

The use of Y_2O_3 coatings in preventing solid-state Si-base ceramic/metal reaction

R. L. MEHAN, M. R. JACKSON, M. D. McCONNELL

General Electric Company, Corporate Research and Development, Schenectady, New York, USA

The use of Y_2O_3 sputtered coatings on the order of $0.1 \mu\text{m}$ thick have been found to greatly reduce the degree of reaction between metals and Si-base ceramics. Even though the Y_2O_3 coating tends to become detached from the sputtered ceramic after one heating cycle, modifications in the surface chemistry of the ceramic continues to provide protection from further attack.

1. Introduction

When Si-base structural ceramics are brought into contact with Ni-base alloys at elevated temperatures, a solid-state reaction occurs between them [1-4]. Such strength-degrading chemical interactions can have severe consequences if the ceramic is to be used as a structural member in hot machinery. The ceramic/metal reaction is particularly severe for ceramics containing free silicon (the reaction bonded Si-SiC ceramics) above about 950°C , where Ni-Si eutectics can form. SiC reacts with metals to a lesser extent, and Si_3N_4 even less so [3, 4]. Particularly for the case of Si-SiC and SiC ceramics, therefore, a coating is required on the ceramic and/or metal in order to prevent these reactions.

Past work [5] has shown that sputtered Y_2O_3 deposited on either the SiC, Si-SiC, or metal can reduce the degree of ceramic/metal reaction to a considerable degree. However, the Y_2O_3 coating was found to spall off both SiC and Si-SiC after being in contact with the Ni-base alloy through a single heating cycle. The presence of metal in contact with the ceramic was found to be a necessary condition for coating detachment; Y_2O_3 coatings on SiC remained intact after 26 thermal cycles between 25 and 1100°C .

The purpose of the present paper is to expand upon the work briefly reported previously [5]. Additional observations and analytical information

on Y_2O_3 stability are now available that permit a more detailed assessment to be made of the effectiveness of Y_2O_3 as a barrier coating between Si-base ceramics and Ni-base alloys.

2. Experimental details

The experimental procedure has been previously described in detail [1, 2]. Briefly, the ceramic discs (6.35 mm diameter \times 3.2 mm) are brought into contact with both sides of the metal discs (12.7 mm diameter \times 3.2 mm) under a compressive stress of 7.0 MN m^{-2} . The reactivity experiments were conducted in air, with heat supplied by a Pt-wound tube furnace. It has been shown [2] that the combination of a tight ceramic/metal contact and the presence of a solid state ceramic/metal reaction is sufficient to exclude oxygen from the interface.

The ceramics used were hot pressed SiC* and two Si-SiC[†] ceramics both of which chemically behaved the same. The metal was a model superalloy consisting of 70 at% Ni, 20 at% Cr, and 10 at% Al. The composition was chosen to resemble the chemistry of a Ni-base superalloy consisting of $\gamma + \gamma'$, neglecting the effects of carbides and borides.

Y_2O_3 coatings on both metal and ceramic were deposited by sputtering. The specimens were thoroughly cleaned in solvent, and the metal was also vapour degreased. Prior to sputtering, the sur-

*Norton Company, USA.

†NC 435, Norton Company, and Silcomp, General Electric Co., USA.

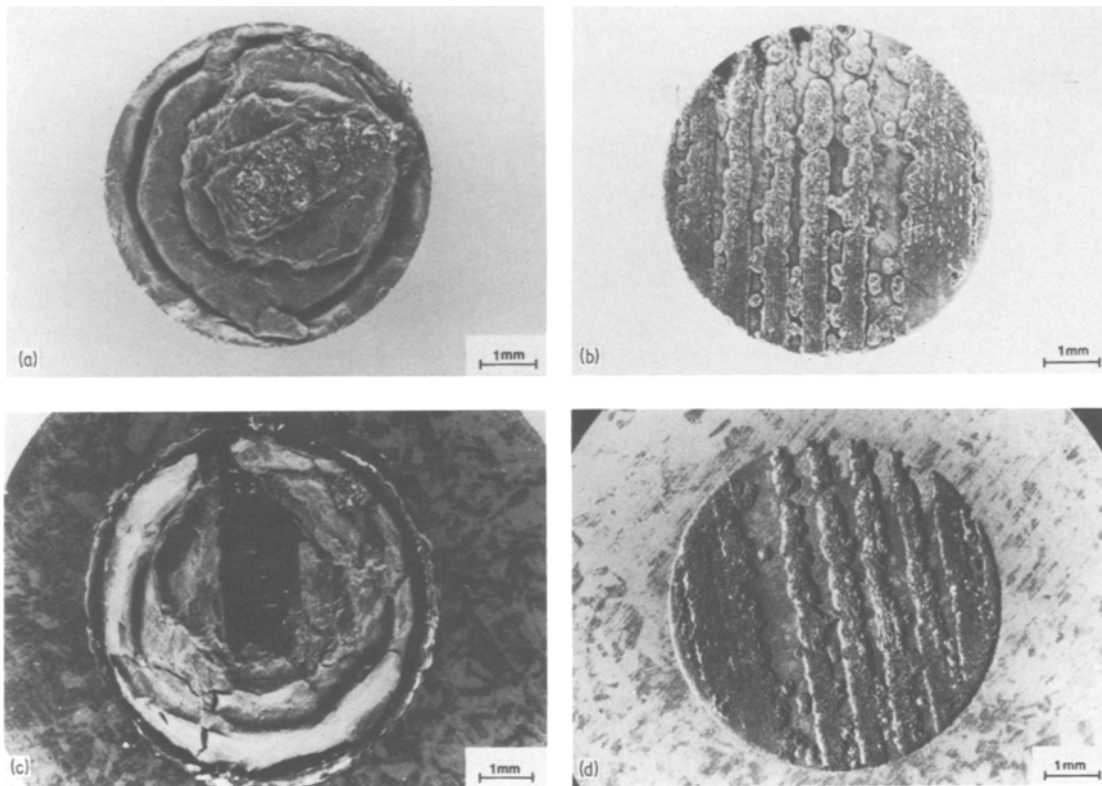


Figure 1 Macrophotographs of uncoated Si-SiC, SiC and NiCrAl alloy after reaction at 1000° C for 1000 h. (a) Si-SiC surface; (b) SiC surface; (c) NiCrAl/Si-SiC surface; (d) NiCrAl/SiC surface. The grooves in (b) and (d) are due to grinding marks in the SiC.

face was sputter-etched for about 5 min. The coatings were about 0.9 μm thick.

