

## THE USE OF A $^{18}\text{O}$ TRACER AND RUTHERFORD BACKSCATTERING SPECTROMETRY TO STUDY THE OXIDATION MECHANISM OF NiAl.

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The oxidation mechanism of NiAl was investigated in the temperature range between 1170 K and 1420 K. Oxidation was performed by alternating exposure of the samples to natural oxygen and oxygen gas enriched with  $^{18}\text{O}$ . The  $^{18}\text{O}$  tracer was profiled by using the reaction with 800 keV protons,  $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ . Rutherford Backscattering Spectrometry of 2 MeV  $^4\text{He}^+$  was used to check the position of noble metal markers.

The  $^{18}\text{O}$  tracer experiments clearly show that up to 1420 K, Al diffusion through the scale is the major material transport mechanism during oxidation, resulting in outside scale growth. Noble metal "marker" experiments however give misleading results by incorrectly suggesting an inside scale growth mechanism.

### 1. INTRODUCTION

Alloys forming protective alumina scales during high temperature oxidation are frequently applied in order to achieve a useful service life in oxidizing environments. The kinetics of alumina scale growth at high temperatures have been described frequently.<sup>1,2</sup> Also the scale morphology has been subject of extensive studies.<sup>3,4</sup> It is reported that alumina scales have a poor adherence to the alloys and that voids formation occurs between the alloy and the oxide scale. Spalling of the alumina scale severely limits the useful service life of the alloy, especially in thermal cycling conditions.<sup>5</sup>

The identification of the diffusing species and the determination of their relative mobilities in the oxide scale are necessary in order to elucidate the oxidation mechanism. However due to the lack of reliable data concerning the transport properties of alumina scales, the oxidation mechanism of Al containing alloys is still not fully understood.

In the present study we investigated the oxidation mechanism of NiAl at temperatures between 1170 and 1420 K. 2MeV  $^4\text{He}^+$  Rutherford Backscattering Spectrometry (RBS) was used to investigate the oxidation kinetics and the oxide scale composition. RBS was also used to determine the position of noble metal markers that were deposited onto preoxidized NiAl. The material transport through the oxide scale (alumina) was studied using a  $^{18}\text{O}$  tracer. This tracer was profiled by making use of the  $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$  nuclear reaction. The "single spectrum" method was followed, with an 800 keV proton beam.

A short introduction to the use of  $^{18}\text{O}$  profiling will be given in this paper prior to the discussion of our experimental results. Besides the relation between  $^{18}\text{O}$  profiles in the oxide scale and various possible oxidation mechanisms will be given.

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## 2. $^{18}\text{O}$ PROFILING

### 2.1. Concept of the method

The concept of and the experimental set up for  $^{18}\text{O}$  profiling much resemble the better known RBS, which has been described in detail frequently.<sup>6,7</sup>

When performing  $^{18}\text{O}$  profiling measurements, the specimen is bombarded with a monochromatic beam of protons. The  $\alpha$ -particles from the nuclear reaction between the protons and  $^{18}\text{O}$  in the specimen,  $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ , are detected. This reaction between  $^{18}\text{O}$  nuclei and protons is exoergic, ( $Q=3.98$  keV). Using classical mechanics it can be calculated that escaping  $\alpha$ -particles will have an energy of 3.40 MeV, if leaving the surface of the specimen at an angle of 170 degrees with the incoming proton beam.<sup>8</sup> This was the detection angle we used in this study. Next to this reaction of the protons, also backscattering of protons will occur. Because of the high energy difference between backscattered protons (<800 keV) and the  $\alpha$ -particles from the  $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$  reaction ( $\sim 3.4$  MeV), the  $\alpha$ -spectrum with relatively low intensity is not disturbed by the high intensity proton spectrum.

