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The solid-state reaction of silicon nitride with an Ni-base alloy

R. L. MEHAN, M. R. JACKSON, M. D. McCONNELL, N. LEWIS
General Electric Company, Corporate Research and Development, Schenectady, New York, USA

The nature of the solid-state reaction between hot-pressed Si_3N_4 and a model Ni-based superalloy was examined and compared to that previously found with SiC. The Si_3N_4 reacted with the metal to a significantly lesser extent than SiC, presumably because of the dependence of the Si_3N_4/metal reaction on the partial pressure of N_2. Products of the reaction in both metal and ceramic were AlN, Ni_2Si, other Ni and Cr silicides, and probably a chromium nitride.

1. Introduction

The solid-state reaction between silicon-based structural ceramics and metals has been under investigation in this laboratory for several years [1–4]. The impetus for this work arises from the fact that if structural ceramics are to be used in hot machinery, at any hot ceramic–metal interface there exists the probability of a chemical reaction between the two materials, degrading the properties of both. An extreme example of such a reaction is shown in Fig. 1. The reaction-bonded Si–SiC has liquid silicon-rich phases present at temperatures above about 960° C, so severe metal–ceramic reactions take place. However, even hot-pressed SiC reacts to a significant extent at 1150° C.

Work conducted to date in this laboratory has concentrated on SiC, Si–SiC/metal combinations. The primary reason for this emphasis is the greater degree of reaction found in these systems as opposed to the Si_3N_4/metal reaction, which makes a greater amount of reacted material available for phase analysis. However, some work has been conducted on the Si_3N_4/metal system, and the purpose of this article is to describe the analysis conducted on this material combination.

2. Experimental procedure

The experimental procedure has been previously described [1], so only a brief review is necessary. The apparatus used is shown in Fig. 2. As-ground and cleaned cylindrical discs (6.35 mm diameter × 3.2 mm) are placed on either side of the metal disc (12.7 mm diameter × 3.2 mm) and the ceramic/metal/ceramic sandwich inserted into the apparatus. A tube furnace (not shown) is raised into place, a compressive stress of $7\,MN\,m^{-2}$ applied, and the assembly brought to temperature. The furnace ends were covered with insulation, but no inert atmosphere was used. To verify that oxygen was excluded from the interface by the tight contact (at least for the case where significant chemical reaction occurred, such as a SiC/metal reaction couple at 900° C), a reaction experiment in a vacuum at 10^{-6} torr was conducted. The same microstructural features were observed in both the air and vacuum experiment [3].

Hot-pressed Si_3N_4 and hot-pressed SiC were obtained from the Norton Co, USA, in billet form and diamond machined and ground into test blanks. The reaction-bonded Si–SiC was either Norton NC-435 or material fabricated in this laboratory.* The metal was a model superalloy, fabricated in this laboratory, consisting of 70 at% Ni, 20 at% Cr, and 10 at% Al. The composition was chosen to model an Ni-base superalloy consisting of γ and γ', neglecting the effects of carbides and borides [2].

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*Silicomp™ – trademark of the General Electric Co, USA.

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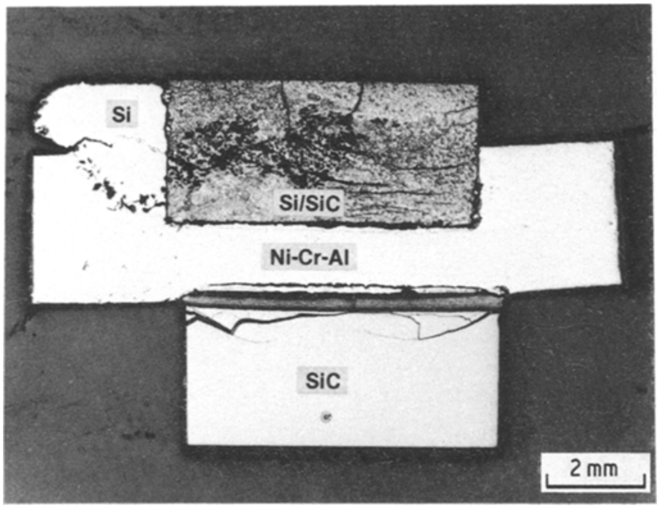

Figure 1 Macrophotograph of the reaction of Si–SiC, SiC, and NiCrAl alloy after 50 h at 1150° C.