3. Results and discussion

Macrophotographs of the surfaces of the ceramics and metal after being in contact, uncoated, for 100 h at 1000° C are shown in Fig. 1. Metallographic cross-sections of the same material combinations are shown in Figs. 2 and 3 (the Si-SiC/metal couple was only exposed for 50 h). Clearly, extensive reaction between the metal and ceramic takes place under these conditions, particularly so for the Si-SiC. In the SiC, the structure consists of alternate dark and light bands, the former consisting of graphite, $\delta\text{-Ni}_2\text{Si}$, and $\text{Cr}_{5-x}\text{Si}_{3-y}\text{C}_{x+y}$ and the latter predominantly $\delta\text{-Ni}_2\text{Si}$. On the metal side a number of silicides and carbides are found; at least 14 individual phases have been identified in this system [2]. Similar phases are found in the Si-SiC, Fig. 3, although metallographically the appearance of the reacted SiC and Si-SiC are different. In the Si-SiC, the silicon

matrix is transformed by reaction with nickel to predominantly Ni_3Si_2 , with some $\text{Ni}_{16}\text{Cr}_6\text{Si}_7$ present. On the metal side, Ni_3Si_2 is also formed, together with $\delta\text{-Ni}_2\text{Si}$, Cr_3Si and other silicides.

The effect of sputter depositing 0.9 μm of Y_2O_3 on SiC and performing reaction experiments

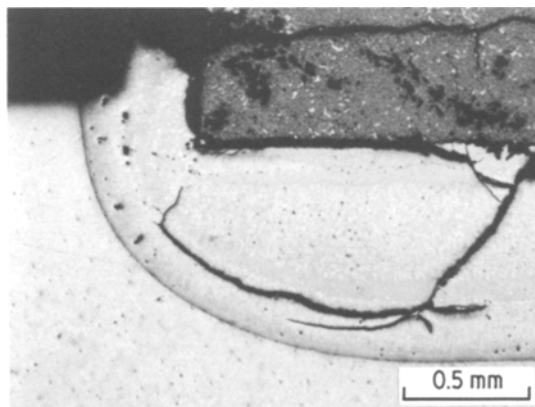


Figure 2 Reaction between Si-SiC and NiCrAl alloy after 50 h at 1000° C.

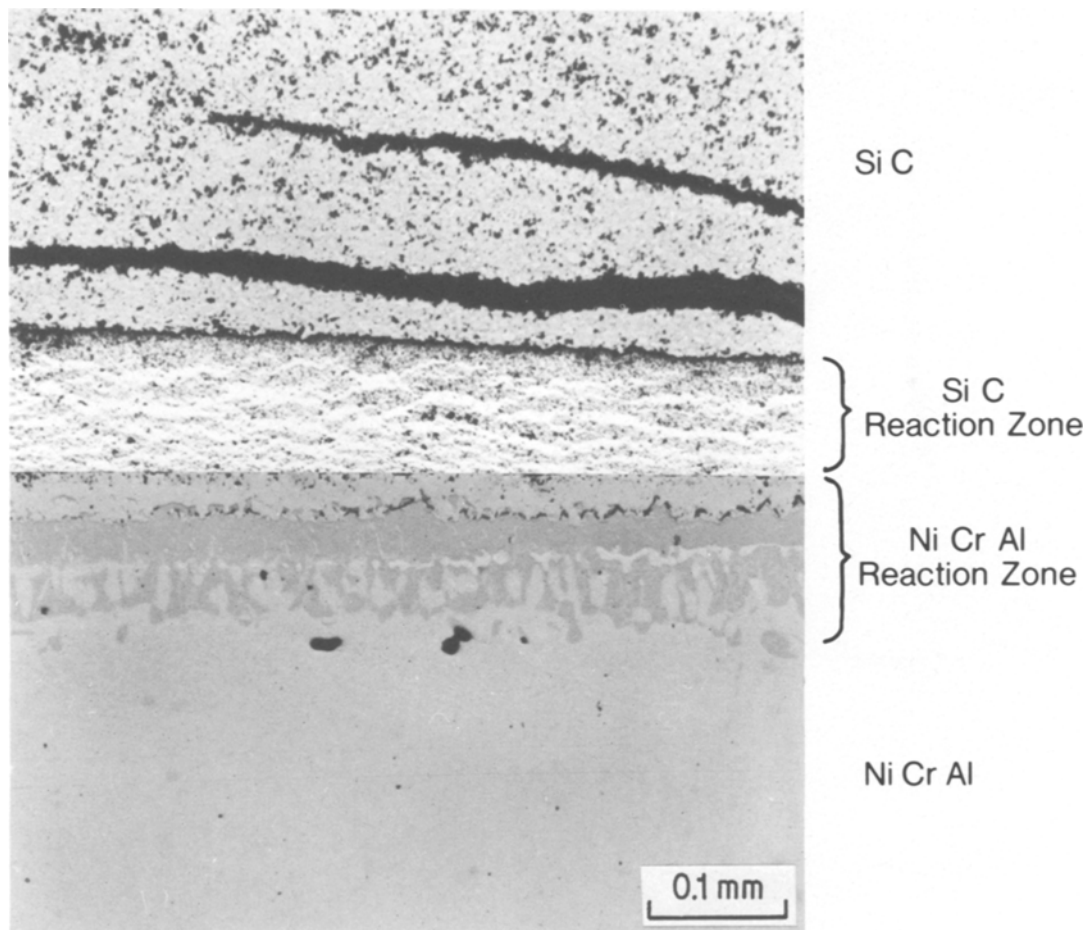


Figure 3 Montage photograph of the reaction between SiC and NiCrAl alloy after 100 h at 1000° C.

at temperatures as high as 1150° C is remarkable. The reaction zones in the metal and SiC for the uncoated case are shown in Fig. 4, for the coated case in Fig. 5. The depression in the metal made by the ceramic is evident, but no sign of reaction products in either the metal or ceramic is present.

Because 1150° C is an unrealistically high ceramic/metal interface temperature, particularly for Si–SiC ceramics, the balance of the experiments were performed at 1000° C and 100 h. Macrophotographs of Y₂O₃ sputtered SiC (0.9 μm thick), the corresponding metal side, coated Si–SiC and metal after the 1000° C exposure are shown in Fig. 6. For the case of the Si–SiC/metal interface, 0.9 μm of Y₂O₃ was applied to both the metal and ceramic. Two features are immediately evident. Firstly, almost complete protection is provided by the Y₂O₃ and secondly, the Y₂O₃ has separated from both the metal and the ceramic. As indicated in the introduction, the presence of the

metal is necessary for coating separation to occur, because the coated ceramic itself can survive at least 26 1100° C to 25° C thermal cycles. The coated metal cannot; spalling occurs after 4 cycles.

