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Some effects of interactions among minor element additions on the high-temperature oxidation behavior of Ni-base alumina-forming alloys

Key routes to improving the oxidation lifetimes of high-temperature alloys are to facilitate the rapid establishment of an α-Al_2O_3 scale, to maximize its adhesion to the alloy substrate, and to minimize its rate of growth. In this regard, it is widely recognized that adding reactive elements (e.g. Y, Zr, Hf, La) [1,2] and/or minimizing the indigenous sulfur content [3] provide beneficial effects. However, few practical guidelines are available on the critical types and amounts of dopants or interstitials that are necessary to optimize performance. The current work presents results for both commercial and model Ni-base alumina-forming alloys on the role of reactive element (RE)additions and interactions with interstitials such as sulfur and carbon.

While Y is considered the prototypical REaddition, it is now recognized that in certain cases the addition of Zr or Hf can produce similar or better benefits. One example is β-NiAl, where Zr and Hf have a higher solubility than Y and thus can be more uniformly present in the alloy and form fewer Ni-rich precipitates. These precipitates are prone to internal oxidation which can produce localized spallation.[4] In the case of Hf, not only has exceptional scale adhesion been observed but also low scale growth rates [5,6] when 0.05at% Hf is added to NiAl.

Model NiCrAl Alloys

Based on the results on Hf-doped NiAl, similar benefits were sought in NiCrAl-base alloys. However, in the case of cast Ni-7at%Cr-13at%(6.5wt%)Al and Ni-20wt%Cr-19at%(10wt%)Al the expected benefits of Hf-doping were not observed. Compared to Y additions, Hf was only marginally effective, Fig. 1. Two ways were found to improve the performance of Hf-doped NiCrAl. First, a dramatic improvement in cyclic oxidation behavior was observed when Ni-7Cr-13Al+Hf was de-sulfurized,[7] at least comparable to a Y addition. A second method was the addition of ≈100ppma Y with 0.05at%Hf. With a Ni-20Cr-19Al

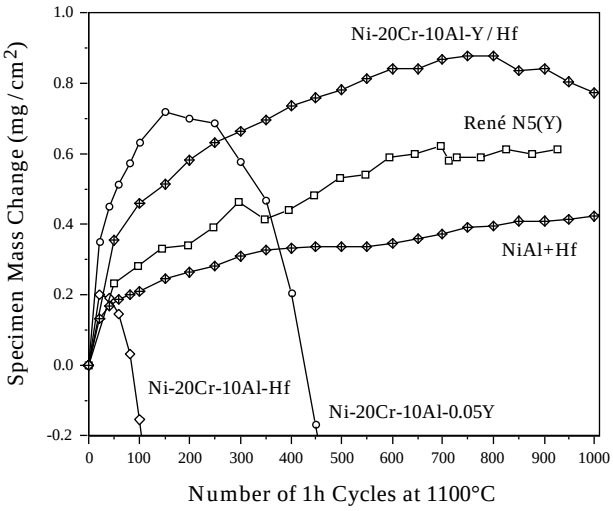

Figure 1. *Specimen mass changes for Ni-20wt%Cr-10wt%Al variants in 1h cycles at 1100°C.*

alloy, the combination of Y and Hf had a longer time to significant scale spallation (noted by mass losses) than either Y or Hf additions alone, Fig. 1. The first result suggests that Hf cannot effectively counter the detrimental effect of S on scale adhesion. The combined benefit of both elements may be due to a solubility argument such as in NiAl. Low levels of Y and Hf in NiCrAl do not form RE-rich precipitates whereas the level of Y alone needed to improved scale adhesion in NiCrAl (≈0.05at%[8]) results in the formation of Ni_xY phases in the alloy.

