INVESTIGATION OF THE SOLID-STATE REACTION BETWEEN NICKEL OXIDE AND ALUMINA BY RUTHERFORD BACKSCATTERING (RBS)

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The reaction of NiO and Al_2O_3 to form $NiAl_2O_4$ was investigated by means of Rutherford backscattering of 3 MeV He^+-ions. The NiO was obtained by oxidation at 900 °C of a nickel film vapour-deposited onto alumina substrates. The reaction of NiO and Al_2O_3 did not proceed markedly at 900 °C. The reaction to form $NiAl_2O_4$ was found to be followed by a reaction of nickel and oxygen ions of the spinel phase with alumina to form $NiAl_2O_4 \cdot xAl_2O_3$. Some NiO was lost by evaporation. Careful calibration of the energy scale and determination of the integrated intensity of bombarding He^+-ions appeared to be essential to get reliable interpretation of the results.

1. Introduction

Radioactive isotopes[1], metallographic techniques[2] and electron microprobe analysis[2-4] have been used to investigate the solid-state reaction between NiO and Al_2O_3. The depth resolution of the first two techniques is rather limited, while it is difficult to obtain accurate values of the concentration profiles with electron microprobe owing to matrix effects. Reliable results can be obtained only when the reaction has proceeded over a considerable depth. The above reaction has accordingly been studied by keeping specimens at temperatures from 1200 to 1500 °C for times up to 300 h.

Evaporation loss of nickel oxide may take place when samples are kept at these elevated temperatures for extended periods[2]. This eliminates the need for an accurate establishment of the contact area on the one hand, but leads to difficulties with porous materials on the other hand. Use of a technique that can give accurate results for small diffusion distances avoids the above difficulties with the contact area and the evaporation. When thin layers are studied, one of the solids can be vapour-deposited onto the other. Vapour-deposition leads to an almost complete coverage of the second solid, provided the thickness of the film is beyond a critical value. In this work we deposited nickel films onto polycrystalline alumina substrates. Subsequent oxidation of the metallic nickel film led to a thin coherent layer of nickel oxide on alumina.

Alumina specimens covered by thin nickel oxide layers have been kept for different times at 1200 °C. Qualitative depth profiles of the chemical composi-

tion of the alumina specimens thus pretreated have been obtained by Rutherford backscattering (RBS) of 3 MeV He^+-ions. RBS appears to be a technique that is sufficiently sensitive to allow the use of very thin layers.

2. Experimental

2.1. APPARATUS

The experimental set-up has been described earlier[5]. To avoid some experimental uncertainties, modifications in energy-scale and current integration control have been provided (see below).

2.2. MATERIALS AND PROCEDURES

The targets investigated were alumina platelets covered by a vapour-deposited nickel layer of a thickness from 60 to 100 nm. The substrates (α-Al_2O_3, superstrate 996 A, Material Research Corporation, Orangeburg, New York, U.S.A.) were cleaned from adhering organic impurities by keeping them at 1200 °C for 24 h in air. In a vacuum system nickel films were vapour-deposited on the substrates from a ceramic crucible, heated by a tungsten filament. The thickness of the nickel films was monitored by the frequency-response of a vibrating quartz crystal mounted beside the substrates. Nickel films of the same thickness were deposited simultaneously on about 20 substrates (source-to-substrate distance 20 cm). By oxidation in air at elevated temperatures the nickel film was oxidized to nickel oxide. This procedure ensures an intimate contact between the two oxides.

Reaction between the oxides was studied at 900 and 1200 °C. To prevent charging in the scattering experiments the heat-treated specimens were cov-

ered by a thin vapour-deposited carbon or gold layer. At 900 °C oxidation to nickel oxide proceeds rapidly, but the resulting nickel oxide did not show any reaction with the alumina, even after several days. At 1200 °C a rapid reaction was observed, as dealt with below.