X-ray analysis of surface scrapings of similar specimens (to be discussed below) indicated that some degree of chemical surface modification took place. To determine if these surface modifications provided protection from further metal/ceramic reactions, the surfaces of the specimens depicted in Fig. 6 were brushed free of loose coating debris and cleaned ultrasonically in acetone. No visual evidence of the coating was present on the SiC or metal, while about half the Si–SiC surface remained coated with the previously applied Y₂O₃. The metal/ceramic couples were re-assembled, placed into the reactivity apparatus for 100 h at 1000° C, disassembled, photographed, and analysed. The surface appearance of ceramic and metal is shown

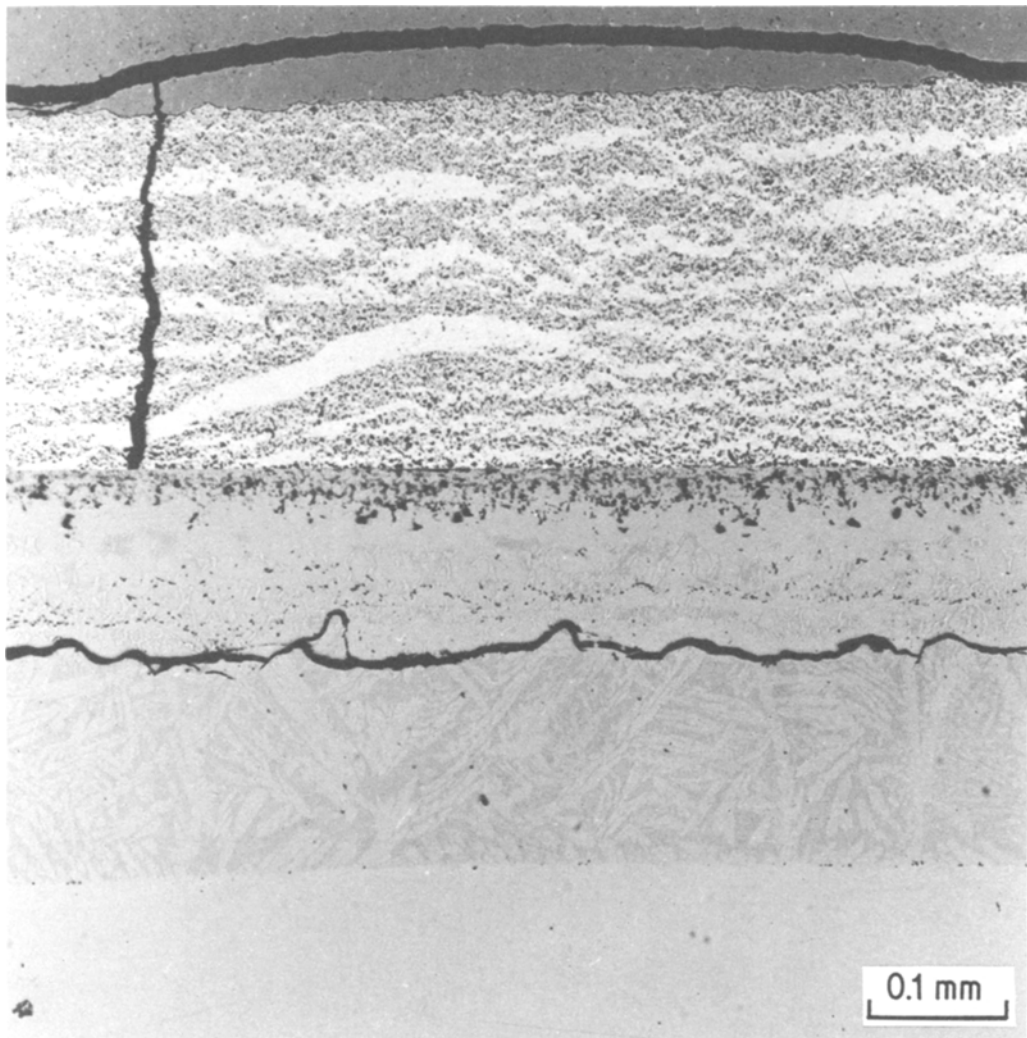


Figure 4 Montage photograph of the reaction between uncoated SiC and NiCrAl alloy after 1000 h at 1150° C. SiC is at top of figure.

in Fig. 7. Clearly, some degree of protection was provided even in areas where no obvious previous presence of Y_2O_3 was observed. In some areas the protection was not sufficient, and a reaction took place. However, when Fig. 1 and 7 are compared, it is evident a profound modification of the surfaces has occurred.

To attempt to determine the mechanisms of these surface changes, the techniques of X-ray diffraction analysis (XRD), X-ray fluorescence analysis (XRF), and Auger electron spectroscopy analysis (AES) were employed. In addition, X-ray maps of the specimen cross-sections were studied in a scanning electron microscope. Considering first the X-ray diffraction findings, analysis of the

spalled Y_2O_3 flakes (taken from the Si-SiC side) showed the presence of Y_2O_3 and, in some cases, a few faint unidentified lines. XRF analysis of the same flakes revealed that yttrium (in a major amount), chromium, nickel, and iron (in minor amounts) were present. Chromium and nickel are the major constituents of the model superalloy, and iron is present as an impurity in the Si-SiC, so some transfer of metal into the coating occurred. Whether this metal diffusion into the Y_2O_3 was the cause of coating spallation is not known.

XRD analysis of surface scrapings of both metal sides and the two ceramics indicated that Y_2O_3 was still present, although it appeared from Fig. 6 to have all flaked off, together with $\alpha-Al_2O_3$, vari-

