Lateral growth kinetics of α-alumina accompanying the formation of a protective scale on (111) NiAl during oxidation at 1100 °C

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During the early stages of oxidation of (111) NiAl at 1100 °C, an alumina scale forms and undergoes a series of allotropic phase transformations. In the final stages of phase development, the metastable Θ-alumina transforms to the equilibrium α-alumina phase. Images formed using the photoluminescence from trace Cr^{3+} impurities in the scale, in conjunction with scanning electron microscopy, indicate that the α-alumina forms by a nucleation and growth process within the Θ-alumina matrix. Lateral impingement of the growing α-alumina islands coincides with the reported drop in oxidation kinetics to those characteristic of long-term oxidation of NiAl. Unlike most interface-controlled transformations, the kinetics of the θ–to–α transformation in the lateral growth are found to be logarithmic. Possible causes of these unusual kinetics are proposed. © *1997 American Institute of Physics.* [S0003-6951(97)01819-6]

The ability of certain metals to grow a protective oxide scale imparts high-temperature oxidation resistance by hindering the progress of subsequent oxidation. Alloys that form an alumina (Al_2O_3) scale offer superior oxidation resistance since this oxide has among the lowest oxygen self-diffusion rates. In the alumina-forming alloys, the long-term oxidation resistance comes from the formation of a continuous α-alumina (corundum) scale over the metal surface.[1–4] However, during the early stages of oxidation, including heating to the oxidation temperature, the kinetics of oxide scale growth are complicated by the formation of a series of intermediate, metastable polymorphs of Al_2O_3. These polymorphs progressively transform from amorphous alumina at low temperatures to the thermodynamically stable α-alumina structure.[1–4] Prior to complete coverage of the surface by α alumina, the oxidation kinetics, although parabolic as measured by thermigravmetric analysis, are reported to be almost two orders of magnitude faster than those of the mature, continuous α-alumina scale.[1,4] This is attributed to the substantially lower diffusivity of oxygen and aluminum through α alumina than through any of the intermediate phases. Although detailed quantitative studies have not been carried out, the kinetics of the phase transformation to α alumina are known to depend on oxidation temperature, composition of the alloys being oxidized, the partial pressure of oxygen, and the applied pressure. In view of the complexity of the parameters involved, the ability to observe the evolving transformation process is essential to quantifying the overall oxidation kinetics and, in particular, the rate at which the surface of the alloy approaches full coverage by the protective α-alumina phase.

NiAl is an oxidation-resistant, alumina-forming alloy whose oxidation behavior has been extensively studied.[3–5] In part, this alloy is attractive for fundamental investigations because the only oxide formed is Al_2O_3 and hence the complications associated with competitive growth of different oxides, such as occurs during the oxidation of Ni_3Al and the MCrAl alloys, is avoided. In this work, we combine photoluminescence imaging with scanning electron microscopy to follow the phase transformation from the monoclinic Θ structure to α alumina, thereby providing the first quantitative data on the polymorphic transformation kinetics accompanying oxide scale growth.

All oxidation experiments were performed in air at 1100 °C using a separate, polished (111) NiAl crystal for each oxidation treatment. Representative secondary electron images of samples oxidized for 0.25, 0.5, 1, and 2 h are shown in Fig. 1. Although the precise mechanisms of electron scattering that give rise to the contrast are not known, they clearly reveal dark circular features whose size increases with oxidation time. (The features are distinguishable by optical microscopy, but their contrast is too low for quantitative studies.) The size distribution of the features is narrow, indicating early site saturation of the nuclei. Additionally, the spatial distribution of these circular features exhibits patterns characteristic of heterogeneous nucleation, as evidenced by a propensity to nucleate along polishing scratches on the metal surface, seen in Fig. 1 for the sample oxidized for 0.5 h.

