Influence of γ-Phase on the High- Temperature Oxidation of NiAl-Fe Alloys

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The oxidation of NiAl, NiAl-20at.%Fe and NiAl-30at.%Fe at 1000-1100 °C in air has been studied. Pure NiAl shows excellent oxidation resistance due to the formation of an Al_2O_3 layer. NiAl-20Fe also shows good oxidation resistance due to the formation of an Al_2O_3 scale on a β-phase substrate. Moreover, some nodules consisting of mixed oxides of Fe and Ni grow over the ductile γ-phase surface incorporated to the β-phase substrate. NiAl-30Fe alloy undergoes a much faster oxidation due to the formation of a non-protective Fe and Ni-rich scale, which is extremely susceptible to spallation. The addition of Fe to NiAl is detrimental to its oxidation resistance.

1. Introduction

NiAl is an intermetallic compound with β structure, which is considered as a candidate for high temperature structural material due to its high melting point, low density, good heat conductivity and excellent oxidation resistance[1,2]. Nevertheless, it has low room-temperature ductility and poor high temperature creep resistance. It has been shown that the addition of Fe to NiAl can improve its high-temperature creep resistance[3] and room temperature ductility[4]. This improvement in ductility is usually achieved by introducing some ductile γ phase in the alloy. Increasing the content of Fe in the alloy will increase the content of γ phase and as a result the alloy shows improved room-temperature ductility. Because the β-phase is rich in Al, but the γ phase is poor in Al, Fe-containing NiAl alloys show a special corrosion behavior, although the alloy has high Al content. Before considering Ni-Al-Fe alloys for practical aplications, it is necessary to understand their corrosion behavior in the possible service environments. The present study examines the high temperature oxidation in air of two Fe-containing NiAl alloys i.e. NiAl-20at.%Fe and NiAl-30at%Fe.

2. Experimental

The materials selected for the present study are pure NiAl, NiAl-20at.%Fe and NiAl-30at.%Fe alloys. The chemical composition of NiAl (atomic percent) is stoichiometric Ni-50Al. NiAl-20Fe (referred to as alloy 20 in the text) is Ni-27Al-20Fe-0.003Y-0.003Ce. NiAl-30Fe (referred to as alloy 30 in the text) is Ni-20Al-30Fe-0.003Y. Rods of the cast alloys contained in a carbon steel pipe were hot-pressed after being preheated to 700 °C and then kept at 1100 °C for 1 h. After hot pressing, the NiAl alloy was heat-treated at 900 °C for 1 h followed by furnace cooling; the alloy 20 was heat treated at 950 °C for 1 h and the alloy 30 at 1050 °C, also for 1 h, and both were air cooling. The oxidation treatment was carried out during 490 h in a high-temperature furnace at 1000 and 1100 °C under air atmosphere. The corroded specimens were analyzed by XRD and SEM coupled with EDAX.

3. Experimental Results

3.1. Alloy composition

Alloy 20 is mainly composed of the β phase (gray) with little γ phase (bright), as shown in Fig. 1a. The composition of the β phase is 31.64%Al, 20.71%Fe, Ni bal. (in atomic percent), and γ is 14.11%Al, 41.02%Fe, Ni bal. Alloy 30 is composed of the β phase (gray) and the γ phase (bright), as

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shown in Fig. 1b. The composition of the β phase is 32.56%Al, 21,55%Fe, Ni bal., and that of the γ phase is Al 14.16, Fe 43.46, Ni bal.

3.2. Scale composition

Scale spallation was not observed during the oxidation of NiAl. Little spallation of the scale grown on alloy 20 was observed. Conversely, alloy 30 underwent servere scale spallation during oxidation, but especially during cooling of the oxidized samples. XRD was used to examine both the spalled oxides and those left on the alloy surface. The surface analysis results showed the presence of a pure α-Al_2O_3 scale on the NiAl surface. Alloy 20 also formed α-Al_2O_3 with little Fe_2O_3, Fe_3O_4 and $NiFe_2O_4$. Instead of an Al_2O_3 scale, a mixed scale containing Fe_2O_3, Fe_3O_4, $NiFe_2O_4$ and $FeAl_2O_4$ oxides were formed on the alloy 30 surface. For alloy 30 the spalled oxides had similar composition to those left on the alloy surface.