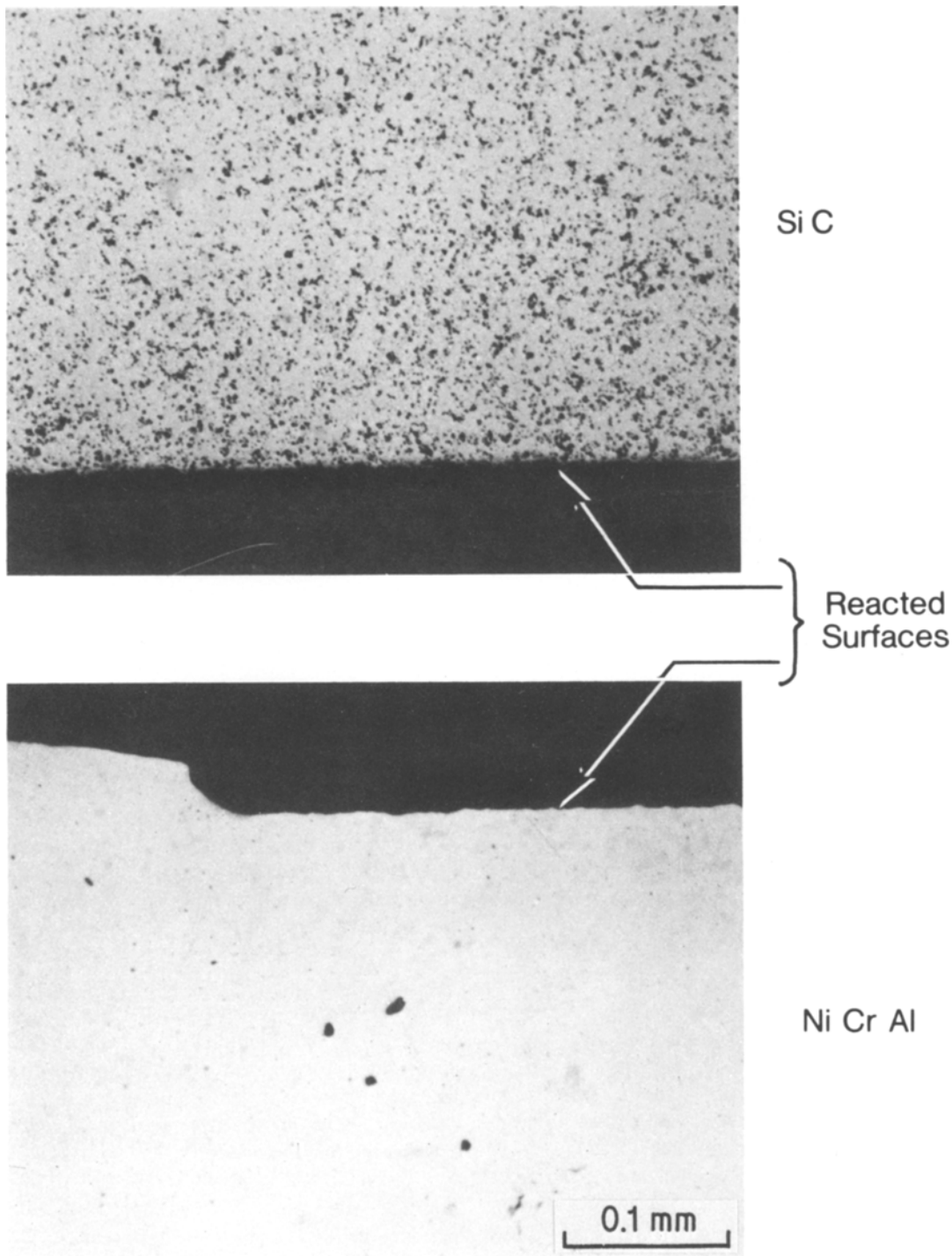


Figure 5 Photograph of Y_2O_3 coated SiC and NiCrAl alloy after 100 h at $1150^\circ C$.

ous spinels with $0.809 \text{ nm} \leq a_0 \leq 0.814 \text{ nm}$, and occasionally a trace of Y_2SiO_5 . These phases were not present on all the surfaces, and were present in various amounts. However, all the surfaces examined had at least some of these phases present.

It seems clear from these data that the previous presence of a Y_2O_3 coating provides protection to both metal and ceramic during elevated temperature exposure, and also leads to surface chemistry modifications.

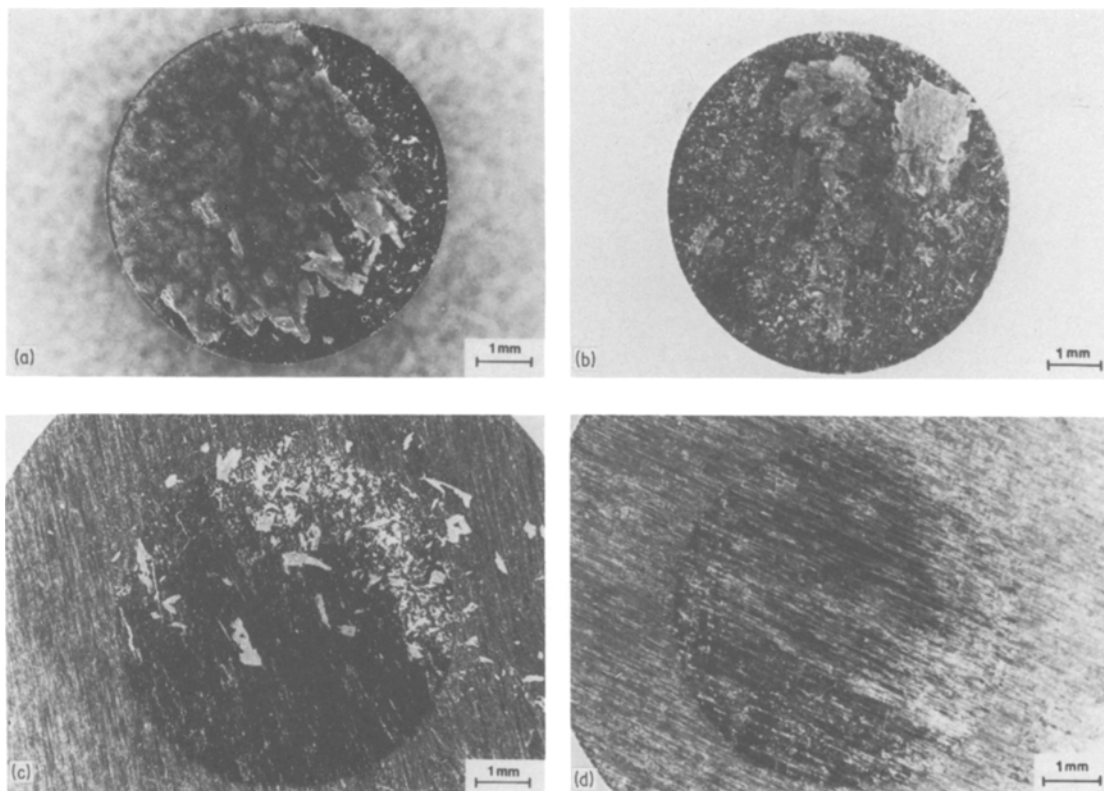


Figure 6 Macrophotographs of Y_2O_3 coated Si-SiC, SiC, and NiCrAl alloy after reaction at $1000^\circ C$ for 100 h. (a) Si-SiC surface; (b) SiC surface; (c) NiCrAl/Si-SiC surface; (d) NiCrAl/SiC surface.

