mined, this and previous data[1] suggest that relatively long exposures to hydrogen environments might be required to embrittle oxide coated stainless steels that were oxidized during the solution annealing treatment.

REFERENCES

1. J. G. Nelson and G. T. Murray: Metall. Trans. A, 1984, vol. 15A, pp. 597-600.
2. W. A. Swansiger, R. G. Musket, L. J. Weirick, and W. Bauer: J. Nuclear Materials, 1974, vol. 53, pp. 307-11.
3. W. A. Swansiger and R. Bastaz: J. of Nuclear Materials, 1979, vol. 85, pp. 335-39.
4. J. M. Stone: Environmental Degradation of Engineering Materials, M. R. Louthan, R. P. McNitt, and R. D. Sisson, Jr., eds., Virginia Polytechnic Institute Press, Blacksburg, VA, 1982, pp. 83-100.
5. G. R. Caskey: Materials Science and Engineering, 1974, vol. 14, pp. 109-14.
6. M. R. Piggott and A. C. Siarkowski: J. Iron and Steel Institute, 1972, vol. 210, pp. 901-05.
7. G. T. Murray: Metall. Trans. A, 1981, vol. 12A, pp. 2138-41.

Adherent Al₂O₃ Scales Formed on Undoped NiCrAl Alloys

JAMES L. SMIALEK

It has recently been proposed that sulfur segregation to the oxide-metal interface accounts for the massive spallation of thermally grown α-Al_2O_3 scales on undoped MCrAl coating alloys.[1,2,3] The evidence for such a mechanism comes from hot stage Auger studies which show that substantial sulfur surface segregation occurs on the undoped NiCrAl alloys which exhibit this spalling. This behavior is in contrast to Y, Hf, or Zr-doped alloys which form strongly adherent scales and show little or no such sulfur segregation. Sulfur is thought to act as a bond weakening agent for the oxide-metal interface in much the same way as it embrittles grain boundaries in superalloys.[1,2] The dopants are sulfur-active and prevent sulfur surface segregation by a bulk gettering mechanism.[1,2,4] The Auger studies have also found surface segregation of the oxygen-active dopants.[3-7] It has therefore been suggested that these elements may actually strengthen the oxide-metal bond.[8,9]

JAMES L. SMIALEK is with the Environmental Durability Branch, Materials Division, National Aeronautics and Space Administration, Lewis Research Center, Cleveland, OH 44135.
Manuscript submitted March 7, 1986.

While the long-standing enigma regarding scale adherence mechanisms is nearly resolved by these proposals, there is still uncertainty regarding the relative importance of bond weakening by sulfur segregation as compared to bond strengthening by Y segregation. For example, it remains to be shown whether adherent scales will form on undoped MCrAl alloys which have no sulfur present. The purpose of this note is to report a dramatic change in the spalling behavior of Al_2O_3 scales formed on an undoped NiCrAl alloy. This change was caused simply by repeated removal of surface layers (polishing) after each oxidation cycle. It is hypothesized that this phenomenon results from the successive depletion of sulfur impurities believed to cause scale decohesion.

Button castings of Ni-15Cr-13Al wt pct were produced by nonconsumable tungsten electrode arc melting from high purity (99.99 pct) starting materials. These alloys were characterized as three phase $\gamma/\gamma'/\beta$ alloys in previous studies.[7,10] The sulfur content was determined to be 10 ppmw by glow discharge mass spectroscopy. Two coupons approximately $1 \times 10 \times 10$ mm were placed in a covered alumina tray, oxidized in air at 1120 °C in a preheated rapid response box furnace, cooled, brushed gently, and weighed every hour. One sample was lightly wet sanded on 600 grit SiC paper each cycle to remove the oxide layer as well as any sulfur enrichment at the oxide-metal interface. The material removed by sanding was only 1.2 mg/cm² per cycle on average (total material removed was 40 μm per side). However, sanding up to 4 mg/cm² per cycle was required after 16 cycles to remove any aluminum depletion zones. The second sample was used as a control and was not sanded after the oxidation cycles.