Enhancement of the backscattering by oxygen in the near surface region is due to the 3.05 MeV resonance in the $^{16}O(\alpha, \alpha)^{16}O$ reaction[6]. This shows up in the presented spectra. The sharp leading edge of the oxygen yield provides an additional identification of the oxidation stage of the nickel.

To detect reliably differences in concentration profiles from spectra exhibited by differently pretreated specimens, the energy scale of every spectrum must be calibrated and the integrated charge Q of the ions intercepted by the specimen must be accurately known. The energy scale was readily calibrated by recording the α-particles emanated by a two-component open α-source mounted permanently in the scattering chamber. We used a ^{230}Th $(E_\alpha = 4.684$ MeV) and ^{239}Pu $(E_\alpha = 5.156$ MeV) source.

At the Utrecht 3 MV accelerator normally an interceptive method for measuring the value of Q is in use. The incoming particles are counted by means of a current integrator[7]. To avoid problems with leakage conductances at the feedthroughs, connectors and cables, we developed a partially interceptive method. A simple and easy to install method was suggested to us by Alderliesten[8]. A schematic diagram is given in fig. 1. The incoming beam is intercepted by a 10 nm thick carbon foil (type S2, Yissum Research Development Corpora-

Fig. 1. Schematic diagram of beam detection and current integration set-up.

tion, Jerusalem, Israel) coated by vapour-deposition by a few monolayers of gold. A fraction of the ions scattered in a forward direction (scattering angle 45°) is collected by solid state detector 1. The signals of the detector are processed by a multichannel analyser. By means of a window around the appropriate gold peak the pulses are counted if and only if they are induced by projectiles scattered by the gold layer. All the measurements of a series are normalized to a preset number of received counts.

The ion beam collimated by a system of apertures, hits the target with a cross sectional area of approximately 0.5×0.5 mm^2. The beam energy had to be corrected for the slight decrease (5–7 keV) due to electronic stopping in the foil. The energy straggling of the beam passing through the foil (calculated at less than 2 keV, standard deviation) is small compared to the 15 keV resolution of the detecting system. We calculated the angular straggling due to multiple scattering of the projectiles in the foil, using the tables listed by Sigmund and Winterbon[9]. The value obtained for the half-angle at half height of the angular distribution is less than 1 mrad. The foil-to-target distance amounts to 20 cm. So there is no significant difference in the size of the beam spot when the beam is caught by the target. Projectiles backscattered from the target are collected by detector 2, and a RBS-spectrum is stored in a second analyser.

3. Results

3.1. FIGURE 2

Figure 2 shows the RBS-spectrum of an alumina specimen covered by a metallic nickel layer of about 60 nm before oxidation. In contrast to the other spectra, which were measured at a scattering angle of 170°, this spectrum was taken at an angle of 165°. Besides peaks due to the nickel layer and a gold layer of 8 nm, edges of aluminium and oxygen are displayed. The aluminium edge is at an energy of 1580 keV and that of oxygen at 1005 keV. Aluminium and oxygen present at the surface of the sample, covered only by the gold layer, should display energies of 1655 and 1085 keV respectively. The energies at which edges are exhibited therefore show that the alumina substrate is completely covered by the 60 nm nickel layer. The completeness of the covering was independently confirmed in the scanning electron microscope. Pictures were taken of the edge of nickel films of thicknesses of
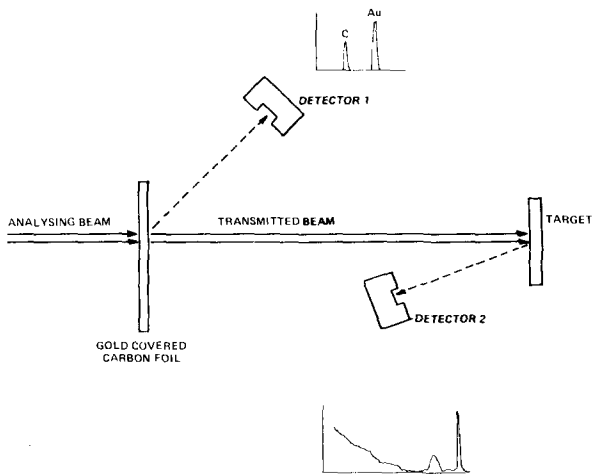
Fig. 2. A backscattering spectrum taken before diffusion has started.