To identify the individual crystallographic phases in the oxide scales, we have used chromium luminescence spectroscopy. The R-line photoluminescence in corundum is identical to the well-known phenomenon of ruby fluorescence. It arises in response to electronic transitions in trace Cr^{3+} impurities incorporated into the alumina scale during oxidation.[6,7] In the present experiments, these transitions were excited by a 514.5 nm argon-ion laser beam. The presence of the α-alumina phase is characterized by a strong R-line doublet at nominal frequencies of 14 432 and 14 402 cm^{-1}, together with a multitude of weaker lines, such as the N lines, related to Cr^{3+}–Cr^{3+} interactions. The Θ-alumina phase exhibits its own characteristic photoluminescence, with a similar but weaker doublet at frequencies of approximately 14 530 and 14 610 cm^{-1}.[8] A luminescence spectrum recorded from a large area of the scale formed after 30 min is shown in Fig. 2. The presence of both doublets in

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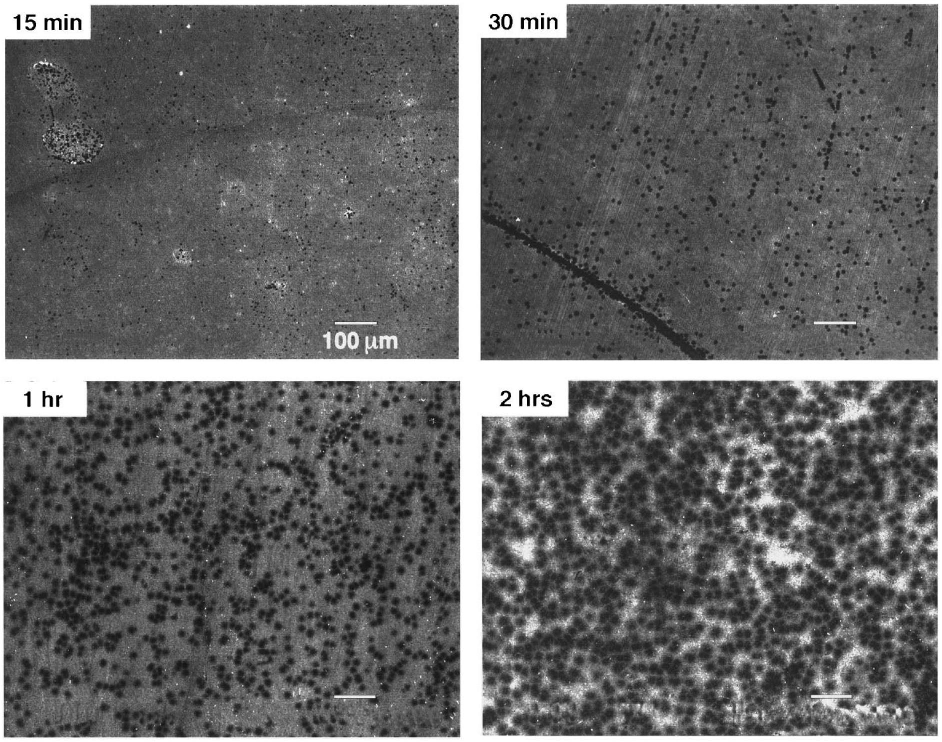

FIG. 1. Scanning electron micrographs of the oxide scale formed on (111) NiAl at 1100 °C after the oxidation times indicated. The image contrast is attributed to contrast between the α-alumina islands (dark) distributed in the metastable Θ-alumina matrix (light) within which it nucleates. Accelerating voltage: 9 kV.

the spectrum indicates that α alumina and Θ alumina coexist in the scale at this stage.

Although the luminescence efficiency of Θ alumina appears to be considerably lower than that of α alumina, it nevertheless suffices for phase identification. By focusing the laser through an optical microscope, photoluminescence from regions in the scale as small as 1 micron across can be probed, allowing the α and Θ phases to be spatially resolved and distinguished. To correlate the features observed under the scanning electron microscope (Fig. 1) to their respective crystallographic phases, spatial maps of the luminescence spectra were collected by stepping the sample under the optical microprobe (using an X-Y stage), acquiring a spectrum at each step. The spatial distribution of the luminescence intensity from the α and Θ phases was subsequently reconstructed from the individual spectra, forming phase maps of the scale.