The profiling of the  $^{18}\text{O}$  tracer in oxides is obtained because  $\alpha$ -particles loose energy when passing through the oxide. Therefore,  $\alpha$ -particles from the reaction  $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$  below the outer surface will reach the detector with a lower energy compared with  $\alpha$ -particles from a surface reaction with protons. Since the energy loss of  $\alpha$ -particles in oxides is known, the depth profile of  $^{18}\text{O}$  in the scale can be calculated from the energy of the detected  $\alpha$ -particles. This energy varies almost linearly with depth. The  $^{18}\text{O}$  distribution down to a depth of several microns can be analysed this way without the need of sputtering or sawing of the sample.

Our spectra were obtained using a surface barrier detector at an angle of 170 degrees

with the primary proton beam. The 800 keV primary beam of protons was 1 mm in diameter and had an intensity of 2 nC/sec. We made no attempts to separate the backscattered protons from the  $\alpha$ -particles (e.g. by use of a mylar foil or a mass spectrometer). Counting was prolonged no more than a quarter of an hour. Within this counting period a sufficient resolution was obtained. In all calculations presented, Ziegler's stopping power data were used, the validity of the Bragg rule was assumed and the mean energy approximation was used.<sup>6</sup> The thickness of alumina scales was calculated assuming the density is equal to that of bulk  $\text{Al}_2\text{O}_3$ .

### 2.2. Possible $^{18}\text{O}$ Profiles

We used the  $^{18}\text{O}$  profiling technique to study the distribution of the  $^{18}\text{O}$  tracer in the aluminum oxide scale on NiAl samples that had been oxidized in an oxygen gas containing 50 %  $^{18}\text{O}_2$  followed by oxidation in natural oxygen (hereafter referred to as  $^{18}\text{O}$  and  $^{16}\text{O}$ ). Alternatively first oxidation in  $^{16}\text{O}$  later in  $^{18}\text{O}$  took place. Depending on the scale growth mechanism different  $^{18}\text{O}$  profiles are to be expected. Four cases will be discussed. Transport occurs by primarily:

- 1- Oxygen lattice diffusion. (Diffusion of oxygen through the bulk of the grains).
- 2- Oxygen short circuit diffusion (e.g. grainboundary diffusion)
- 3- Aluminum lattice diffusion.
- 4- Aluminum short circuit diffusion.

If the transport through the scale can be described by short circuit diffusion, alternating oxidation in  $^{18}\text{O}$  and  $^{16}\text{O}$  will result in two separate oxide regions. One region will next to  $^{16}\text{O}$  contain 50%  $^{18}\text{O}$  oxide, the other will be  $^{18}\text{O}$  oxide free. (Hereafter reported as  $\text{Al}_2^{18}\text{O}_3$  and  $\text{Al}_2^{16}\text{O}_3$ .) Figure 1 shows the expected distribution of  $^{18}\text{O}$  in the oxide scale and the expected  $\alpha$ -spectrum for such a scale, in case that short circuit

diffusion of Al is responsible for the scale growth. The scale shown is developed when oxidation takes place first in  $^{16}\text{O}$ , followed by  $^{18}\text{O}$ . Also the  $\alpha$ -spectrum using 800 keV protons has been given.

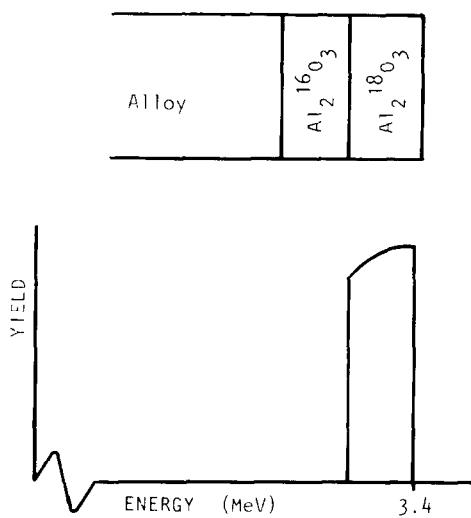


FIGURE 1

Scale developed for Al short circuit diffusion and  $\alpha$ -spectrum (800 keV protons) (First  $^{16}\text{O}_3$ , later  $^{18}\text{O}_3$ )