Fig. 3. The nickel layer is oxidized. At the right-hand edge of the aluminium and the left-hand edge of the nickel, the beginning of the diffusion process is perceptible.
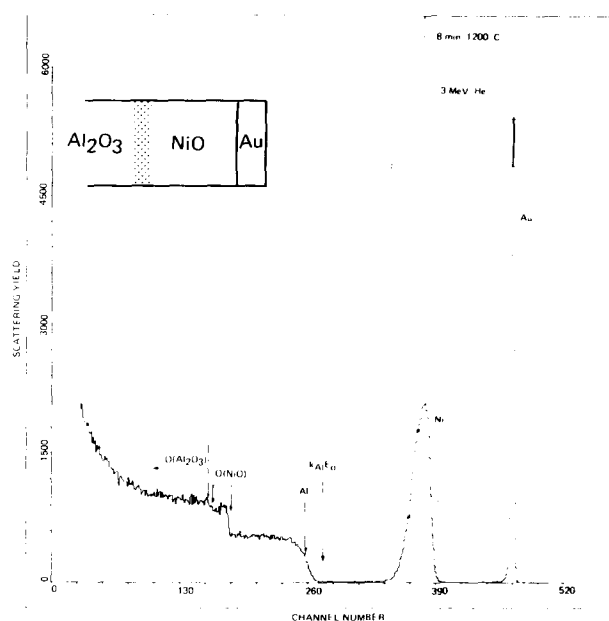
10, 20 and 30 nm; a sharp edge was obtained by covering part of the alumina substrate with a razor blade to intercept the depositing nickel atoms. Pictures with secondary electrons did not exhibit a difference between uncovered and covered parts of the alumina substrates. Backscattering of electrons depends on the nuclear charge of the atoms of the specimens. The picture of the backscattered electrons (silicon ring detector) clearly showed the difference between the covered (more bright) and the uncovered parts of the substrate. The covered part displayed a sharp boundary also with a film of a thickness of 10 nm only. Hence the use of backscattered electrons was demonstrated to be a sensitive means of searching for discontinuities in the film of nickel. None were seen.

3.2. FIGURE 3

In fig. 3 the RBS-spectrum of a specimen kept for 8 min at 1200 °C is represented. The positions of the gold and the nickel peaks are in accordance with the computations. The nickel peak is lower and broader than that of fig. 2. The oxygen yield now displays two edges, one at an energy of 1080 keV and another one at 960 keV. An edge at 1080 keV is expected for oxygen atoms at the surface covered only by the 8 nm gold layer. Figure 3 thus shows that the nickel layer has been oxidized by keeping the specimen for 8 min at

1200 °C. The oxidation dilutes the nickel layer with oxygen. Owing to this the density of the nickel atoms at the surface has decreased and the nickel atoms are present in a layer of a larger thickness. Owing to the oxygen ions in the oxidized nickel layer the edge of the oxygen yield of the Al_2O_3, which contains more oxygen than NiO, has shifted to a lower energy, viz. from 1005 to 960 keV. The edge due to aluminium ions is no longer straight. It is centered at an energy of about 1540 keV, which is about 40 keV lower than the edge displayed before oxidation of the nickel layer. The oxygen and the aluminium edges therefore have shifted over about the same distance. The onset of the aluminium edge is situated at an energy of 1610 keV. This indicates that aluminium ions have already markedly migrated into the nickel oxide layer during the time of 8 min the specimen was kept at 1200 °C. The aluminium edge not being straight is due to a gradual drop in the aluminium concentration towards the surface or to the thickness of the aluminate layer not being uniform. The marked formation of nickel aluminate also contributes to the broadening of the nickel peak.

