EVOLVED GAS ANALYSIS FOR EXAMINATION OF SURFACE OXIDES ON ALLOYS

D. B. Goldman*

NATIONAL INSTITUTE FOR MATERIAL RESEARCH, CSIR, P.O.BOX 395, PRETORIA 0001, SOUTH AFRICA

Temperature programmed reduction in a hydrogen flow with simultaneous evolved gas analysis was employed to determine surface oxides on oxide dispersion strengthened (ODS) nickel containing TiO_2, Al_2O_3 or Cr_2O_3 particles, and on a Ni—2OCr alloy, after exposure to air at elevated temperatures. Oxides on particles of water-atomized (WA) Ni—2OCr powder were analysed similarly. Significant differences in starting temperatures of the reaction between hydrogen and phases present in oxide layers made identification of the phases possible. NiO or NiO doped with Ti, Al or Cr are the major constituents of the scale formed on ODS Ni. $NiTiO_3$, $NiCr_2O_4$ and $NiAl_2O_4$ are formed as a result of a reaction between TiO_2, Al_2O_3 or Cr_2O_3 particles in the scale with NiO. The oxide layer formed on Ni—2OCr alloy consists of Cr_2O_3 and of NiO doped with Cr. Surface oxides on WA Ni—2OCr contain Cr_2O_3 and a small amount of NiO.

Evolved gas analysis has previously been used for the qualitative and quantitative determination of phases present in powder oxide mixtures [1–3]. Reduction of oxides takes place when they are exposed to a reducing atmosphere, e.g. hydrogen. Temperature limits of reduction are different for various oxides. For example, reaction with hydrogen for Cu, Fe or Ni oxides takes place at relatively low temperatures, reduction of oxides of Cr, Ti, Mn requires higher temperatures, while oxides of Al, Ca, Mg are not reducible, even at very high temperatures [4]. The starting temperature of the reaction of oxides with hydrogen increases with the increase in the strength of the bond between cations and oxygen [5–9]. To a certain extent the temperature of the start of reduction is characteristic of an oxide. The phenomenon was exploied in studies of solid state reactions between oxides [2, 10]. The starting temperature of the reduction by hydrogen for the components initially involved in a reaction differs from that of the reaction products. Water vapour

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* New address: Howmet Turbine Components Corporation Technical Center, 699 Benston Road Whitehall, Michigan 49461 U.S.A.

evolves as a result of the reduction of oxides in hydrogen. The amount of water evolved is directly proportional to the amount of oxide reduced. By reducing a sample with a continuous increase in temperature and with simultaneous analysis of the gas evolved, the beginning of the reduction of an oxide phase can be established. The quantity of the phase can be determined by measuring the amount of the gas (water vapour) evolved during the reduction of a phase [2]. This method of analysis was applied before to determine surface oxides on particles of water-atomized iron-base alloys [11, 12].

In the present work, the analysis was employed to identify oxide phases on the surface of ODS nickel containing TiO_2, Al_2O_3 or Cr_2O_3 particles and on a Ni—20Cr alloy, exposed to air at elevated temperatures. Oxides on the surface of particles of water-atomized Ni—20Cr were also analysed.

Oxidation of Ni with TiO_2, Al_2O_3 or Cr_2O_3 dispersions at temperatures between 800 and 1200° in air was studied in [13, 14]. NiO containing Ti, Al or Cr was found to be the major constituent of the oxide scale on the alloys. The scale on a Ni—20Cr alloy consists of NiO, Cr_2O_3 and $NiCr_2O_4$. The latter can be formed as a result of the reaction between NiO and Cr_2O_3 [15, 16]. Formation of these oxides can also be expected on the surface of particles of water-atomized Ni—20Cr alloy.