In this case, the new  $^{18}\text{O}$  oxide is found at the surface, because the high energy edge in the  $\alpha$ -spectrum is situated at 3.4 MeV. The peak has a limited width because of the finite thickness of the covering  $\text{Al}_2^{18}\text{O}_3$  layer. The yield of  $\alpha$ -particles slightly decreases at lower energies. This is caused by the decreasing reaction cross-section, with decreasing proton energy (Protons also loose some energy during penetration into the alumina scale). In an experimentally obtained  $\alpha$ -spectrum the edges will be less sharp because of the limited energy resolution of the detection system, energy straggling of the  $\alpha$ -particles and protons and due to the non-uniform thickness of the scale in the beam spot area ( $1 \text{ mm}^2$ ). Of course, when first oxidation in  $^{18}\text{O}$  and later in  $^{16}\text{O}$  takes place,  $\text{Al}_2^{18}\text{O}_3$  will be found at

the alloy/scale interface covered with  $\text{Al}_2^{16}\text{O}_3$ . No  $\alpha$ -particles with 3.4 MeV will be detected, and the peak in the spectrum will be found at lower energies.

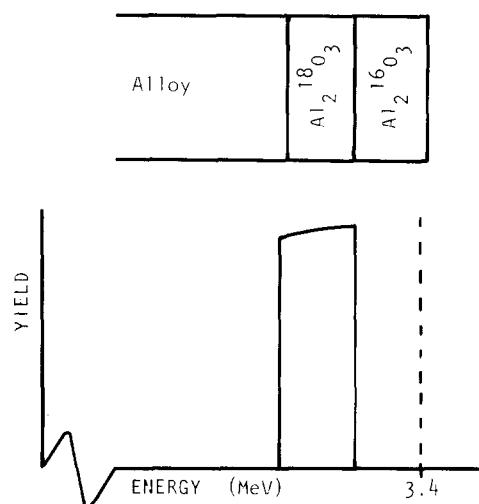


FIGURE 2  
Scale developed for O short circuit diffusion and  $\alpha$ -spectrum (800 keV protons) (First  $^{16}\text{O}_3$ , later  $^{18}\text{O}_3$ )

In Figure 2 the expected profiles are given (of  $^{16}\text{O}$  oxidation followed by  $^{18}\text{O}$ ), assuming that oxygen short circuit diffusion is responsible for scale growth. The scale grows at the alloy/oxide interface. The new ( $^{18}\text{O}$ )oxide will develop underneath the already existing ( $^{16}\text{O}$ ) scale. A small amount of  $^{18}\text{O}$  will be found at the grainboundaries of the  $\text{Al}_2^{16}\text{O}_3$  layer. Although it is not very likely that, at these relatively low temperatures (1170 - 1420 K), lattice diffusion of Al or O plays an important role in mass transport, we did not exclude the possibility a priori. If oxygen lattice diffusion through the grains is responsible for the scale growth, oxidation in  $^{16}\text{O}$  followed by  $^{18}\text{O}$  results in an  $^{18}\text{O}$  diffusion profile in the scale. This is schematically shown in Figure 3. Although the growth of new oxide takes place at the alloy/oxide interface,  $^{18}\text{O}$  is still found at the surface of the scale.

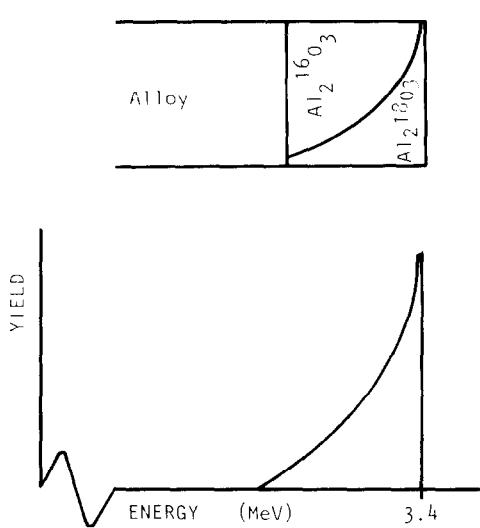


FIGURE 3

Scale developed for O lattice diffusion and  $\alpha$ -spectrum (800 keV protons)(First  $^{16}O$ , later  $^{18}O$ )

Finally, if the transport process is determined by Al lattice diffusion, scale growth is observed at the scale/gas interface again. The profile of the scale and the expected spectrum are alike those obtained if Al diffuses along short circuit diffusion paths.