Figure 2 shows the cross-sectional morphology of NiAl alloy oxidized at 1100 °C: a thin Al_2O_3 layer forms on the alloy surface. Some cracks exist across the scale and voids are present along the scale/alloy substrate interface.

Alloy 30, oxidized at both 1000 °C and 1100 °C, shows similar cross-sectional morphologies. Figure 3a. and b show the cross-sections of alloy 30 oxidized at 1100 °C for 490 h. The outer layer is mainly composed of Fe an Ni-rich oxides, containing Fe oxides (gray) and $NiFe_2O_4$ (bright) (Fig. 3a.). Al-containing oxides such as $FeAl_2O_4$ are present in the inner layer. Moreover, an Al_2O_3-rich scale (black) forms along the discontinuos scale/substrate alloy interface. In addition, oxidation develops into the alloy, forming mainly $FeAl_2O_4$ and Al_2O_3 (Fig. 3b).

The cross-sections of alloy 20 corroded at 1100 °C (Fig. 4) shows the formation of an Al_2O_3 scale on the alloy surface (Fig. 4a.), and of an Al-depleted layer in the alloy substrate. Meanwhile, nodules rich in Fe and Ni oxides also

formed on the alloy surface, which mainly developed over the γ phase incorporated to the β-phase substrate(Fig. 4b). Moreover, oxidation along the γ phase developed deep into the alloy substrate, forming Al-rich oxides. The Al-depleted layer developed under Al_2O_3 scale may join with the γ phase.

4. Discussion

Pure NiAl alloy has an excellent oxidation resistance due to the formation of a protective Al_2O_3 layer, just as observed in the present study. The oxidation of pure NiAl has been widely discussed in many studies[5-7].

The addition of Fe to NiAl obviously has a detrimental effect on its oxidation resistance. The addition of Fe changes single β-phase structure of NiAl into a two-phase structure (β + γ). A change in the Fe content of the alloy will directly affect the difference between the amount of the β and γ phases in the alloy. The change of the alloy
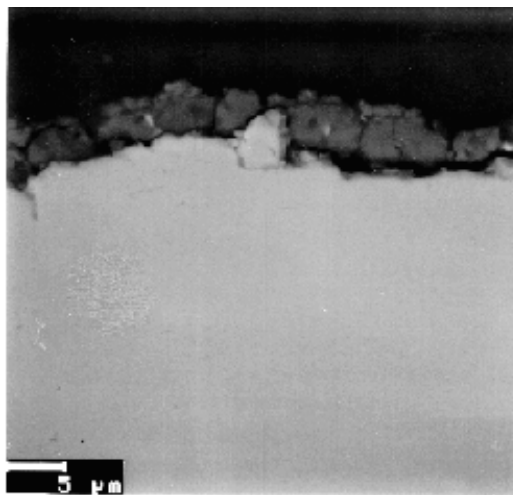

Figure 2. Cross-sectional morphology of NiAl after oxidation at 1100 °C for 490 h.
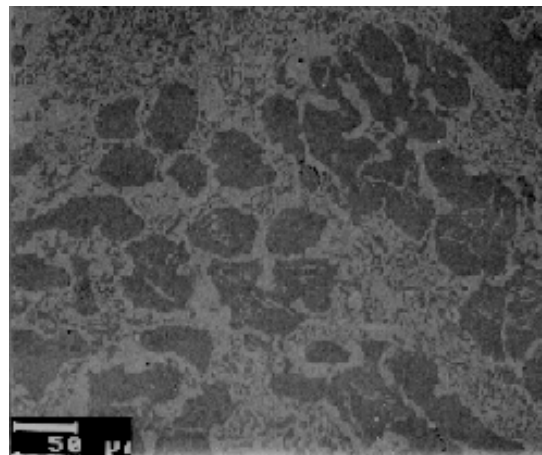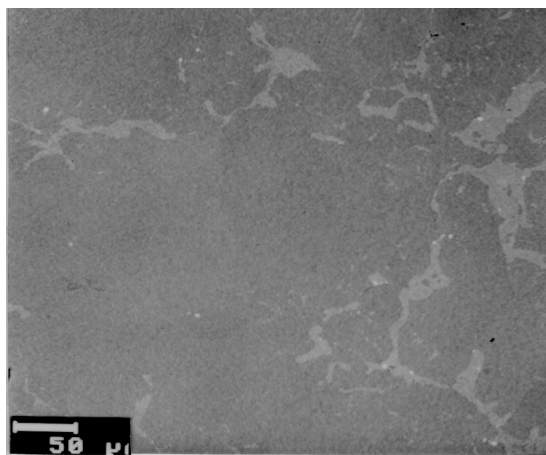