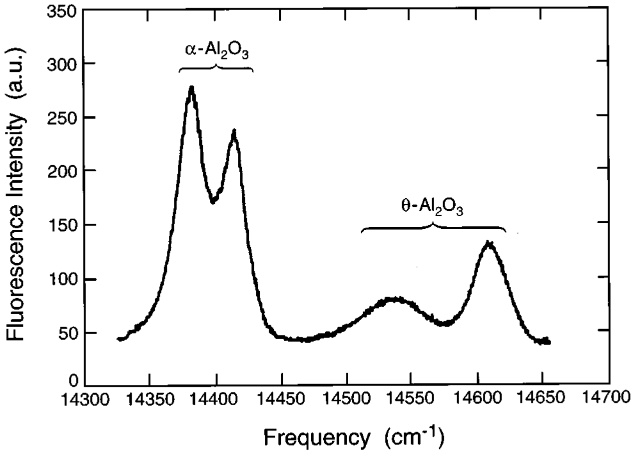

FIG. 2. Photoluminescence spectrum recorded from a typical scale, showing the R-line doublet from α-alumina grains, together with the doublet from the Θ-alumina matrix phase.

Data on the radius of the features measured from the scanning electron micrographs of Fig. 1 shows substantial agreement with the luminescence images (e.g. Fig. 3), demonstrating that the circular islands correspond to α-alumina crystallites growing in a Θ-alumina matrix. The mean radius of the α-alumina regions is plotted in Fig. 4 as a function of oxidation time. Because the α- islands span the entire scale thickness, the lateral growth rate is taken to correspond directly to the kinetics of the Θ–to–α transformation. The data also indicates that the average radius, R, of the α-alumina islands exhibits a logarithmic dependence on oxidation time. These kinetics correspond to an interface velocity that diminishes with the inverse of the oxidation time. A linear regression fit gives a kinetic relation of the form:

$$R = A + B \log t,$$

where A and B are constants ($A = 7.0$ and $B = 8.0$ μm) and time, t, is in hours. This dependence is in marked contrast to the linear growth kinetics expected for an interface-controlled transformation, such as observed for the amorphous-to-crystalline transformation in metal silicide thin films,[9] and reported for unconstrained γ–to–α alumina phase transformation.[10] Logarithmic growth kinetics have rarely been observed, a notable exception being the recrystallization of heavily deformed metals after long annealing times when, presumably, the driving force for recrystallization has been significantly reduced.[11,12]

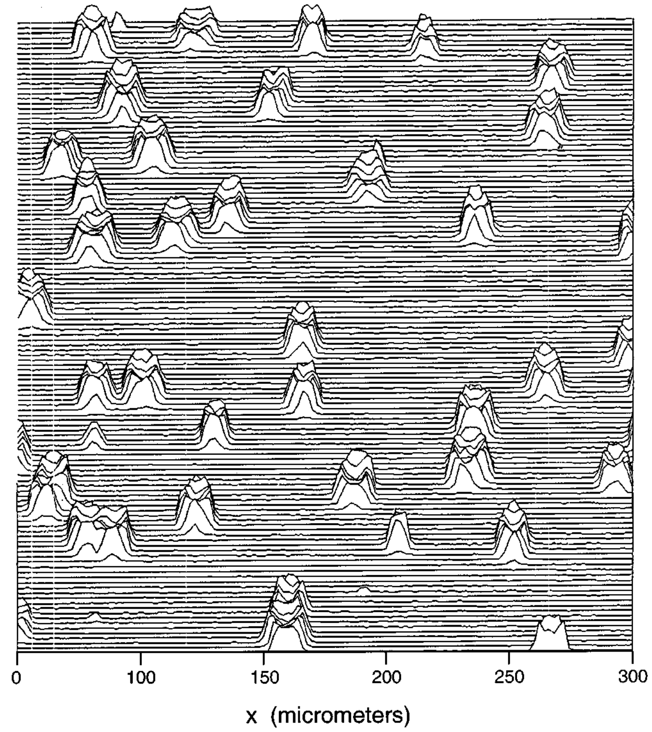

FIG. 3. Map of the α-alumina R-line intensity recorded from the scale formed after 1.0 h at 1100 °C. The contours correspond to differences in intensity.

We partially attribute the observed lateral growth kinetics to interface pinning by accumulating voids formed at the transformation front as a result of the approximately 9.5% molar volume shrinkage associated with the transformation.[13] This effect would not have been observed in prior studies on the transformation of submicron alumina powders. An alternative possibility is that the constraint from the Θ-alumina matrix and underlying NiAl causes a stress in the growing α-alumina grains, altering the transformation kinetics.