### 3. EXPERIMENTAL

Buttons of NiAl were produced by melting pressed tablets of mixed Ni and Al powder (50/50 at.%) in Argon gas using induction heating. The buttons were cut to pieces of about 5\*5\*1mm<sup>3</sup> with cooled slow speed diamond saw. One side of every piece was carefully polished through 1μ diamond paste. Oxidation of the specimen in natural oxygen was carried out in a tube furnace in dried flowing oxygen. Oxidation in  $^{18}O$  was performed in a sealed quartz ampoule. The samples were slowly reheated and furnace cooled after each oxidation treatment. At 1170 K, oxidation up to 100 hours was examined. Oxidation at 1420 K was only performed for some hours. Also thin noble metal markers were used on some of the samples.

In these cases thin Pd or Pt films were deposited onto preoxidized materials. These samples were then given an oxidation treatment. The position of the marker in the scale was measured with  $^4He^+$  RBS. We reported on the application of this method before.<sup>9</sup> Next to the application of these "surface markers", some oxidation experiments were performed with noble metal markers covered with a synthetic alumina scale (Al deposition in a moderate vacuum).

### 4. RESULTS

#### 4.1. Oxidation at 1170 K

In Figure 4 a typical experimentally obtained  $\alpha$  spectrum is shown for a sample that has been oxidized first in  $^{18}O$  for 4 hours afterwards in  $^{16}O$  for 16 hours at 1170 K.

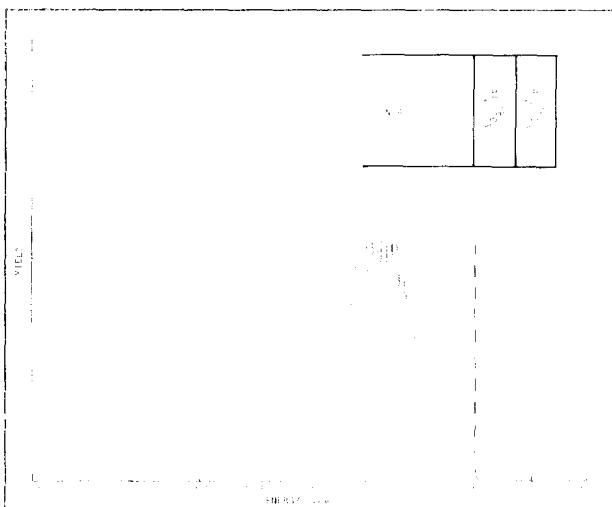


FIGURE 4  
 $\alpha$ -spectrum (800 keV protons) of NiAl oxidized T=1170 K, first 4h  $^{18}O$  later 16h  $^{16}O$

It can be concluded from this spectrum that no  $^{18}O$  is present at the oxide/gas interface (no  $\alpha$  particles with an energy of 3.4 MeV are detected). The  $Al_2^{18}O_3$  layer has been covered with the newly formed  $Al_2^{16}O_3$  oxide. The average thickness of the covering  $Al_2^{16}O_3$  layer

(340 nm) was calculated from the energy shift of the leading edge of the peak in the spectrum. From the width of the peak the average thickness of the  $\text{Al}_2\text{O}_3$  layer (350 nm) was calculated. The total scale thickness calculated this way corresponds quite well with the overall scale thickness calculated from a  $^4\text{He}^+$  RBS spectrum of the same sample (not given). (Here the scale thickness was calculated from the energy shift of the Ni-leading edge<sup>7</sup>).