The next analytical technique employed was AES, which is a very surface sensitive analytical technique capable of obtaining chemical information in the 0.5 to 2.0 nm region near the surface. Oxidation states of the atom can sometimes be determined because the Auger emission often involves valence electrons, and Auger peak shape and electron energy may change. An *in situ* argon ion gun is used both for sputter cleaning any airborne contaminants from the surface and for depth profiling. AES was performed on three of the mating surfaces previously described as having a second $1000^\circ C$ heat treatment (Fig. 7).

Auger spectra of the cleaned surface of the SiC specimen contains peaks for silicon, yttrium and oxygen (see Fig. 8). Using the argon ion gun a depth profile was made through this reaction layer to determine its approximate thickness. Fig. 8 shows a plot of this profile indicating a gradual decrease in yttrium until the SiC substrate is reached. Sputtering rates on a rough surface such as this are very difficult to determine. The roughness of the surface tends to lengthen the sputtering time and to smear out any sharp interfaces: these

effects must be considered when interpreting the profile in Fig. 8. We can say that there is a silicon, yttrium and oxygen layer on the silicon carbide substrate with an approximate thickness of several tens of nanometres.

The Auger spectra from the Ni-Cr-Al side of the Ni-Cr-Al/SiC interface are shown in Fig. 9. Elements present on this rough surface include nickel, chromium, aluminium, oxygen and yttrium. After 30 min of sputtering on this rough surface, little change in these elemental concentrations was observed, indicating the affected surface layer is at least several tens nanometres deep.

The Ni-Cr-Al side of the Ni-Cr-Al/Si-SiC interface was also examined, and showed the presence of Y_2O_3 with a small amount of nickel (see Fig. 9). After 30 min of sputtering on this rough surface, there was no change in composition of this oxide layer. This is consistent with the X-ray images shown below in Fig. 10, which identify the yttrium layer to be 1 to $2\ \mu m$ thick. These observations on the two metal surfaces are consistent with the experimental procedure. On the Si-SiC side, the metal had been initially Y_2O_3

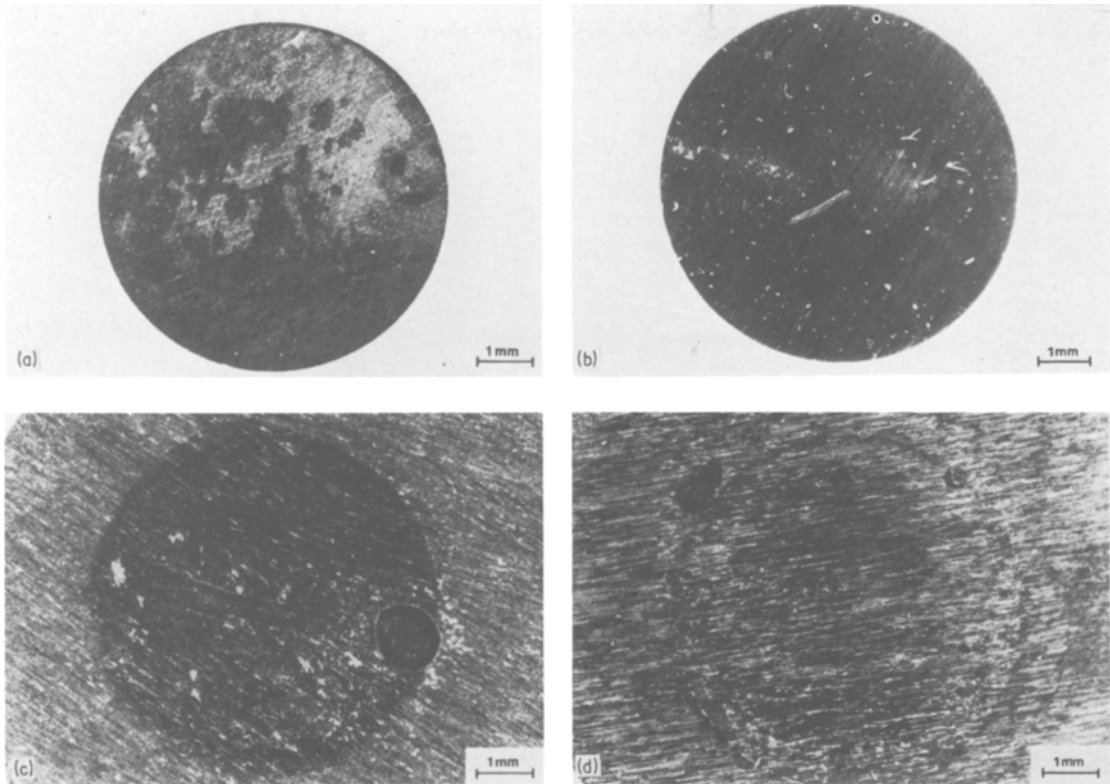


Figure 7 Macrophotographs of previously coated Si-SiC, SiC, and NiCrAl alloy after a second reaction exposure at 1000° C for 100 h. (a) Si-SiC surface; (b) SiC surface; (c) NiCrAl/Si-SiC surface; (d) NiCrAl/SiC surface.

sputtered, and after heating and apparent Y_2O_3 spallation, some Y_2O_3 was still present (also confirmed by XRD analysis). On the SiC side, however, the only constituents that can enter the surface must come from the SiC, because this side had not been previously coated with Y_2O_3 . The yttrium found on this side, then, came from the Y_2O_3 -coated SiC, either as yttrium or Y_2O_3 .

Additional chemical information concerning the surface can be obtained from qualitative and/or quantitative analysis of metallographic cross-sections of reacted samples in the scanning electron microscope. Quantitative electron microprobe analysis (EMPA) has been extensively used in past work in this laboratory dealing with ceramic/metal reactions [1, 2, 4, 5]. In the present case, the areas of interest in Y_2O_3 -coated SiC, Si-SiC, and NiCrAl alloy were very small in extent, making the use of quantitative EMPA analysis difficult. Consequently, qualitative X-ray maps of the various elements of interest (nickel, chromium, aluminium, silicon, yttrium and oxygen) were obtained in cross-sections of the two ceramics and

the alloy after the second temperature exposure. The cross-sections were taken away from the areas where a reaction did occur (see Fig. 7). In essence, all the samples showed the same features; no indication of large scale diffusion of silicon into the metal or nickel, chromium and aluminium into the ceramic. Where Y_2O_3 had been applied, yttrium X-ray maps showed yttrium to be present. The lack of large scale diffusion is in marked contrast to the case where no coating was present [1, 2].