$NiTiO_3$ is the only binary compound formed in the NiO—TiO_2 system [17–19] below 1000°. The composition of the compound can deviate slightly from stoichiometry [18, 19]. Solubility of TiO_2 in NiO is limited to about 2 mol%. $NiAl_2O_4$, the composition of which can vary considerably in favour of Al_2O_3, is the only compound formed in the NiO—Al_2O_3 system [20, 21]. Solubility of Al_2O_3 in NiO at 1000° is about 1 mol% [21]. $NiCr_2O_4$ is the only compound found in the NiO—Cr_2O_3 system. The solubility of Cr_2O_3 in NiO is lower than that of TiO_2 and Al_2O_3, and is below 1 mol% at 1000° [22].

Experimental

The experimental apparatus is shown schematically in Fig. 1. A specimen in a quartz or alumina boat is placed inside a quartz reactor in a stream of hydrogen, supplied at a flow rate of 4 dm^3/h. The reactor is heated by a tube furnace. The temperature is increased at a constant rate of 15 deg/min. The temperature of a sample is measured by a thermocouple placed near the sample. The reactor is connected to a thermal conductivity detector (TCD). The signal from the detector is proportional to the water concentration in the hydrogen flow and is recorded vs. temperature on an X–Y recorder. During treatment of an alloy in hydrogen, reactions other than oxide reduction may occur, e.g. reduction of sulfides and decarburization, and gases such as H_2S or CH_4, can be formed. A cold trap, placed

between the reactor and TC-detector, when cooled to the temperature of solid CO_2, removes water vapour from the hydrogen stream. Peaks of water then disappear from the diagram, but peaks of H_2S or of CH_4 remain, thus making the identification of peaks possible. Since the response of the detector is proportional to the concentration of water in the stream, the area under a peak on a diagram of the analysis is proportional to the amount of water evolved as well as the amount of oxygen removed from the surface of a sample. Figure 2 shows the dependence of the analysis peak area on the amount of oxygen removed. To establish this dependence,
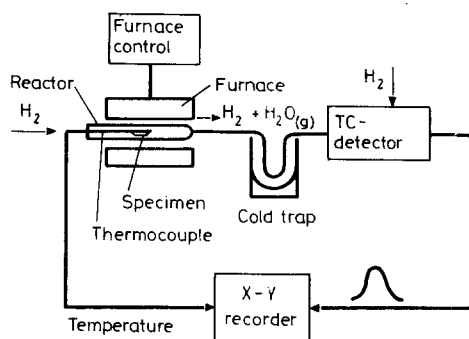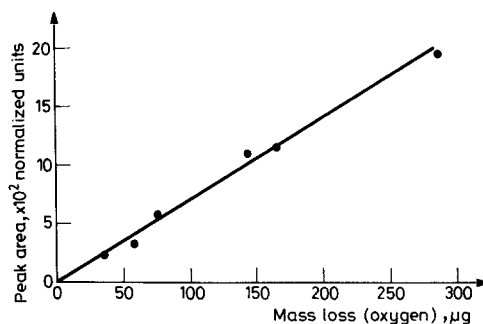
Fig. 1 Apparatus for analysis of surface oxides

Fig. 2 Dependence of the peak area of the analysis on the amount of oxygen removed from an alloy surface

samples of nickel foil with varying surface areas were used. The samples were oxidized in air at 700° for one hour before the analysis. The mass losses after the analysis were determined by using a microbalance (sensitivity 0.001 μg).

Nitrates of nickel, aluminium, chromium [$Ni(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$] "pro analysis" grade and TiO_2 "laboratory" grade, E Merck AG, FRG, were used in the preparation of Ni, ODS nickel, containing 5 vol% Al_2O_3 ($Ni5Al_2O_3$), 10 vol% Cr_2O_3 ($Ni10Cr_2O_3$), 5 vol% TiO_2 ($Ni5TiO_2$), and of binary compounds ($NiTiO_3$, $NiAl_2O_4$, $NiCr_2O_4$). Water solutions of the nitrates