3. Results and discussion

The microstructure of Si_3N_4 and the NiCrAl model alloy after reaction at 1150° C for 100 h is shown in Fig. 3. For comparison, an SiC/NiCrAl couple, reacted under the same conditions, is shown in Fig. 4 [3, 4]. The SiC–metal reaction is more severe and complex. The banded region consists of graphite, δ-Ni_2Si, and $Cr_{5-x}Si_{3-y}C_{x+y}$ (dark bands); the light bands are predominantly δ-Ni_2Si. In the metal a variety of silicides are found. In all, 14 individual phases have been identified in this five-component (Si, C, Ni, Cr, Al) system [3, 4].

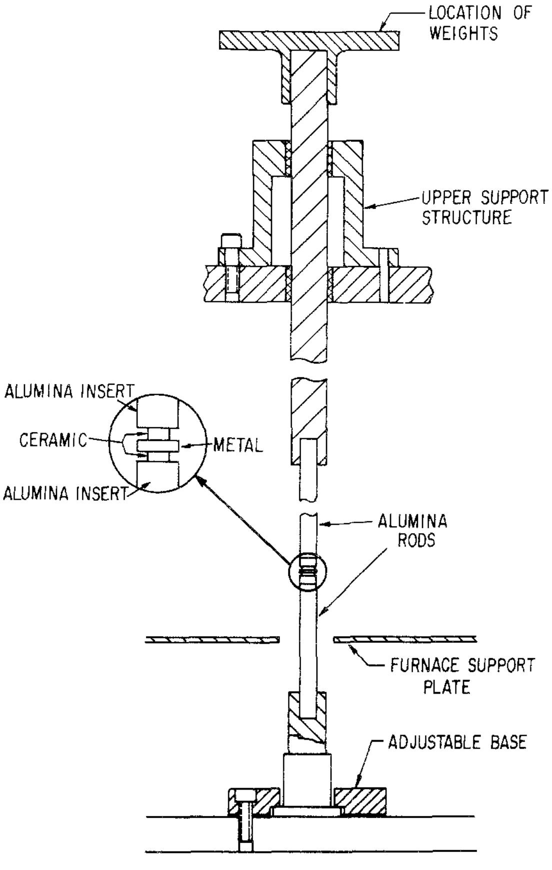

Figure 2 Experimental apparatus.

Considering now the Si_3N_4/NiCrAl reaction, the most salient observation is that it is less severe than that observed in the carbide systems and is discontinuous rather than continuous even at 1150° C. The maximum depth of reaction into the Si_3N_4 after exposure to the NiCrAl metal at 1150° C for 100 h is about 100 μm, as compared to 320 μm for the case of SiC. The reaction is barely detectable in the Si_3N_4 after a 264 h exposure at 1000° C (about 2.5 μm), while for SiC a depth of reaction of 160 μm is obtained under identical conditions. No reaction was observed in the Si_3N_4 at 100, 50, and 3 h at 1000° C, and no metallographic evidence of a reaction between Si_3N_4 and NiCrAl was found below 1000° C. The SiC/NiCrAl system has been found to be diffusion-controlled over the temperature range 700 to 1150° C [3, 4]. Although the data for the Si_3N_4/NiCrAl system are meagre, the lack of parabolic reaction behaviour at 1000° C and no evidence of a reaction below 1000° C make it unlikely the Si_3N_4 metal reaction is diffusion-controlled. A similar conclusion concerning the Si_3N_4/FeCr, Si_3N_4/Hastelloy X, and Si_3N_4/Nimonic 75 systems at 1000° C was reached by Bennett and Houlton [5].

The reason for the smaller reaction depth for Si_3N_4 as compared to SiC, and possibly for the different rate-controlling process, is the difference