The above may be illustrated by the most complex structure found; the NiCrAl side of the NiCrAl/Si-SiC interface, which had been Y_2O_3 coated. These maps are shown in Fig. 10. Adjacent to the metal is an aluminium and oxygen-rich layer, probably Al_2O_3 . Aluminium is available from the NiCrAl base material, and the reaction which in the uncoated case prevented O_2 migration into the diffusion couple does not occur in this case. This is followed by a zone of nickel and chromium, and then a chromium and oxygen-rich layer, perhaps a chromium oxide. Finally, a yttrium-rich layer is present on the outside surface. It appears that a

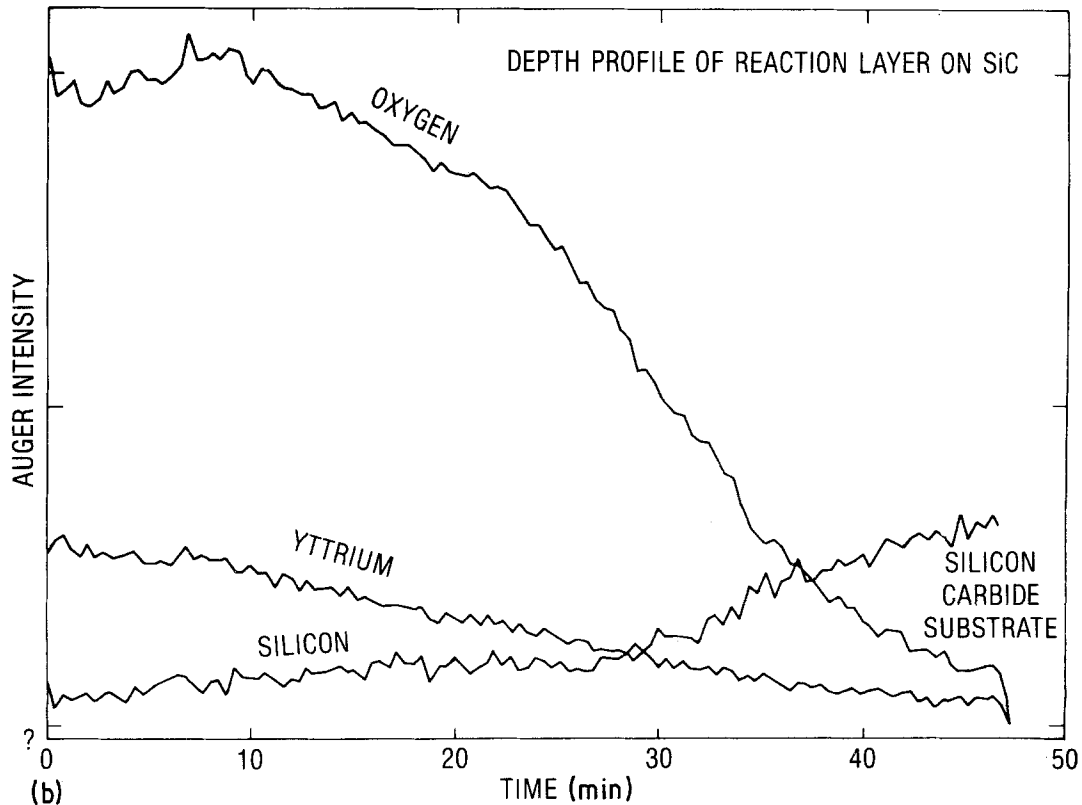
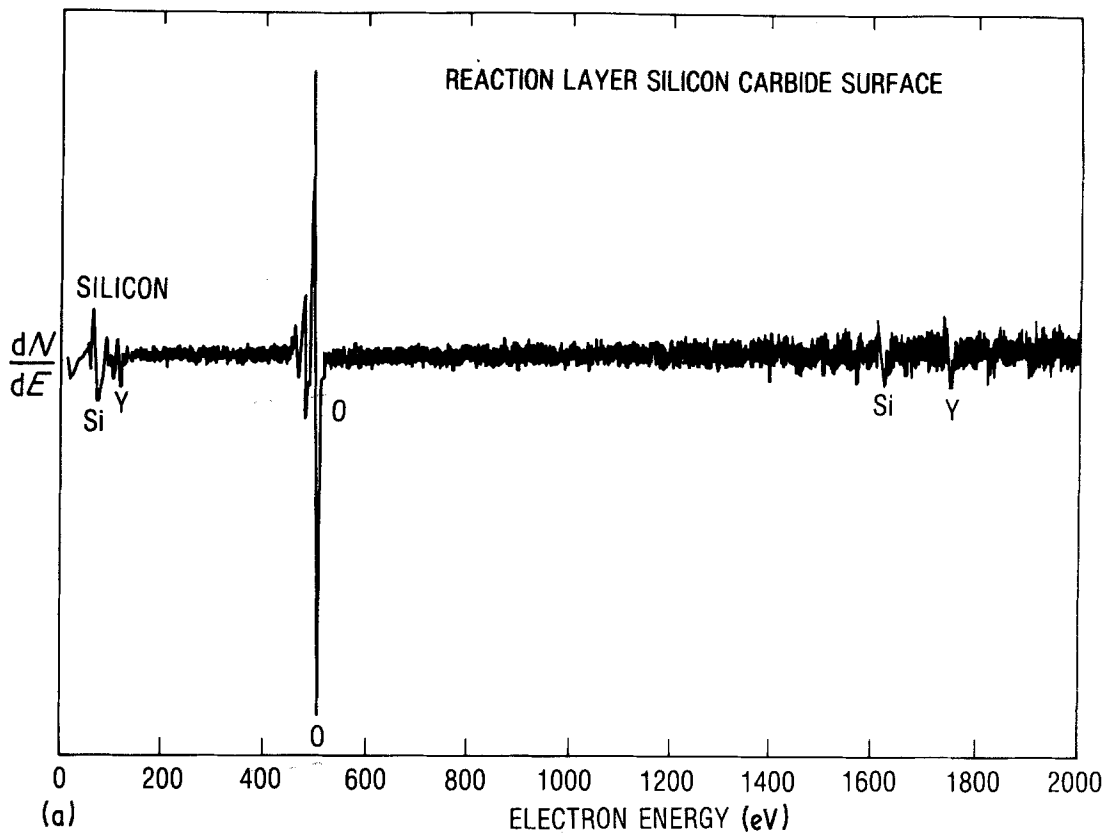


Figure 8 Auger derivative spectra of the reaction layer on the SiC surface (upper figure) and the depth profile through the reaction layer.