The results of a 25-cycle experiment are shown in Figure 1. Here the cumulative weight change after N cycles for the sanded specimen is contrasted against weight change for the control. (Cumulative weight change is given by $^N\Sigma_{i=0}(\Delta w_i/A)$, where i is the cycle number and Δw_i is the weight gain of the i-th cycle.) During the first cycle both samples form an easily removed, white flakey oxide. The
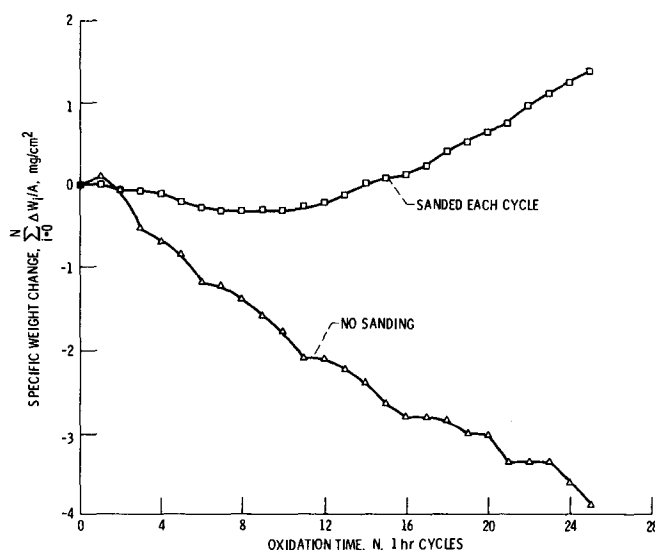

Fig. 1 — Cumulative weight changes for 1120 °C cyclic oxidation of undoped NiCrAl samples. (a) Lightly sanded after each 1-h cycle. (b) No sanding.

spalled oxide from the sanded specimen changed from large white flakes to small segments over the next few cycles. However, spalling always took place after the samples had cooled appreciably and always revealed the reflective surface of the underlying metal. The control sample, however, began to show dark green oxides, probably containing NiO and $Ni(Al, Cr)_2O_4$, after only the second cycle. This trend continued throughout the test and the control sample exhibited considerable weight loss as measured previously.[8]

The sanded specimen also continued to lose weight for the first 8 cycles, but at a lower rate due to the thinner Al_2O_3 scales formed on the freshly sanded surface. Small segments of adherent grey oxide were first visually apparent after 8 cycles. At 13 cycles the sanded specimen retained nearly 100 pct of its surface scale on cooldown, and this dramatic turnaround in spalling behavior continued throughout the test.

Macrographs of the two samples after 25 cycles are shown in Figure 2. The uniform adherent scale on the sanded specimen i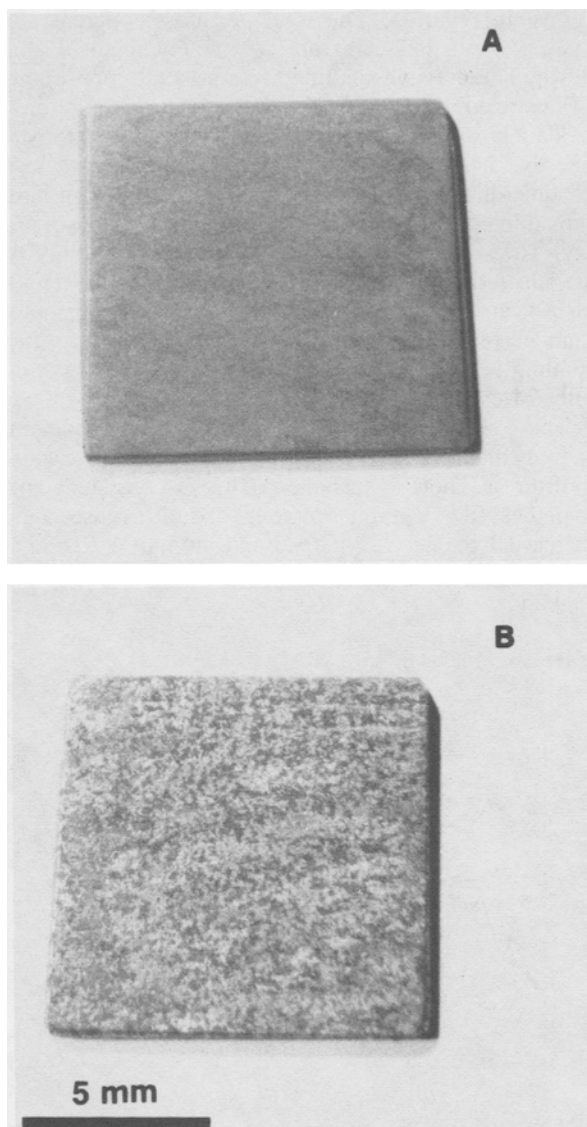s clearly in contrast to the speckled, spalled scale on the control sample. X-ray diffractometer scans have identified only α-Al_2O_3 on the sanded specimen and α-Al_2O_3 and $Ni(Al, Cr)_2O_4$ ($a_0 = 8.15$ Å) on the control sample.