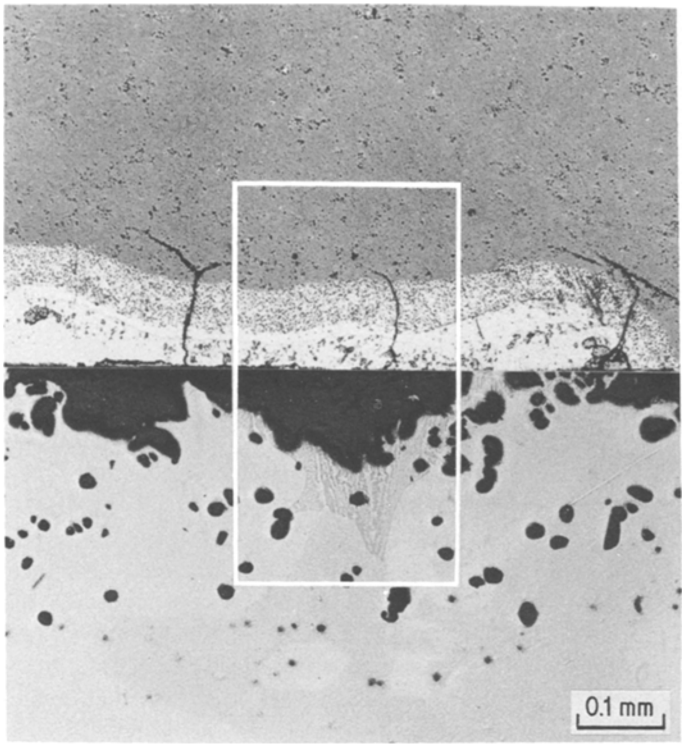

Figure 3 Reaction zones in Si_3N_4 and NiCrAl after 100h at 1150° C. Si_3N_4 is at the top of the figure. The area shown in the box was analysed by microprobe measurements.

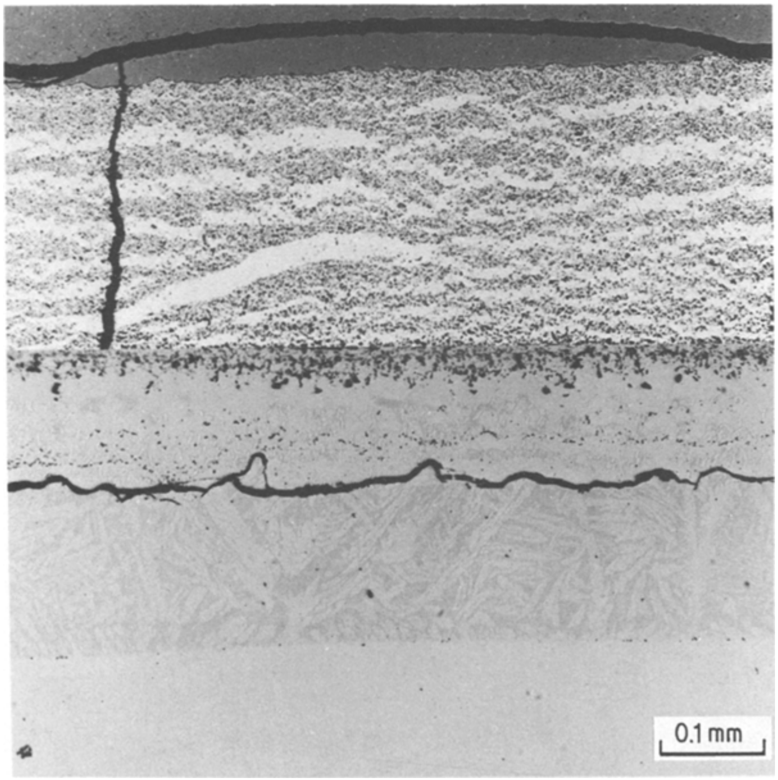

Figure 4 Reaction zones in SiC and NiCrAl after 100 h at 1150° C. SiC is at the top of the figure.

in the decomposition mechanisms. Silicon carbide decomposes via solid-state reactions, such as $SiC + Ni \rightarrow NiSi + C$, which are thermodynamically favourable for most Ni, Cr, and Fe silicides [6]. The decomposition of Si_3N_4, on the other hand, is strongly dependent on the environment, particularly the N_2 partial pressure. This was clearly shown by Andrews *et al.* [7], who demonstrated that reactions of the type $Si_3N_4 + 3Ni \rightarrow 3NiSi + 2N_2$ could be suppressed by a sufficiently high N_2 partial pressure. Although there is some danger in applying the above equation to more complex systems where nitrides may be formed, to a first approximation it should be applicable for silicide formation in the Si_3N_4/NiCrAl case. For the case of SiC/NiCrAl, if O_2 is initially excluded from the interface by the tight intimate contact between the mating surfaces, protective oxide films will not form* and the solid-state metal/ceramic reaction will occur and proceed independently of atmosphere. For Si_3N_4/NiCrAl, the reaction is probably governed by the N_2 partial pressure, which must be less than about 10^{-5} to 10^{-6} atm (for Si_3N_4/Ni at 1100° C) in order to proceed [7]. It seems reasonable that reactions at the metal/ceramic interface will occur only in localized areas, and this is indeed found to be the case. For the carbide ceramics, on the other hand, the reaction occurs over the entire interface for $T \geqslant 900°$ C, while at lower temperatures it occurs at local spots (for SiC) presumably because O_2 has had time to reach the interface and form oxide films.