3.3. FIGURE 4

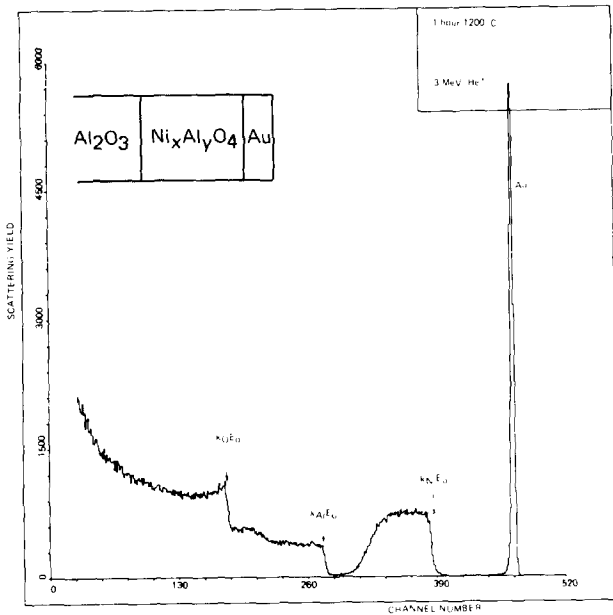Keeping a specimen for 1 h at 1200 °C led to the spectrum displayed in fig. 4. The nickel peak has

Fig. 4. In a rapid process a spinel has been formed. The aluminium has reached the surface of the heated sample.

was calculated from the heights of the edges. The ratio turned out to be Al/Ni = 2.05.

3.4. FIGURE 5

A marked change in the spectrum was observed only after keeping the specimen for 21 h at 1200 °C. The spectrum observed from this specimen is shown in fig. 5. It appears that the scattering yield of oxygen and aluminium are almost the same as they were in fig. 4. The aluminium yield has slightly increased. The yield of nickel has decreased at higher energies and has slightly decreased at lower energies, while the leading edge due to nickel ions has remained at the same energy. At the surface the Al-to-Ni ratio has become higher, viz. 2.45.

When the specimens were kept at 1200 °C for a longer period, the nickel content at the surface continued to drop. The nickel yields no longer showed a horizontal plateau behind the leading edge. The yield had a character analogous to that of aluminium in that of fig. 3. After 215 h the Al-to-Ni ratio at the surface rose to 3.2.

now substantially decreased and broadened, which indicates the diffusion of the nickel ions into the alumina over an appreciable distance. The position of the nickel edge has remained at 2280 keV, which shows that nickel ions are still present at the surface. The aluminium yield displays a two stage profile. The first sharp edge is at 1655 keV. Aluminium ions present at the surface of a specimen covered by a gold film of 8 nm are calculated to exhibit an edge at an energy of 1650 keV. Figure 4 therefore shows that the aluminium ions have migrated to the surface of the specimen at 1200 °C within 60 min. Since a nickel layer of 60 nm leads to a nickel oxide layer of 80 nm, a nickel oxide layer of this thickness must have reacted to nickel aluminate, as the solubility of Al_2O_3 in NiO is very small. The gradual increase in the mean aluminium concentration is evidenced from the gradual rise in the scattering yield of the aluminium ions. The nickel ion concentration must likewise decrease gradually, which can also be seen in fig. 5. Owing to the resonance scattering of oxygen surface ions, the structure of the oxygen edge has disappeared in fig. 4. It has been observed that the RBS-spectrum did not change when the specimens were kept at 1200 °C for 2 and 3.5 h. The recorded spectra precisely coincided with the spectrum of fig. 4. The Al-to-Ni atomic ratio at the surface of the specimen