The observations reported here provide both a visual and quantitative picture of the early stages of formation of the protective α-alumina scale. They indicate that the α-alumina nucleates within the metastable Θ-alumina scale and grows laterally by the radial migration of the transformation front until impingement. In this respect, our microstructural observations are consistent with the detailed microscopy studies[3,5] that identified α-alumina grains growing in the transient-phase scale. The observation of preferential nucleation of α alumina on superficial scratches in the NiAl supplements these TEM studies by indicating heterogeneous nucleation. The lateral growth of the α-alumina grains occurs concurrently with the oxide scale thickening. It is significant that the time at which α-alumina coverage is essentially complete at 1100 °C closely coincides with the transition to the substantially slower parabolic oxidation kinetics for NiAl, as reported on the basis of thermogravimetric measurements.[1,4] The logarithmic kinetics of the lateral growth are therefore of considerable practical significance, in that the formation of a continuous α-alumina diffusion barrier takes longer than would be expected based on the usual linear kinetics for interface migration.

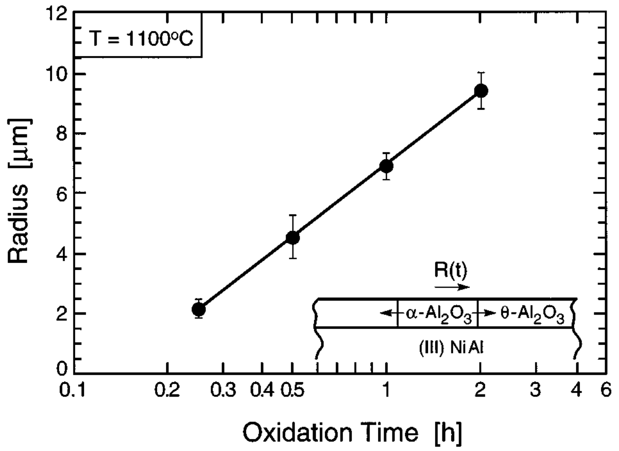

FIG. 4. The measured mean radius of α-alumina islands plotted as a function of oxidation time. As the least squares fit demonstrates, the Θ–to–α transformation follows logarithmic kinetics.

In summary, we have shown that photoluminescence from trace chromium impurities in oxidized alloys can be used to image the Θ–to–α transformation in a thermally growing oxide scale on a NiAl alloy. These observations provide quantitative information concerning the rate of lateral growth (and therefore the transformation kinetics) of the protective α-alumina phase. The observed logarithmic kinetics of the lateral growth of α alumina are quite distinct from the parabolic oxidation kinetics of the alloy as a whole, such as measured by weight gain or the thickening of the oxide scale with time.

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[1] B. Pieraggi, Oxid. Met. **27**, 177 (1987).

[2] G. C. Rybicki and J. L. Smialek, Oxid. Met. **31**, 275 (1989).

[3] J. Doychak, J. L. Smialek, and T. E. Mitchell, Metall. Trans. A **20**, 499 (1989).

[4] M. W. Brumm and H. J. Grabke, Corros. Sci. **33**, 1677 (1992).

[5] J. Doychak and M. Rühle, Oxid. Met. **31**, 431 (1989).

[6] D. M. Lipkin and D. R. Clarke, Oxid. Met. **45**, 267 (1996).

[7] D. M. Lipkin, D. R. Clarke, M. Hollatz, M. Bobeth, and W. Pompe, Corros. Sci. (in press).

[8] This fluorescence was first noted by J. Bohandy, J. Solid State Chem. **3**, 467 (1971), who mistakenly assigned its origin to γ alumina.

[9] A. Cros, K. N. Tu, D. A. Smith, and B. Z. Weiss, Appl. Phys. Lett. **52**, 1311 (1988).

[10] C. J.-P. Steiner, D. P. H. Hasselman, and R. M. Spriggs, J. Am. Ceram. Soc. **54**, 412 (1971).

[11] A. T. English and W. A. Backofen, Trans. Metall. Soc. AIME **230**, 396 (1964).

[12] G. R. Speich and R. M. Fisher, in *Recrystallization, Grain Growth, and Textures* (American Society for Metals, Metals Park, 1966).

[13] Joint Committee for Powder Diffraction Standards (JCPDS) card Nos. 42-1468 (α), 35-121 (Θ) (1992).