The nature of the reaction between Si_3N_4 and the NiCrAl model alloy was examined at 1150° C, where a sufficient amount of reaction product was available for analysis. Figs 5 and 6 show a series of X-ray maps of the region indicated in Fig. 4. The maps were obtained using a Cameca MBX electron microprobe with crystal spectrometers. The maps of the metallic elements were taken with an accelerating voltage of 15 kV and a specimen current of 30 nA. The N maps were taken at 5 kV and 500 nA in order to optimize the peak-to-background signals. The use of crystal spectrometers and small acceptance windows on the amplifier enhances the peak-to-background ratios of the elements and makes the X-ray image a good representation of the true elemental distribution. In addition to the X-ray maps, quantitative analyses (EMA) were performed on the separate phases using a Cameca MS46 microprobe. X-ray diffraction data (XRD) were also obtained on scrapings of the reaction products on a similar reacted specimen.

Considering the metal half of the reaction couple first (Fig. 5), examination of the X-ray maps reveals that the N_2 from the Si_3N_4/NiCrAl reaction enters the metal to form AlN (Fig. 5b and c), also identified by XRD results. No evidence for CrN or Cr_2N is evident (Fig. 5e). This is not surprising in view of the higher negative free energy of formation of AlN than either CrN or Cr_2N (− 64, − 28, and − 26 kcal g^{-1} at^{-1}, respectively) [9]. In addition, Al is available to form AlN because it does not form silicides, while Cr can form a number of silicides. Nickel, of course, does not form a nitride.

Immediately beyond the AlN, there is a fine precipitate high in Si and Ni (this area is clearer in the optical photograph, Fig. 3, than the secondary electron image of Fig. 5a). Based on EMA data, the composition of this region is approximately Ni 70 at%; Si 28 at%; Cr 2 at%; Al 0.4 at%. This area appears to contain Ni_2Si, probably δ-Ni_2Si based on previous work with SiC/NiCrAl reaction couples [3, 4]. The small amount of Cr detected may be present in the Ni_2Si lattice. Other than these two areas, one composed almost entirely of AlN and the other containing predominantly Ni_2Si, the Si, Ni and Cr are uniformly distributed, probably as various silicides.

Turning to the Si_3N_4 side of the couple shown in Fig. 6, there is again evidence of the presence of AlN, both on the surface and in the form of the same particle-like precipitate found on the metal side (Fig. 6a, b and c). Al does not diffuse into the ceramic to as great a distance as does Ni and Cr. There is an Ni-rich (Fig. 6d) layer roughly corresponding to the area containing the AlN which, based on EMA data, is probably rich in Ni_2Si (Ni 71 at%; Si 28 at%; Cr 1.0 at%; Al 0.5 at%). Finally, there is a Cr-rich area (Fig. 6f) adjacent to the unreacted ceramic. EMA analysis shows about 38 at% Cr present, and 55 at% N (by difference). This is not inconsistent with the presence of a chromium nitride such as CrN, together with a small amount of Ni silicides. Admittedly, quantitatively determining the presence of an element by difference is not exact; however, only the areas containing AlN (Fig. 6b) and those high in Cr (Fig. 6f) showed high N values from EMA analysis by difference.

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*Pre-oxidizing the SiC and NiCrAl reduces, but does not prevent, the SiC/NiCrAl reaction at $T \geqslant 1000°$ C [8].