or of nickel nitrate and TiO_2 were mixed in the ratios required to provide the desired composition of an alloy or compound. After dehydraton and decomposition of nitrates in air at 500°, NiO and the oxide mixtures intended for alloy preparation were exposed to a hydrogen stream at 800° to produce Ni powder and mixtures of Ni with a corresponding oxide. The oxide mixtures containing 1:1 mol ratio of corresponding oxides were calcinated in air at 1350° to produce the binary oxides. Compacts, 6.5 mm dia and about 0.5 mm thick, were prepared from the nickel-oxide mixtures under 6 kbar pressure. Ni, $Ni5Al_2O_3$ and $Ni10Cr_2O_3$ compacts were sintered in hydrogen, and $Ni5TiO_2$ in argon at 1050°. After this treatment the compacts were cold-sintered [23] under 30 kbar pressure. Densities close to theoretical were obtained. Samples 6.5 mm dia and 0.2 mm thick were annealed at 800° in hydrogen. Samples $15 \times 7.5 \times 0.2$ mm^3 of a commercial Ni—20Cr alloy with composition in wt%: Ni — 78.1, Cr — 20, Si — 1.7, Mn — 0.1, C — 0.019, and samples of Ni and of ODS Ni were polished with 1200 grit SiC paper and washed in acetone before oxidation. Surface oxides on particles of water-atomized Ni—20CR (Nichrom) alloy, BSA Metals Co., UK, containing (wt%) O — 0.259, S — 0.07 and C — 0.014 were analysed.

Other materials used in the experiments were: GPR grade Ni foil, 0.15 mm thick, and electrolytic Cr, 99.5% purity, BDH Co., UK; Cr_2O_3, 99% purity, Cerac Co., USA. Hydrogen used in experiments had a reported purity >99.99% with oxygen <1 ppm and a dew point < −72°. Argon used in preparation of the alloys had purity >99.995% with oxygen <3 ppm and water <1 ppm.

Results and discussion

Figure 3 shows diagrams of the analysis for NiO, TiO_2 and Cr_2O_3 powders (Al_2O_3 is not reducible even at very high temperatures). A significant difference in the starting temperature of the reduction of NiO and TiO_2, and between NiO and Cr_2O_3 was observed. The reduction of NiO starts at 255°. TiO_2 and Cr_2O_3 start to react with hydrogen at 880 and 960° respectively. For the binary oxides the values are between those for NiO and for a corresponding oxide (Fig. 4). Values are 580° for $NiTiO_3$, 670° for $NiCr_2O_4$ and 820° for $NiAl_2O_4$.

The diagrams of the reduction of oxides, formed on the surfaces of Ni and Cr after exposure to air for three hours at 700 and 1000° respectively, are shown in Fig. 5. NiO and Cr_2O_3 are the only oxides found on the surfaces of pure Ni and Cr [24]. The temperatures of the beginning of reduction are very close to those for NiO and Cr_2O_3 powders, and are 260 and 950° respectively. The starting temperature of the
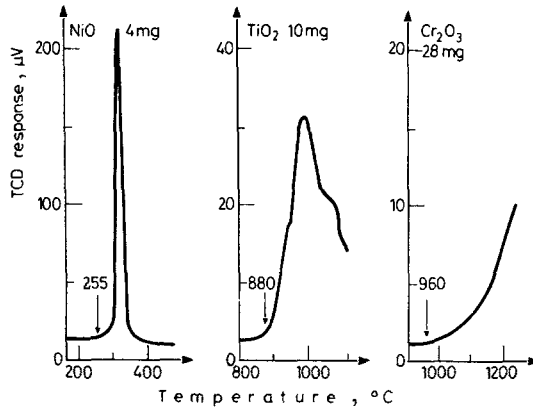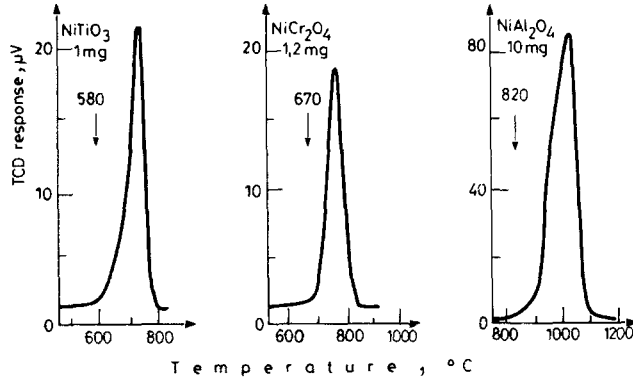
Fig. 3 Diagrams of the analysis for NiO, TiO_2 and Cr_2O_3 powders

Fig. 4 Diagrams of the analysis for $NiTiO_3$, $NiCr_2O_4$ and $NiAl_2O_4$ powders

reduction of 280° was measured for Ni samples oxidized at 900°. It can probably be explained by changes in composition of NiO with variation in temperature [25].