Commercial NiCrAl Alloys

An almost identical combination of Y and Hf is also found in commercial Ni-base superalloys such as René N5+. Similar to the observations in cast, model alloys, both the addition of Y and the removal of S improve oxide scale adhesion, Fig. 2. When the Y is not added, resistance to scale spallation is lost (alloy N5-A in Fig. 2), even though the alloy still contains approximately 500 ppma Hf. However, when no addition of Y is made, and the S level is significantly reduced (by in-melt processing) an improvement in resistance to scale spallation is observed, as shown for alloys N5-B, -C, and –AH. In fact, the very significant improvement shown by alloy N5-AH (desulfurized by a hydrogen treatment) appears to have resulted from the removal of S and C. The performance of this alloy was somewhat better than that of René N5+ since it exhibited improved scale spallation resistance and a decreased rate of oxidation.[9] The fact that Hf forms a very stable carbide perhaps prevents it from exerting the expected RE effects on oxidation behavior. If the level of Hf in excess of that required to tie up the C (and N and O) in the alloy is considered, it can be seen from Table I that the low-C alloy (N5-AH) is the only one with available Hf.

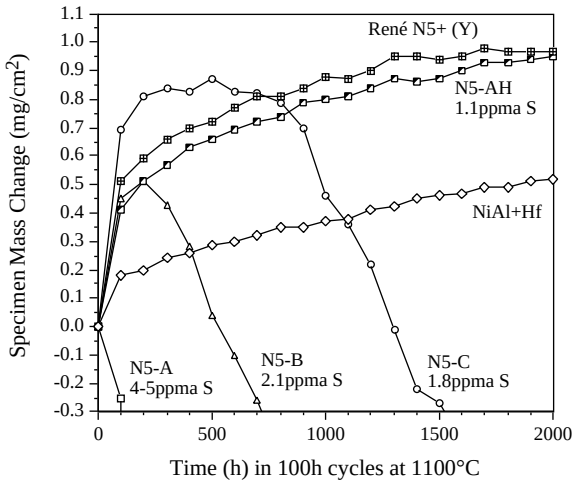

Figure 2. *Specimen weight changes for René 5 variants in 100 h cycles at 1100°C*

Table I. Relative levels of 'excess'Hf in the René N5 variants

Alloy	S, ppma	C, ppma	Hf, ppma	XS Hf [a]
René N5+[b]	7.5	2494	537	0.21[c]
N5A [b]	5.5	2467	398	0.16
N5B [d]	2.1	4449	159	0.04
N5C [d]	1.8	5282	137	0.03
N5AH [d]	1.1	24	169	3.36

[a] XS Hf = Hf/(C+0.5xO+N)
[b] analysis by plasma-coupled arc
[c] contains 34 ppma Y (30 ppma free Y)
[d] GDMS analysis

Another commercial alloy with excellent scale adhesion is Haynes 214 (Ni-17at%Cr-9Al-3Fe). This alloy contains ≈25ppma Y and 125ppma Zr indicating that a similar co-doping benefit can be achieved with very low levels of Y and Zr.

In the case of Hf-doped NiAl, nominal S and C are <4ppma and <0.04at% respectively. When alloys were cast with higher levels of Sand C, the performance deteriorated, Fig. 3. A sulfurcontent of 41ppma caused rapid attack and is probably not a realistic comparison. (Acomparison casting with 10ppma S would be more useful.) However, when the XS Hf was decreased from 1.53 to 0.91 by increasing the Ccontent (while maintaining <4ppma S), a significant increase in the amount of scale spallation was noted (difference between the total and specimen mass gains in Fig. 3.) These results suggest a critical importance of knowing the REadditions as well as the Sand C contents in order to optimize the oxidation performance of Ni-base alloys at high temperature.

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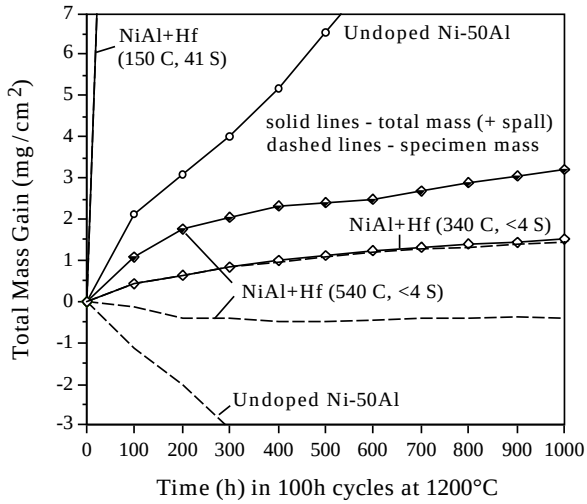

Figure 3. *Total and specimen mass changes for NiAl variants in 100h cycles at 1200°C.*