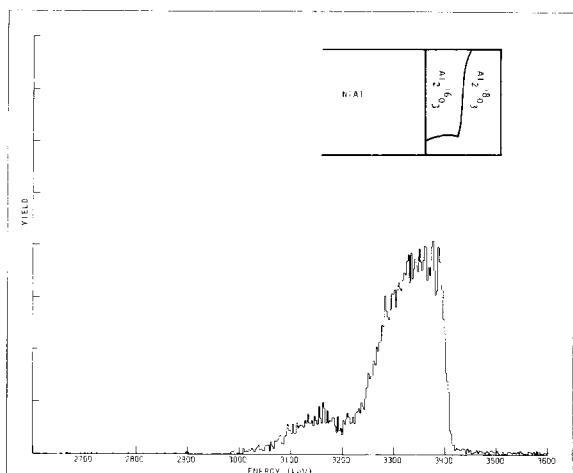


FIGURE 5  
 $\alpha$ -spectrum (800 keV protons) of NiAl oxidized  
 $T=1170$  K, first 4h  $^{16}\text{O}$  later 16h  $^{18}\text{O}$

The above described observations suggest an outside growth mechanism. The spectrum shown in Figure 5 confirms this suggestion. In this figure the spectrum of a sample first oxidized in  $^{16}\text{O}$  (4h) followed by oxidation in  $^{18}\text{O}$  (16h) is shown. The new  $\text{Al}_2\text{O}_3$  oxide is found in a layer of 380 nm thickness at the outer surface. If bulk diffusion of  $^{18}\text{O}$  were predominant we would expect profile like Figure 3. However a small amount of  $^{18}\text{O}$  is observed at lower energies corresponding with  $\text{Al}_2\text{O}_3$  formation at a larger depth. The maximum penetration

depth was calculated to be 840 nm. This corresponds with the total scale thickness calculated from an RBS spectrum. It can be concluded therefore that some of the  $^{18}\text{O}$  has penetrated up to the alloy/oxide interface. Although the main transport mechanism is the outward diffusion of aluminum, also some inward diffusion of oxygen along short circuit diffusion paths seems to occur. Moreover during long term oxidation (up to 100 h), the outside growth mechanism persists, as is clearly shown in Figure 6. The thin  $\text{Al}_2\text{O}_3$  layer, formed during initial oxidation in  $^{18}\text{O}$  for 4 h, is found at large depth (low energies), 1600–1700 nm, after an extra 88 hours of oxidation in  $^{16}\text{O}$ .

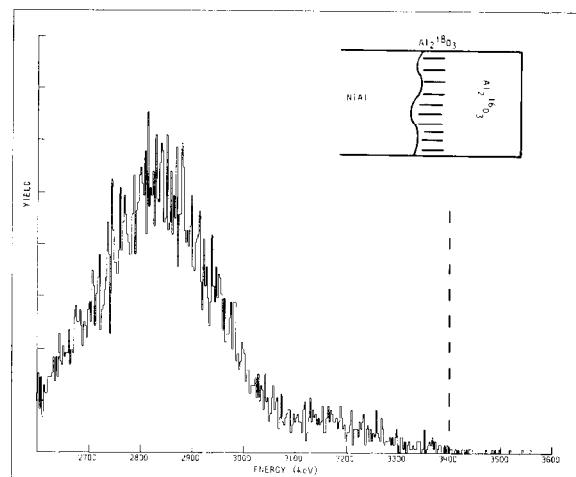


FIGURE 6  
 $\alpha$ -spectrum (800 keV protons) of NiAl oxidized  
 $T=1170$  K, first 4h  $^{18}\text{O}$  later 88h  $^{16}\text{O}$

Surprisingly it was observed that inert markers remained at the outer surface of the specimen after oxidation. This can be seen in the RBS spectrum shown in Figure 7. After an extra 4 hours oxidation the Pt "marker" material is still found at the specimens outer surface (Pt edge in the spectrum is at its

surface energy). SEM observations of this surface show the presence of small islands of Pt on the surface after the extra oxidation treatment. It can be calculated that most of the broadening of the Pt peak can be attributed to the island formation. Therefore we can conclude that hardly any diffusion of Pt into the scale occurred.