Figure 1. Microstructure (BEI) of NiAl-20Fe (a) and NiAl-30Fe (b) alloys. Dark phase: β; light phase: γ.
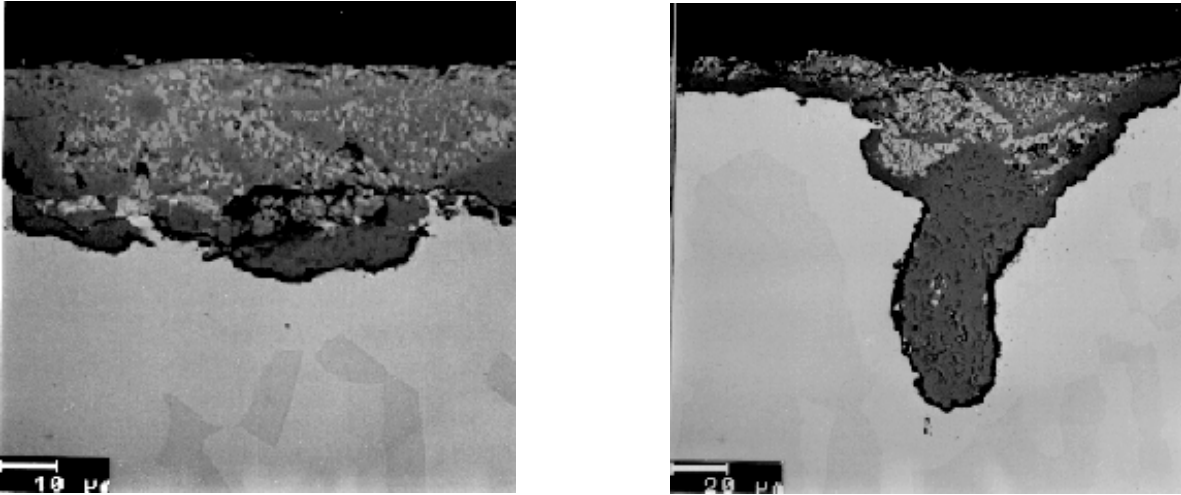
Figure 3. Cross-sectional morphologies of NiAl-30Fe alloy after oxidation at 1100 °C for 490 h.
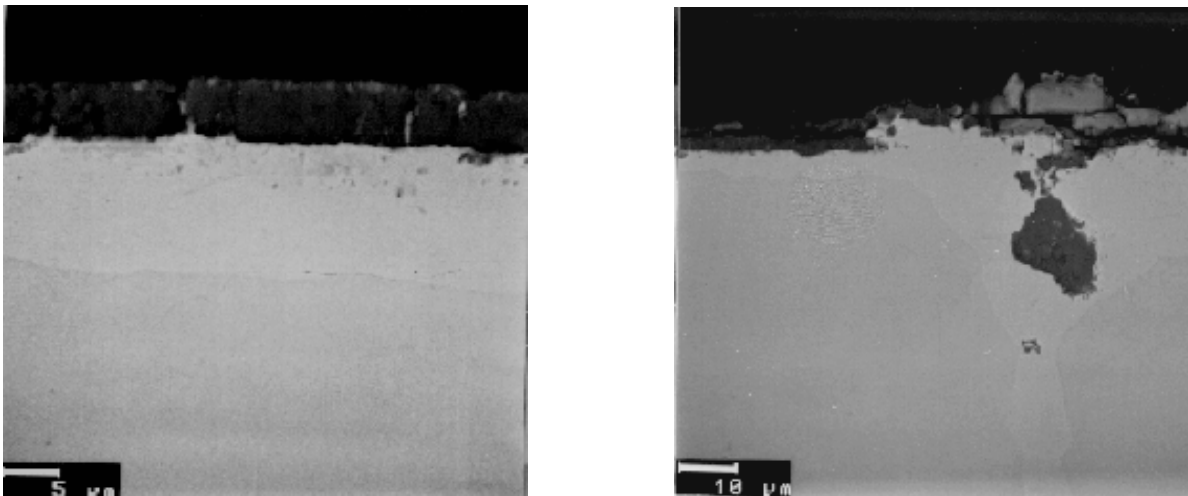