The adherent scale formed on the sanded specimen is shown in greater detail in Figure 3. Here only limited areas of spallation were observed, most of which were caused by water immersion as will be discussed later. The overall scale otherwise showed none of the features typical of undoped NiCrAl's — buckling, delamination, or interfacial voids in the metal. In contrast, the control sample shows numerous spall fragments as well as diverse scale morphologies (Figure 4). The colonies of large angular crystallites are consistent with the identification of spinel in the scale by XRD.

The evolution of these oxide structures will be the subject of a subsequent study, which includes the effects of repeated surface removal on Y and Zr-doped NiCrAl's as well.[11] It is noted here that no obvious morphological changes took place between the initial and final cycles for the undoped sample exhibiting this change in adherence. The only change was a reduction in the bulk sulfur content from the initially low value of about 10 ppmw to 3 ppmw after 25
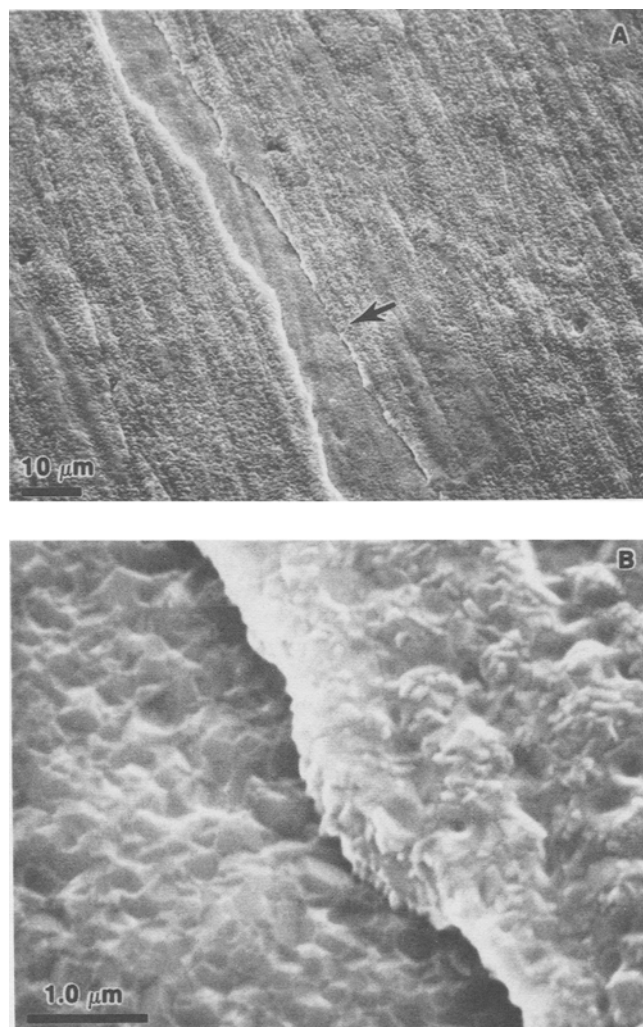

Fig. 2 — Contrasting scale appearance for undoped NiCrAl samples, oxidized at 1120 °C for 25 cycles. (a) Sanded each 1-h cycle. (b) No sanding.