Diagrams of the analysis for $Ni5TiO_2$ samples exposed to air for three hours at 700 and 900° are shown in Fig. 6. Two peaks are observed on each diagram. For the sample oxidized at 700° reduction starts at 270°, which is almost the same value observed for pure Ni. Reduction of samples oxidized at 900° starts at a higher temperature, 350°, indicating that TiO_2 was dissolved in NiO [2]. The second peak appeared at higher temperatures and was recorded with an increased sensitivity of the detector (as indicated on the diagrams). The peaks represent reduction of $NiTiO_3$. The latter was formed as a result of the reaction, during oxidation, between TiO_2 particles and the NiO matrix. The temperature of the start of the
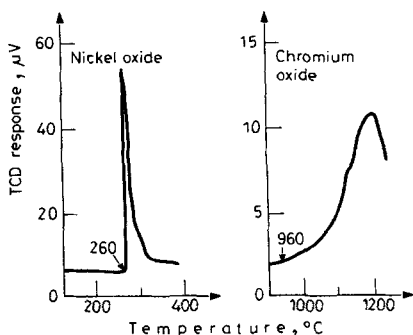
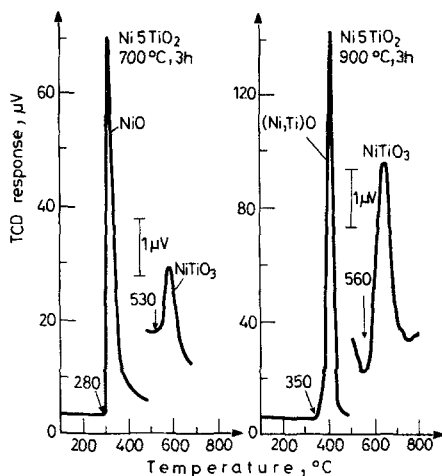**Fig. 5** Diagrams of the analysis for oxides on the surfaces of Ni and Cr

Fig. 6 Diagrams of the analysis for oxidized surfaces of Ni5TiO$_2$ alloy

reduction of the compound is lower than observed for sintered NiTiO$_3$ and probably is a result of the deviation in composition in favour of NiO [19].

In Fig. 7 diagrams of the analysis for oxidized surfaces of Ni5Al$_2$O$_3$ alloys are presented. Formation of NiO—Al$_2$O$_3$ solid solution in the oxide layer was observed already after exposure to air for three hours at 700°. The corresponding peak appeared on the diagram at a temperature of about 400°. For the sample
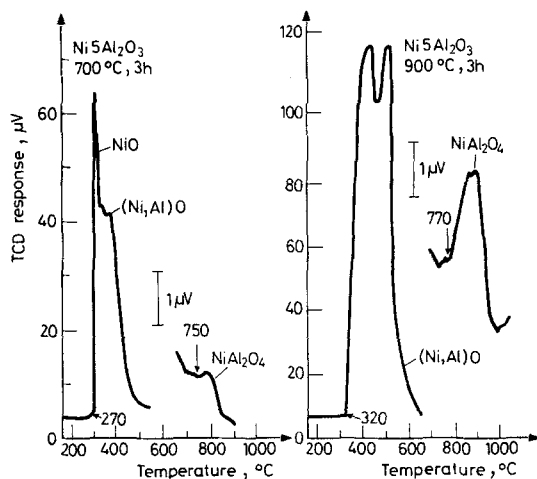

Fig. 7 Diagrams of the analysis for oxidized surfaces of Ni5Al$_2$O$_3$ alloy

oxidized at 900° no pure NiO was detected in the scale. The presence of two reduction peaks for the solid solution indicates that solutions with differing Al_2O_3 contents are present in the scale, probably a different distances from the alloy surface. Formation of $NiAl_2O_4$ took place as a result of the reaction between Al_2O_3 particles and the NiO matrix. The lower values for starting temperatures of the reduction, when compared with the sintered compound, can probably be ascribed to a variation in the composition of the compound [21].