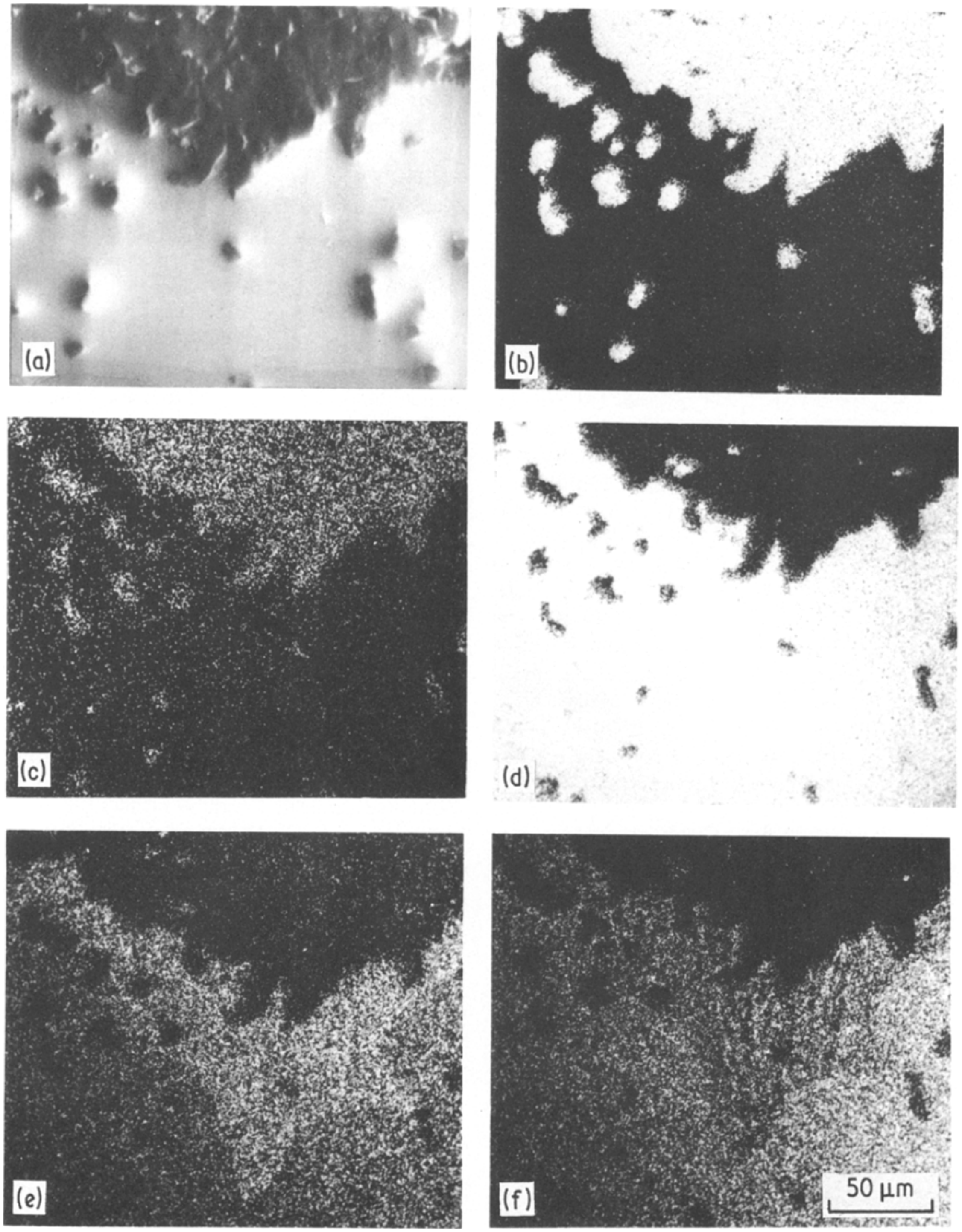

Figure 5 X-ray maps of reaction in NiCrAl after exposure to Si_3N_4 for 100 h at 1150° C: (a) secondary electron image; (b) Al X-ray map; (c) N X-ray map; (d) Ni X-ray map; (e) Si X-ray map; (f) Cr X-ray map.