Fig. 3 — SEM micrographs of the uniform scale morphology on the sanded NiCrAl specimen, 25 cycles at 1120 °C. (a) Polishing scratches and local spalled region (arrow). (b) Oxide imprints in metal at spalled region.
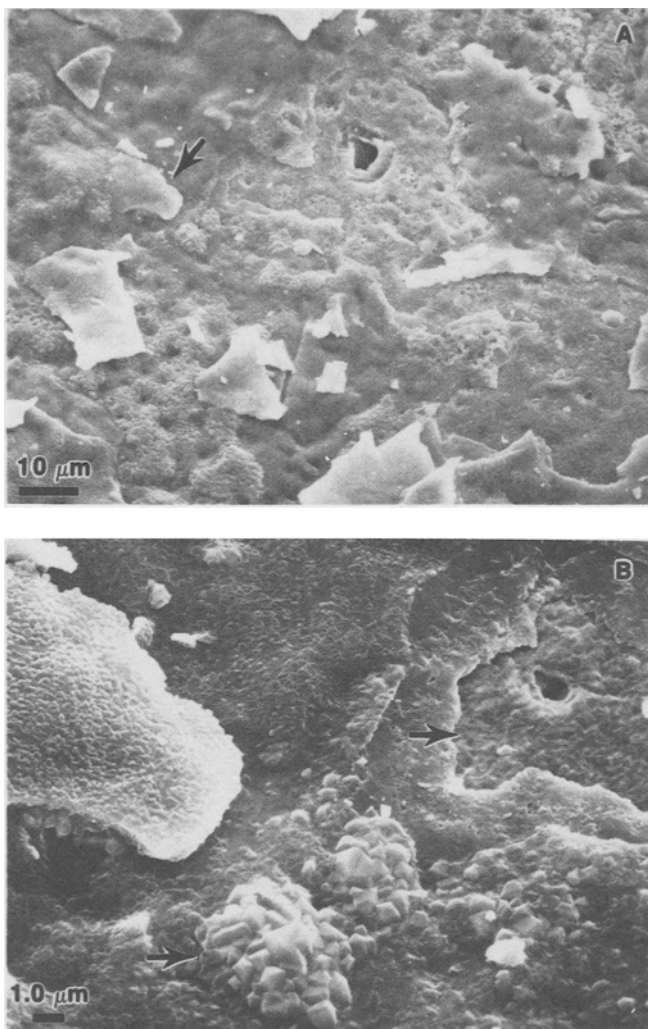
Fig. 4 — SEM micrographs of the complex scale morphology on the unsanded specimen, 25 cycles at 1120 °C. (a) Numerous spall fragments (arrow). (b) Oxide imprints in metal (upper arrow), multiple scale layers, and a colony of large oxide grains (lower arrow).

purging cycles. (Accuracy of the sulfur analyses is approx. ±25 pct of reported values.) More detailed sulfur analyses of purged NiCrAl alloys will be presented in the subsequent study.[11]

The change from nonadherent to adherent Al_2O_3 formation simply by repeated oxidation and surface removal (i.e., sulfur purging) is a new observation regarding oxide adhesion. It cannot be easily explained on the basis of the conventional oxide-adherence mechanisms (growth stress, vacancy sink, scale plasticity, or pegging). None of these models would predict any difference in oxidation behavior after the first cycle as compared to the 25th cycle. No permanent or cumulative effects from repeated polishing are believed to be important because of rapid dislocation mobility in NiCrAl at 1100 °C.[7]

It is therefore proposed that the recent chemical bond mechanism of adhesion provides a compelling and consistent explanation of these results. Namely, spallation is influenced by interfacial segregation of sulfur as shown previously,[1-4,8] and repeated oxidation and surface removal merely serves to gradually deplete the alloy of its sulfur

impurity content. It can be shown that less than 40 cycles would be required to completely remove the sulfur in this specimen, given that a segregation level of about half a monolayer occurs each cycle.[4,8] The observed adherence after only 13 cycles indicates that total sulfur removal may not be necessary for the first onset of scale retention.

This new phenomenon also suggests that Y, Hf, Zr, Th, etc. dopants or finely dispersed oxides are not necessary for adherence, while they are indeed sufficient — a fact seemingly inconsistent with the previously proposed models. It may also be inferred that any increased chemical bonding in doped alloys due to segregation of the dopants themselves[8,9] is of second order importance compared to the decreased bonding in undoped alloys caused by sulfur segregation. The quantitative degree to which bonding is increased by sulfur removal as compared to any possible further increase caused by dopant segregation is not clear from this study. This is an important question to address in future work.