The starting temperature of the reduction of oxidized surfaces of the $Ni10Cr_2O_3$ alloy (Fig. 8) is very close to that for pure oxidized Ni. Only a broadening of the first
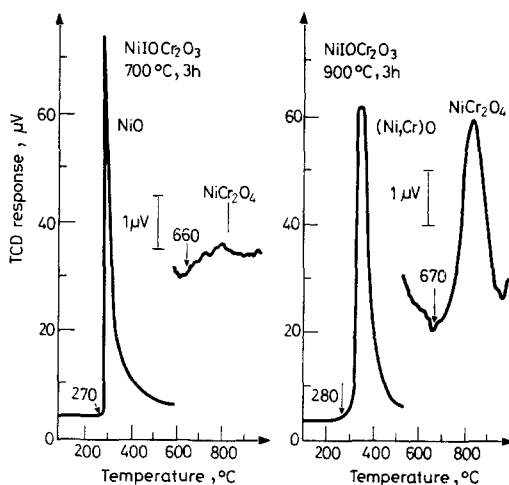

Fig. 8 Diagrams of the analysis for oxidized surfaces of $Ni10Cr_2O_3$ alloy

peak on the diagram for the sample oxidized at 900° indicates that a certain amount of Cr_2O_3 was dissolved in the NiO matrix. Reaction between Cr_2O_3 particles in the scale and NiO, which results in the formation of $NiCr_2O_4$, takes place at 700 and 900°.

NiO and Cr_2O_3 are the constituents of the scale formed on the surface of a sample of Ni—2OCr alloy exposed to air at 900° for two hours. The diagram of the analysis is shown in Fig. 9. During the analysis decarburization of the sample takes place above 1000° simultaneously with Cr_2O_3 reduction. A higher temperature of the start of the reduction of the surface oxides, when compared with a pure NiO, indicates that NiO in the scale was doped with chromium. The starting temperature of the reduction of Cr_2O_3 in the scale of 910° is lower than observed for pure Cr_2O_3, thus confirming that Ni was dissolved in Cr_2O_3 [15].
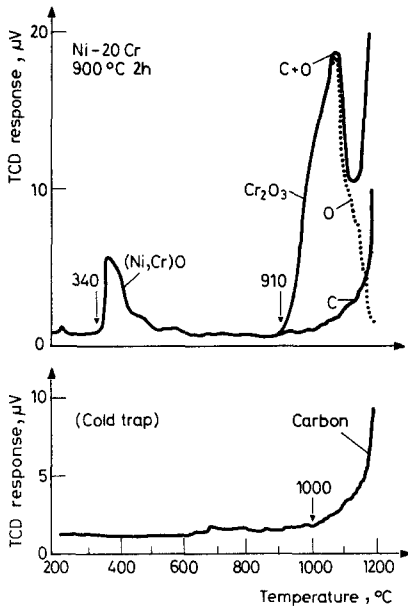
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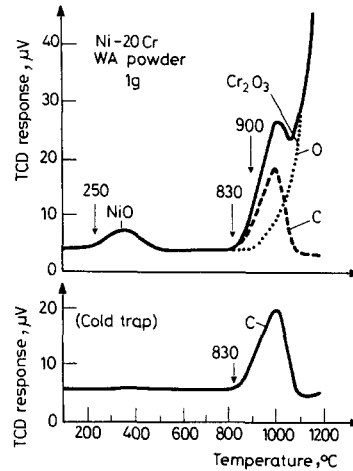**Fig. 9** Diagrams of the analysis for oxidized surface of Ni—2OCR alloy

Fig. 10 Diagrams of the analysis of water-atomized Ni—2OCr powder

Surface oxides on water-atomized powder of Ni—2OCr alloy consist of Cr_2O_3, which is the major component of the scale, and a small amount of NiO (Fig. 10). Reduction of chromium oxide on the particle surfaces starts at 900°, indicating that the oxide contains a certain amount of dissolved Ni. Decarburization of the powder takes place simultaneously with the reduction of surface oxides above 830°.