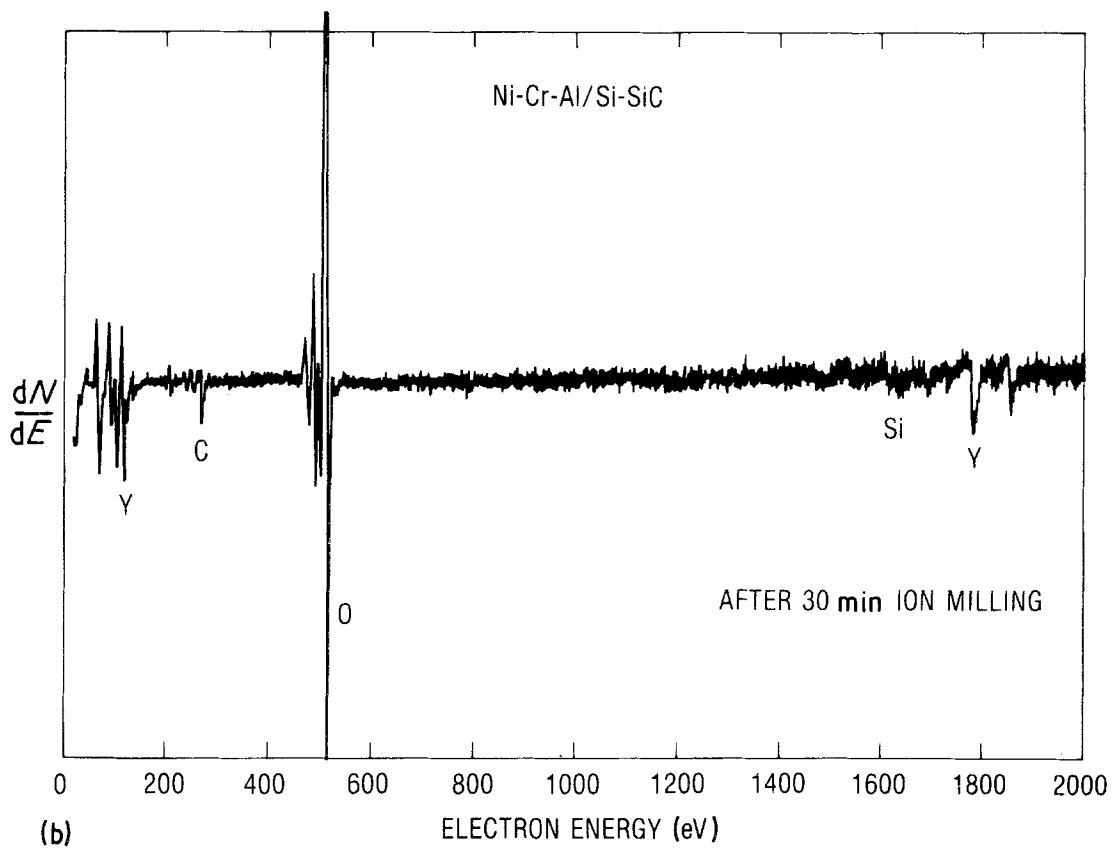
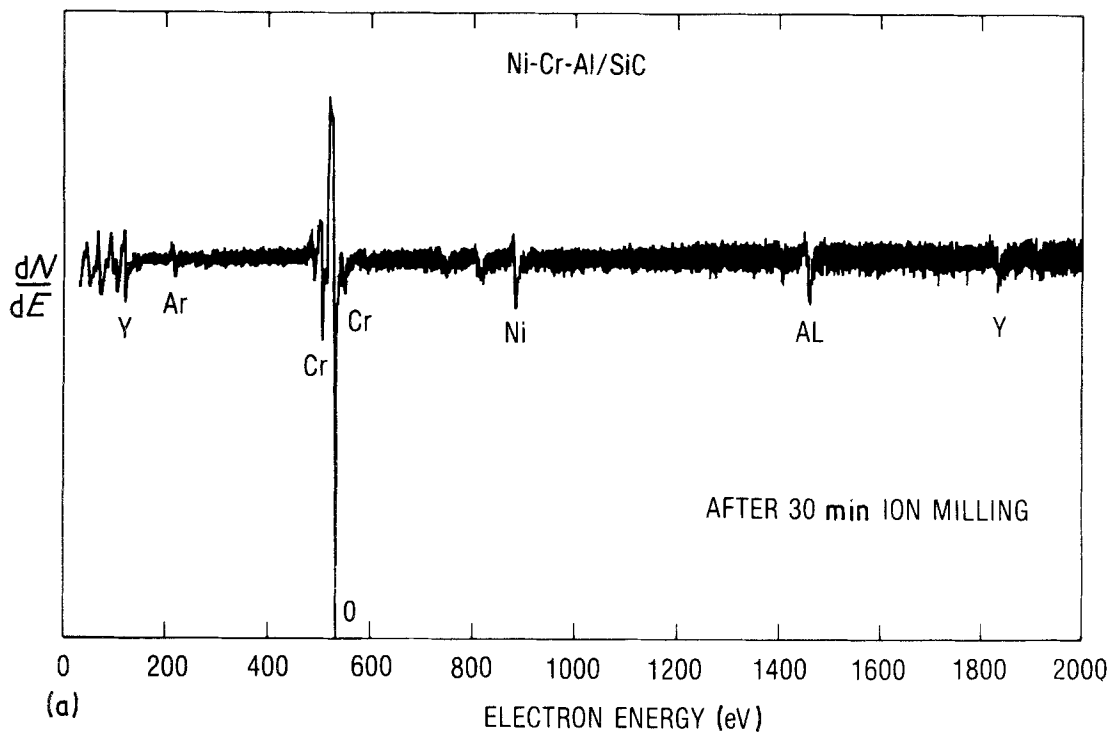


Figure 9 Auger spectra of the reaction layers on the NiCrAl specimen after reaction with SiC (upper figure) and Si-SiC.