Also relevant to scale adhesion is the fact that when the scales first become partially adherent (~cycle #8), they are completely destroyed by moisture. Water immersion after each oxidation cycle can cause an appreciable weight loss as shown in Figure 5. The effect is most apparent after 13 cycles, when the scales are completely retained on cooldown. The massive spalling to bare metal upon immersion is illustrated in Figure 6. Here a duplicate sample run for 15 oxidation/sanding cycles after immersion is compared to one that has not been immersed. The oxide is most susceptible directly after cooldown, when even high humidity (breathing on the sample) is sufficient to initiate some spalling. The scales become more resistant to humidity if they are allowed to set a few hours before immersion. The scales also become more resistant to immersion with increasing number of sulfur purging cycles; this moisture-induced spalling begins to diminish after 20 cycles and is minimal after 24 cycles (Figure 5).

These observations suggest that even though adherence is initially maintained on cooldown, the added stress caused by moisture cannot be sustained. This is consistent with the hypothesis that a gradual removal of sulfur causes a gradual increase in the Al_2O_3-NiCrAl bond strength. After 25 cycles the bond is sufficiently strong to resist this moisture-induced spallation.
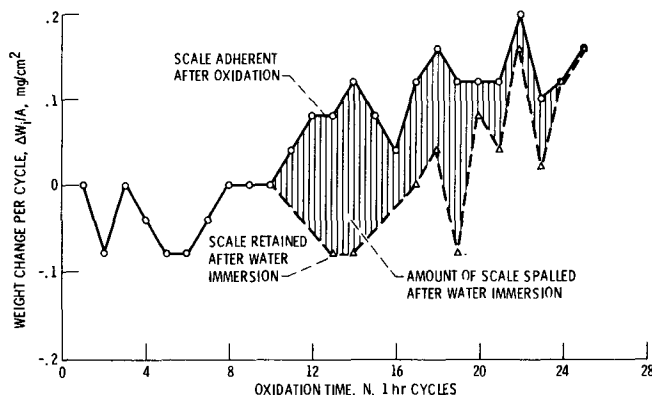

Fig. 5 — Weight change per individual cycle before and after spalling induced by water immersion; sanded NiCrAl specimen, 1120 °C oxidation, 1-h cycles.
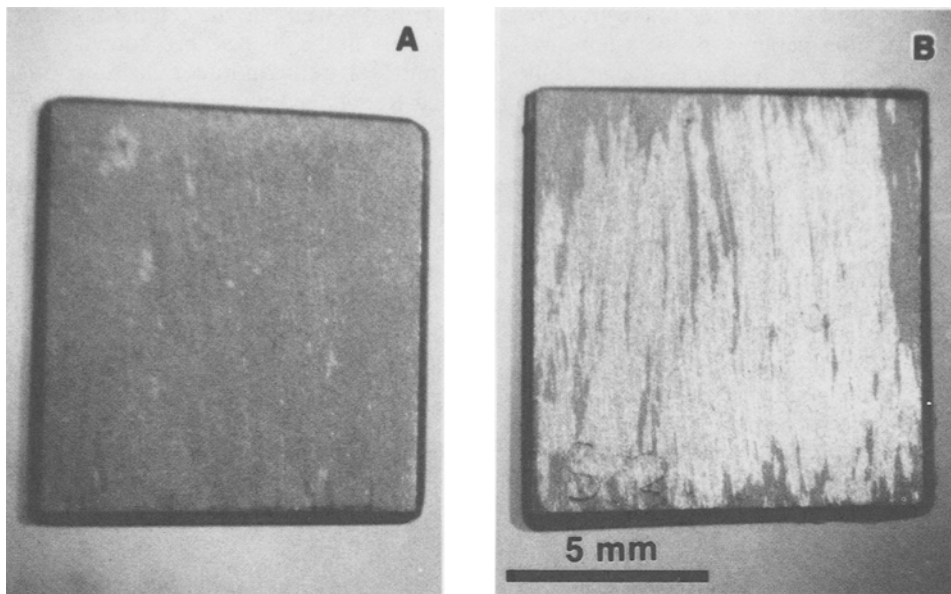
Fig. 6—Adherent and spalled alumina scales produced on sanded NiCrAl specimens oxidized at 1120 °C for 15 cycles; (a) after cooldown. (b) Duplicate sample, after cooldown and water immersion.