Conclusions

Temperature programmed reduction in a hydrogen flow with simultaneous evolved gas analysis was used to examine surface oxides on ODS nickel containing TiO_2, Al_2O_3 or Cr_2O_3 particles, and on a Ni—2OCr alloy, after exposure to air at elevated temperatures. Oxides on particles of water-atomized Ni—2OCr powder were also analysed. The significant differences in the temperatures of the beginning of the reaction with hydrogen of the oxide phases present in the oxide layers (NiO; NiO doped with Ti, Al or Cr; TiO_2; Al_2O_3; Cr_2O_3; $NiTiO_3$; $NiAl_2O_4$; $NiCr_2O_4$) made identification of the phases possible. The high sensitivity of the method permits analysis of oxide scale on samples with a small surface area. The method may find an application in controlling the processing of metal powders.

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Zusammenfassung — Temperaturprogrammierte Reduktion im Wasserstoffstrom wurde zusammen mit gleichzeitiger Analyse des in Freiheit gesetzten Gases dazu benutzt, um Oberflächenoxide an Nickel enthaltenden TiO_2-, Al_2O_3- oder Cr_2O_3-Partikeln mit verstärkter Oxiddispersion (ODS) und an einer Ni—2OCr-Legierung nach Behandlung in Luft bei erhöhten Temperaturen zu bestimmen. Oxide auf Partikeln von wasser-zerstäubtem (WA) Ni—2OCr-Pulver wurden auf ähnliche Weise analysiert. Signifikante Unterschiede in der Starttemperatur der Reaktionen zwischen Wasserstoff und der in den Oxidschichten vorliegenden Phasen ermöglichen die Identifikation der Phasen. NiO oder mit Ti, Al oder Cr gedoptes NiO sind die Hauptbestandteile des auf ODS—Ni gebildeten Belags. $NiTiO_3$, $NiCr_2O_4$ und $NiAl_2O_4$ treten als Produkte der Reaktion von TiO_2-, Al_2O_3- oder Cr_2O_3-Partikeln mit NiO im Belag auf. Die auf der Ni—2OCr-Legierung gebildete Oxidschicht besteht aus Cr_2O_3 und aus mit Cr gedoptem NiO. Oberflächenoxide auf WA-Ni2OCr enthalten Cr_2O_3 und geringe Mengen an NiO.

Резюме — Метод температурно-программированного восстановления в потоке водорода, совмещенный с анализом выделяющегося газа, был использован для определения поверхностних окислов на никеле, дисперсионно упрочненном окисью, и содержащем частицы двуокиси титана, окиси алюминия или окиси хрома, а также на сплаве Ni—2OCr, после выдерживания их на воздухе при повышенных температурах. Подобным образом были анализированы окислы на частицах распыленного водой сплава Ni—2OCr. На основе значительных различий начальных температур реакций между водородом и фазами, присутствующими в окисных слоях, проведена идентификация возможных фаз. Главными компонентами окалины, образующейся на дисперсионно упрочненном никеле, являются окись никеля или окись никеля, легированная титаном, алюминием или хромом. Соединения $NiTiO_3$, $NiCr_2O_4$ и $NiAl_2O_4$ образуются в результате реакции, происходящей в окалине между окисью никеля и двуокисью титана, окисью алюминия или окисью хрома. Окисный слой, образующийся на поверхности сплава Ni—2OCr, состоит из окиси хромя и окиси никеля, легированного хромом. Окисные поверхности на распыленном водой сплаве Ni—2OCr содержат окись хрома и небольшое количество окиси никеля.