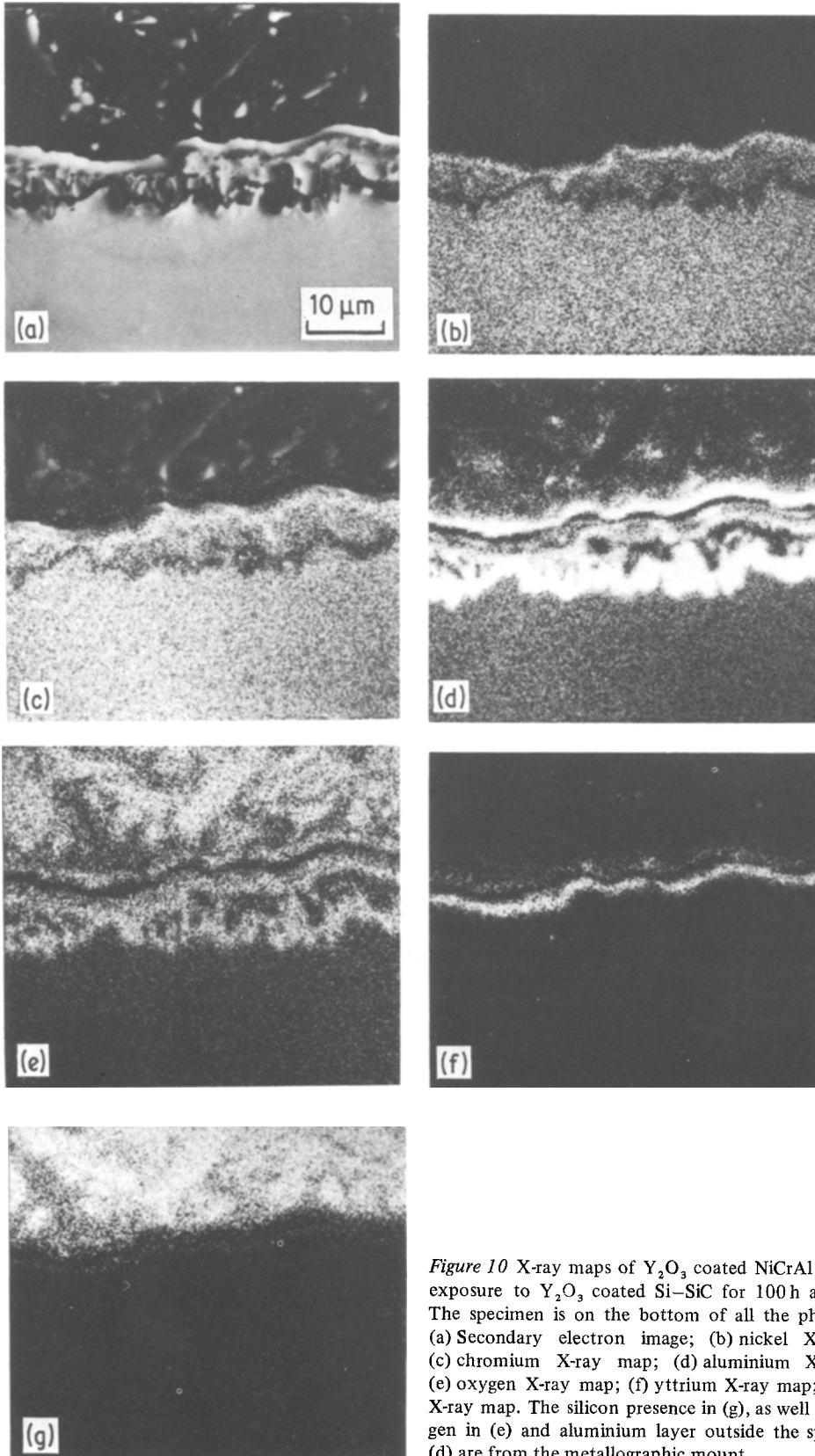


Figure 10 X-ray maps of Y_2O_3 coated NiCrAl alloy after exposure to Y_2O_3 coated Si-SiC for 100 h at $1000^\circ C$. The specimen is on the bottom of all the photographs. (a) Secondary electron image; (b) nickel X-ray map; (c) chromium X-ray map; (d) aluminium X-ray map; (e) oxygen X-ray map; (f) yttrium X-ray map; (g) silicon X-ray map. The silicon presence in (g), as well as the oxygen in (e) and aluminium layer outside the specimen in (d) are from the metallographic mount.

small amount of silicon may be present in the yttrium-rich area, suggesting the presence of the yttrium silicate detected by X-ray scrapings, but this apparent silicon signal could also be due to a change in background radiation.

The NiCrAl/SiC interface is similar to that described above, except the yttrium is absent. Both ceramics show the presence of a yttrium-rich phase, and no metal penetration (except, of course, in the areas where the protective film broke down).

The above analytical information can be summarized in terms of the protective mechanism of Y_2O_3 in reducing the ceramic/metal reaction. It seems clear that upon the first heating cycle when Y_2O_3 was present as an intact layer, its presence almost completely inhibited any gross reaction (see Fig. 5). At the same time during this heating period, Y_2O_3 probably reacted with other compounds or elements on both the ceramic and metal surfaces. Because of its high thermodynamic stability, it is unlikely that Y_2O_3 decomposed into its constituent elements. Indeed, the high negative free energy of formation of Y_2O_3 is the reason for choosing this oxide as a barrier coating [6]. Rather, it is likely that Y_2O_3 reacted with available elements such as silicon to form compounds such as Y_2SiO_5 . Other structures, although not identified by XRD, are possible.

Probably a variety of surface reactions took place, resulting in the formation of various yttrium compounds, including Y_2O_3 , on most of the surfaces involve. These compounds extended below the surface to a depth not exceeding about $10\mu m$, and in some cases no more than several tens of nanometres. In addition to these yttrium compounds, Al_2O_3 and various spinels were formed.

During the second heating cycle, where most of the original Y_2O_3 coating was no longer present (except for a portion on the Si-SiC), these surface modifications involving yttrium compounds, Al_2O_3 , and spinel almost entirely prevented gross ceramic/metal reaction (see Fig. 7). In a few areas, protection was not sufficient and Si from the ceramic entered the metal, and metal constituents diffused into the ceramic, leading locally to the type of metal/ceramic reaction previously observed [1, 2]. It is possible that a longer initial heating cycle of the ceramic/metal couple in the presence of Y_2O_3 would lead to more surface reactions extending deeper into the materials, and hence afford a greater degree of protection. However,

this is conjectural and needs experimental verification.

4. Conclusions

Based on the results presented above, the following conclusions may be drawn:

1. Y_2O_3 is an effective diffusion barrier in preventing Si-base ceramic/metal reactions at temperatures of $1000^\circ C$ and, for the case of SiC, at $1150^\circ C$.

2. The presence of the Y_2O_3 causes chemical surface modifications that provide additional protection, even though the Y_2O_3 coating appears to become detached from metal and ceramic after a single heating cycle.

3. The nature of this surface modification is not known in detail, but involves the reaction of Y_2O_3 with other elements and compounds to form compounds such as Y_2SiO_5 .

4. An additional degree of protection may be due to Al_2O_3 and/or spinel layers in the metal, which can form because of the absence of large scale silicon diffusion.

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