yttrium has the same positive effects on the corrosion of pure nickel in molten carbonates as dysprosium, except for the occurrence of fast selective oxidation along the phase $Ni_{17}Y_2$, just as observed in air oxidation.

4. CONCLUSIONS

Two-phase Ni-Dy alloys were oxidized faster than pure nickel at 923K and 1023K in air, except for Ni-1Dy at 1023K, forming a scale composed of NiO with a trace of Dy_2O_3. The oxidation behavior of Ni-Dy is related to the following aspects. On the one hand, the dissolution of Dy ions with higher valence than Ni^{2+} may increase defect concentration of NiO, and thus the growth rate of NiO. Meanwhile, the oxidation of reactive element Dy may make a contribution to the increased weight gain of the alloys to a certain extent. On the other hand, however, the presence of Dy ions along the grain boundaries may reduce the diffusion of Ni and thus the formation of NiO. 1-5% Dy additives can further favor the lithiation process of NiO in molten $(Li, K)_2CO_3$ and therefore the electrical conductivity. Ni-Dy alloys showed similar air oxidation and molten carbonates corrosion to Ni-Y alloys except that the Dy-containing precipitates of the alloys did not suffer from fast preferential corrosion during air oxidation and in molten $(Li,K)_2CO_3$ at 923K.

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