The cause of moisture sensitivity of Al_2O_3 scales is not known, but has been observed for undoped NiAl.[12] Here a weight loss of 0.44 mg/cm^2 per hundred hours was produced by cyclic oxidation at 1100 °C and exposure to moisture after each cooldown as compared to 0.12 mg/cm^2 for samples not exposed to moisture. The effect was discussed in relation to a moisture-assisted crack growth phenomenon (stress corrosion) reported for bulk Al_2O_3.

In conclusion, the present study shows that adherent scales can form on undoped NiCrAl alloys by repeated heating and sanding, presumably due to the successive removal of interfacial segregants such as sulfur. While adherent scales form after 13 purging cycles, spalling can still be caused by water immersion. With further purging this susceptibility is also diminished. Any additional strengthening of the oxide-metal bond for doped NiCrAl alloys due to segregation of the oxygen-active dopants themselves is not required for scale retention during cycling and consequently appears to be a secondary effect. The results therefore strongly support the model proposed by Smeggil and co-workers that (1) trace levels of sulfur in undoped MCrAl alloys are sufficient to cause Al_2O_3 scale spallation, (2) removal of sulfur from the alloy is sufficient to allow scale adhesion, and (3) one major effect of oxygen-active dopants on adhesion is to prevent sulfur segregation at the interface.

REFERENCES

1. A. W. Funkenbusch, J. G. Smeggil, and N. S. Bornstein: *Metall. Trans. A*, 1985, vol. 16A, p. 1164.
2. J. G. Smeggil, A. W. Funkenbusch, and N. S. Bornstein: *Metall. Trans. A*, 1986, vol. 17A, p. 923.
3. K. L. Luthra and C. L. Briant: *Electrochem. Soc. Extended Abstracts*, 1984 Spring Mtg., Cincinnati, OH, p. 26.
4. R. Browning, C. Park, F. A. Marks, J. L. Smialek, and C. Papageorgopoulas: NASA Ames, Nasa Lewis, unpublished research, 1985.
5. L. A Larson, M. Prutton, H. Poppa, and J. L. Smialek: *J. Vac. Sci. Technol.*, 1982, vol. 20, p. 1403.
6. M. M. El Gomati, C. G. H. Walker, D. C. Peacock, M. Prutton, H. E. Bishop, R. M. Hawes, and J. L. Smialek: *Surf. Sci.*, 1985, vol. 152/153, p. 917.
7. M. M. El Gomati, C. Walker, D. C. Peacock, and M. Prutton: *Corr. Sci.*, 1985, vol. 25, p. 351.
8. J. L. Smialek and R. Browning: in *Symp. Proc. on High Temperature Materials Chemistry III*, Z. A. Munir and D. Cubicciotti, eds., Electrochemical Soc., Pennington, NJ, 1986, p. 258; also NASA TM 87168, 1985.
9. A. B. Anderson, S. P. Mehendru, and J. L. Smialek: *J. Electrochem. Soc.*, 1985, vol. 132, p. 1695.
10. J. L. Smialek and R. Gibala: *Metall. Trans. A*, 1983, vol. 14A, p. 2143.
11. J. L. Smialek: in Proc. N. L. Peterson Mem. Symp. on "Oxidation of Metals and Associated Mass Transport," AIME, in press.
12. J. L. Smialek: *Metall. Trans. A*, 1978, vol. 9A, p. 309.

Cellular-Dendritic Transition in Directionally Solidified Binary Alloys

S. N. TEWARI and V. LAXMANAN

It is important to study the microstructural development during solidification because the physical and mechanical properties of castings are determined mainly by their microstructure. Directional solidification of binary alloys with a positive temperature gradient (G) at the liquid-solid inter-

S. N. TEWARI is Visiting Associate Professor, Department of Chemical Engineering, Cleveland State University, Cleveland, OH 44115. V. LAXMANAN is with the Department of Metallurgy and Materials Science, Case Western Reserve University, Cleveland, OH 44106, and Visiting Scientist, NASA-Lewis Research Center, Cleveland, OH 44135. Manuscript submitted March 28, 1986.