4. Conclusions

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

(1) Si_3N_4 reacts to some extent with an NiCrAl model alloy, but to a significantly lesser degree than carbide-base ceramics;

(2) the reaction is probably not diffusion-controlled as in the case of SiC in contact with

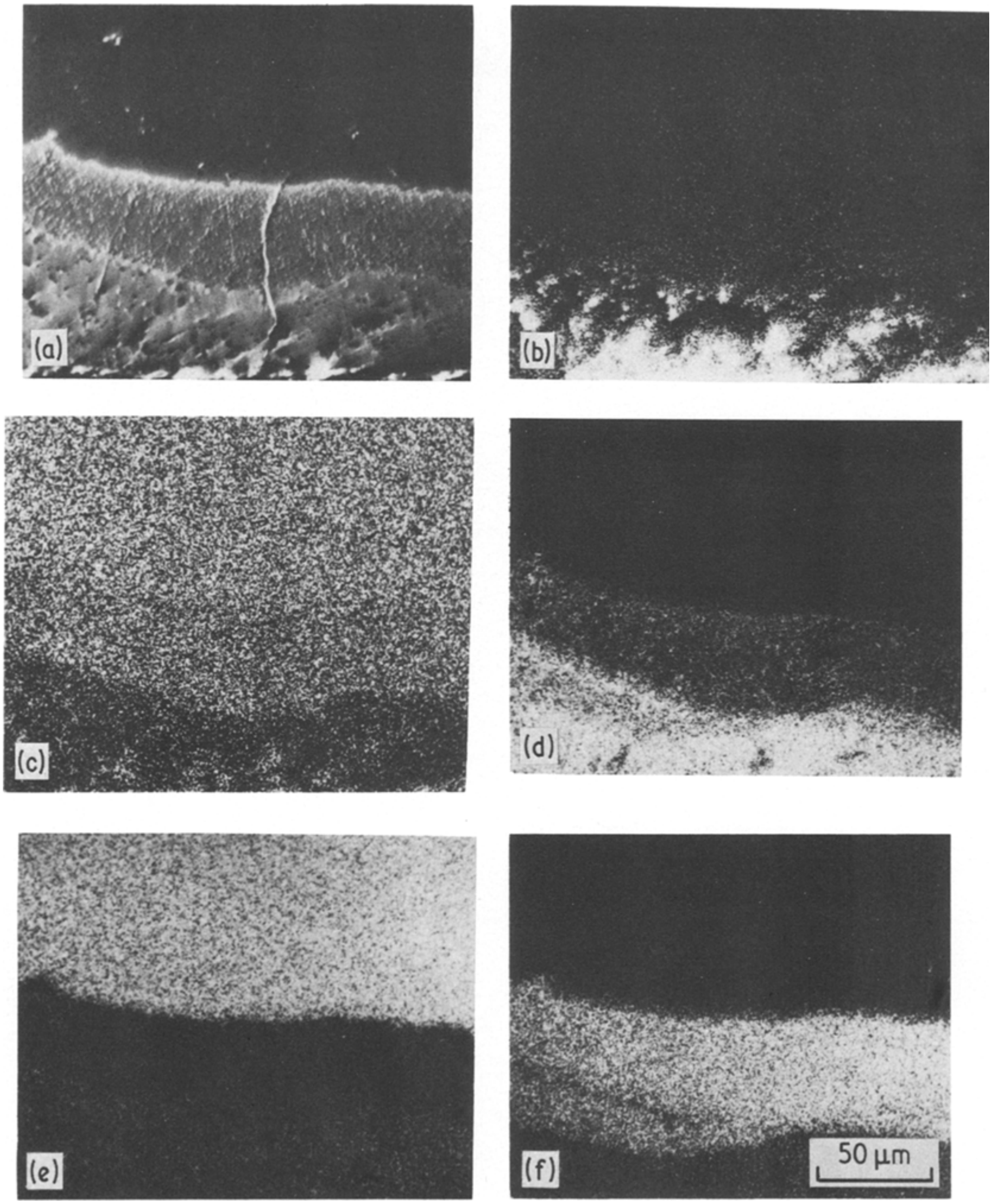

Figure 6 X-ray maps of reaction in Si_3N_4 after exposure to NiCrAl for 100 h at 1150° C: (a) secondary electron image; (b) Al X-ray map; (c) N X-ray map; (d) Ni X-ray map; (e) Si X-ray map; (f) Cr X-ray map.

the same alloy, and is strongly dependent on the local partial pressure of N_2;

(3) the primary products of reaction in the metal half of the couple are AlN, Ni_2Si, and other Ni and Cr silicides. On the ceramic half, AlN and Ni_2Si are again present, together with other silicides and probably a chromium nitride.

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