Figure 4. Cross-sectional morphologies of NiAl-20Fe alloy after oxidation at 1100 °C for 490 h (a) and 100 h (b)

microstructure also affects its oxidation mechanism, since the two phases will be exposed to the oxidizing atmosphere simultaneously. In fact, an Al_2O_3 scale can grow more easily on the β phase surface because the β phase has a higher Al content. Conversely, a scale rich in Fe and Ni oxides tends to form on the γ phase surface due to its lower Al content.

For alloy 20, the β phase is the main constituent alloy, so that an Al_2O_3 scale can form rapidly on its surface, producing an Al depletion in the base alloy. Because of the slow growth rate of Al_2O_3 and of the rapid growth rate of Fe and Ni oxides, a mixed scale rich in Fe and Ni may grow over the γ phase, forming oxides nodules at places where the γ phase is exposed to air. Furthermore, this kind of oxidation can develop deep into the alloy substrate, forming internal oxides. The spallation of the scale during the

experiment is mainly associated with these nodules. The formation of an Al-depleted layer under the Al_2O_3 scale is detrimental to the alloy oxidation resistance because the alloy substrate may not be able to provide enough Al for the formation of a new Al_2O_3 scale if the initial Al_2O_3 scale spalls off. Thus, it is very important to improve the adhesion of the Al_2O_3 scale. The fact that the Al_2O_3 scale grown on the β phase does not undergo spallation during the experiment may be related due to the presence of the rare earth elements in the alloy.

For alloy 30, the γ phase is the main constituent of the alloy. During oxidation, a mixed scale rich in Fe and Ni oxides can grow rapidly on this phase. Theoretically, an Al_2O_3 scale should form on the β phase surface. Accordingly, the surface scale should be composed of a mixture of Fe and Ni-rich oxides and Al_2O_3. However, only a

surface scale rich in Fe and Ni oxides is observed, which may be atributed to the rapid growth of the Fe and Ni oxides and to the slow growth of the Al_2O_3 scale. The formation of a mixed scale may cause the enrichment of Al of the alloy surface, and as a result an Al_2O_3 rich scale may form in the inner layer. Because the mixed scale is extremely susceptible to spallation, the whole oxide spalls off frequently during the experiment, especially under heating and cooling cycles. After spallattion, the alloy surface is again exposed to air starting a new oxidation process. This process is repeated promoting a very fast alloy oxidaton.

The ductility improvement of NiAl is usually acchieved by the presence of the ductil γ phase, which also transforms the single structure of NiAl into a two-phase structure. However, the above results show that these two-phase alloys, especially for high Fe contents, usually do not show a good oxidation resistance. For common superalloys such as the Ni and Fe-based alloys, the formation of a protective Al_2O_3 scale usualy does not require very high Al contents. Compared to those superalloys, alloys 20 and 30 have higher Al contents, but they hardly form a continuous Al_2O_3 layer especially for the 30 alloy. This may be due to the two-phase structure of the alloys, but also to the presence of intermetallic phases which may decrease the Al activity in the alloy, due to a strong chemical bond, as observed in other systems containing intermetallic compounds[8].

5. Conclusions

NiAl shows excellent oxidation resistance due to the formation of a protective Al_2O_3 oxide layer. The addition of Fe to NiAl affects the microstructure and the oxidation behavior of the alloys. The NiAl-20Fe alloy, which is almost a single phase alloy, shows good oxidation resistance. On the other hand, the oxidation of the NiAl-30Fe alloy is much faster than for NiAl. The two-phase structure of the Fe containing NiAl alloys is detrimental to their corrosion resistence. A proctetive coating is needed for their high temperature aplications.

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