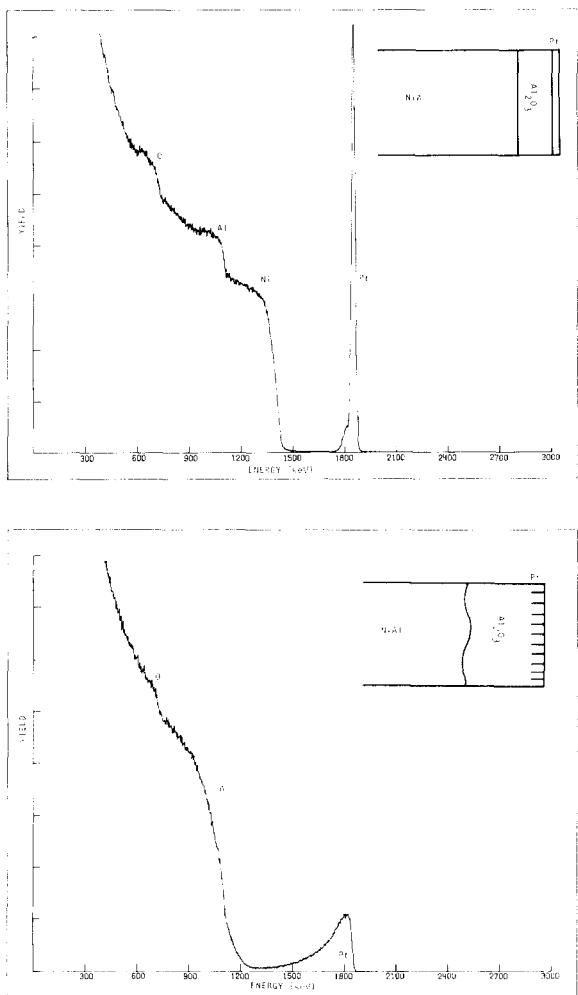
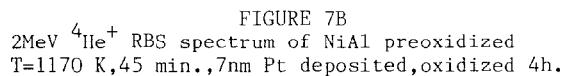


FIGURE 7A  
2MeV  $^4\text{He}^+$  RBS spectrum of NiAl preoxidized T=1170 K, 45 min., 7 nm Pt deposited



Such an observation, markers remaining at the specimen surface during oxidation, is commonly interpreted as evidence for inside scale growth. However, in experiments in which the marker material was covered by synthetic alumina prior to the extra oxidation treatment, new oxide was observed to form on top of this marker, thus indicating outside growth.

#### 4.2. Oxidation at 1420 K

Apart from the fact that the rate of scale growth is larger at 1420 K, also the oxidation mechanism differs. In Figure 8 the spectrum of a sample oxidized first in  $^{16}\text{O}$  (1 h) and later in  $^{18}\text{O}$  (2 h) is shown. It can be seen that, although still  $\text{Al}_2^{18}\text{O}_3$  has grown at the

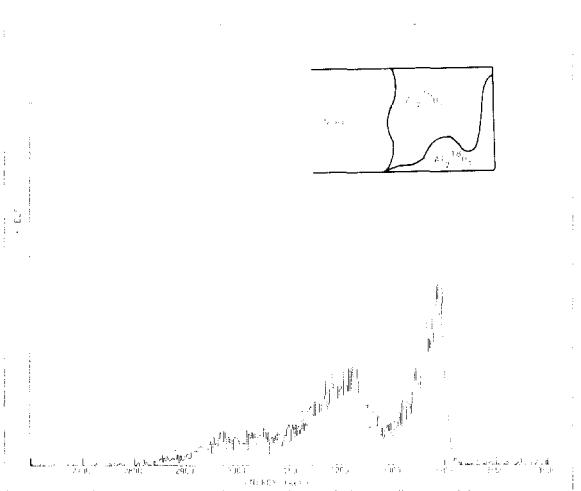


FIGURE 8  
 $\alpha$ -spectrum (800 keV protons) of NiAl oxidized T=1420 K, first 1h  $^{16}\text{O}$  later 2h  $^{18}\text{O}$ .

outside, inward transport of oxygen gained importance compared with oxidation at 1170 K. Also at this higher temperature, noble metal marker materials deposited onto preoxidized samples (without synthetic alumina cover) remained at the surface. Thus again incorrectly suggesting pure inside growth mechanism.