4. Discussion

The spectra demonstrated that the solid-state reaction of NiO and Al_2O_3 proceeds at 1200 °C at a marked rate. This agrees with results obtained by
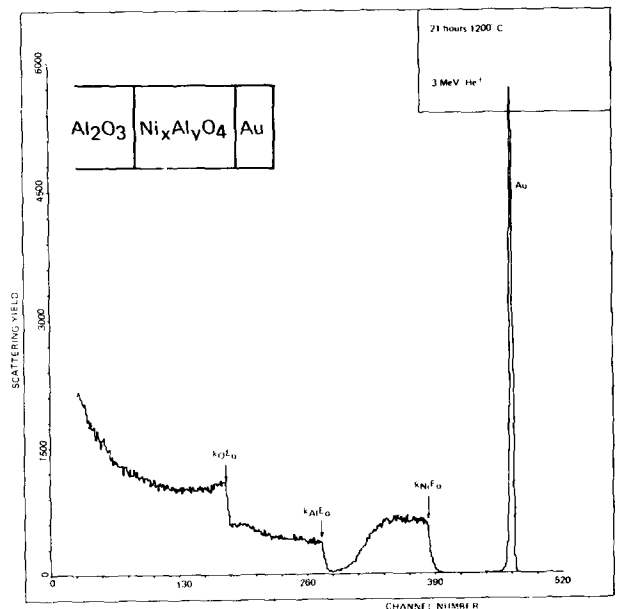

Fig. 5. Nickel from the aluminate reacts with Al_2O_3 to more spinel. The nickel plateau is lowered by a factor of 0.85 relative to the 1 h spectrum.

Pettit et al.[2]) who used a metallographic technique. From the data of these authors it can be concluded that within 1 h at 1200 °C a spinel layer of a thickness of 520 nm should be formed and that formation of a spinel layer of 80 nm calls for 1.5 min. Since we did not observe complete reaction of a NiO layer of about 80 nm within 8 min, our samples display a less rapid reaction.

Within 1 h the nickel oxide layer appeared to react to a spinel exhibiting a Al-to-Ni ratio of about 2. Phillips et al.[10]), studying the phase diagram of the NiO-Al_2O_3 system found that Al_2O_3 dissolves into $NiAl_2O_4$ up to a Al-to-Ni ratio of about 3. Earlier Iida[11]) observed the same ratio, while Pettit et al.[2]) found a ratio of 2.84 of the spinel that was in equilibrium with Al_2O_3. NiO, on the other hand, does not dissolve Al_2O_3 beyond about 1 mol %.

The gradual decrease in the nickel yield towards lower energies and the rise in the aluminium yield indicate that the mean concentration of nickel and aluminium gradually changes with the depth below the surface. This might be ascribed to a continous decrease in the nickel concentration. Since the spinel can only accommodate Al_2O_3 up to $NiAl_2O_4 \cdot 0.4 Al_2O_3$, the nickel concentration cannot drop continously to zero. Owing to the porous character of the substrate (grains of about 1 μm) the nickel concentration does not remain uniform. At some sites the reaction to the spinel has penetrated more in the substrate then at other sites.

Our results indicate a relatively rapid formation of stoichiometric $NiAl_2O_4$ followed by a much slower process in which nickel ions migrate from the $NiAl_2O_4$ to the Al_2O_3-phase to form more aluminate. The horizontal plateau of a large part of the nickel yield indicates that during this process the composition of the spinel phase remains uniform. The rate-determining step is the migration of nickel

and oxygen ions into the alumina phase. The small increase in the aluminium yield shows that there must be a loss of nickel from the solid which gives rise to the appreciable decrease in the total nickel yield. The loss of nickel is presumably caused by evaporation of nickel oxide. According to Pettit[2]) the composition of the resulting spinel phase is $NiAl_2O_4 \cdot 0.4 Al_2O_3$. When this limiting composition has been reached, further evaporation of nickel oxide would demand the formation of alumina nuclei. Now the mean nickel concentration at the surface is no longer uniform, which leads to the disappearance of the flat level of the nickel yield behind the leading edge.

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