## 5. DISCUSSION AND CONCLUSIONS

In most of the literature concerning the growth mechanism of alumina scales it is agreed upon that the primary transport occurs by rapid grainboundary diffusion of oxygen.<sup>4,10</sup> Inert marker experiments were used to confirm this inside growth model.<sup>5,11</sup> It was suggested by Golightly, Stott and Wood that aluminum diffusion through the bulk of the grains occurs simultaneously. But in their model Al does not reach the gas/oxide interface.<sup>12</sup> Reddy, Smialek and Cooper performed  $^{18}\text{O}$  tracer oxidation experiments on Zr doped NiCrAl alloys at 1370 K. They concluded that oxygen grainboundary diffusion was the primary transport mechanism. But, especially for the low Zr doped alloys, some outward transport of Al upto the oxide/gas interface was observed as well.<sup>13</sup> Using  $^4\text{He}^+$  RBS as an analytical technique, we recently reported outside scale growth due to Al transport through Y doped alumina scales at temperatures between 1170 and 1370 K.<sup>9</sup> The tracer experiments, presented in this paper, show that during the oxidation of pure NiAl (without rare earth-like dopants), Al diffusion is a major transport mechanism. The experiments also show that inert marker experiments are very unreliable. Although surface markers, when not previously covered with  $\text{Al}_2\text{O}_3$ , suggest incorrectly inside growth,  $^{18}\text{O}$  tracers clearly show that a substantial part of the scale growth takes place at the oxide/gas interface. A poor adherence of the marker to the oxide surface seems probable explanation for the failure. The Pt islands seem to flow on the (new) oxide. As noted before, from the  $^{18}\text{O}$  distribution profiles, we cannot distinguish between Al lattice diffusion and Al short circuit diffusion. But since the transport of aluminum takes place at considerable rate at relatively low temperatures, it is commonly assumed that this transport occurs along short circuit diffusion paths. It has been put

forward by Golightly et al that Al moves along short circuit paths within the grains (e.g. dislocation pipes), while O moves along the grainboundaries<sup>12</sup>. According to this model, cations would move outwards along different paths than anions moving inwards. This might explain our observation that oxygen penetrates down to the alloy/oxide interface while Al moves up to the gas/oxide interface. As pointed out by Golightly et all, it would be very unlikely that Al and O could pass each other moving along the same path, e.g. the grainboundaries.<sup>14,15</sup> However, we also observed, especially at higher temperatures (1420 K), that new oxide is being formed within the scale. Thus the possibility that some grainboundary transport of Al occurs as well resulting in oxide growth at the grainboundaries, cannot be excluded.

It is clear anyhow that in any discussion of various oxidation experiments the oxidation temperature at which the various experiments were performed should be stressed. The relative contribution of the two species (Al and O) to the total mass transport, depends on the oxidation temperature. This was to be expected since the two diffusion processes will undoubtedly have a different activation energy. (Not taking into account the possibility of the formation of different alumina phases.) Therefore, at higher temperatures ( $>1170$  K) oxygen transport will gain importance relative to the aluminum. Only at very high temperatures ( $>1420$  K) the alumina scale growth will probably take place as described by Golightly et all. Their model was based on oxidation experiments at 1470 K. At lower temperatures the alumina scale grows by an outside growth mechanism. As to the 'value' of surface "markers" we would like to conclude that it is probably better to use implanted markers, if markers are to be used at all. We hope to report on the use of implanted markers in near future.

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