MASTER

A STUDY OF SOLID METAL/CERAMIC REACTIONS

Progress Report

3/17/80 to 1/15/81

on

Contract No. DE-AC02-79ER10413

U.S. Department of Energy
Chicago Operations Office
Argonne, Illinois 60439

by

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January 26, 1981

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I. Introduction

This study is concerned with the solid state reactions between silicon-based structural ceramics and a simple model superalloy. Such reactions are likely to occur if these ceramics are used in contact with metals in hot machinery operating over an extended period of time. A model superalloy was chosen to simplify the ceramic/metal reaction, yet remain representative of conventional superalloys. The intent of the study is to gain a fundamental understanding of the nature of these reactions in terms of phase equilibria concepts.

The first year of the program was devoted to the examination of the reactions occurring between SiC, Si/SiC, Si₃N₄, and a model NiCrAl superalloy⁽¹⁾. The extent and severity of these reactions was determined as a function of time and temperature, and some preliminary microanalysis information was obtained. Based on this somewhat limited analytical information, and using a hypothetical Si-C-Ni ternary diagram, tentative reaction paths in this system were proposed. However, the lack of firm identification of the phases present made this analysis somewhat tenuous.

During this past year, considerable effort was devoted to phase identification using microprobe, x-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM) analysis techniques. The relatively simple Si-C-Ni-Cr-Al system was found to be even more complex than anticipated, with at least 14 individual phases identified in the metal/ceramics reaction zone region. Nevertheless, by preparing diffusion couples consisting of SiC and Ni, NiCr, and NiCrAl, and reacting them at various temperatures, a reasonably satisfactory understanding of the overall reaction mechanism has been obtained. Obviously, in view of the complexity of the system, a complete analysis of the reaction would require far more work and, in our view, is unnecessary for solving the problem addressed; namely, what is the nature of the reaction, what constituents are most responsible, and how can it be avoided.

Our understanding of the Si-SiC/metal reaction is on reasonably firm ground, but some analyses are still in progress. Very little additional information has been obtained in the Si₃N₄/metal system, and work in this area is proposed for the coming year.

In the following sections, a brief description of the results obtained on reaction-bonded Si₃N₄/NiCrAl and SiC/NiCrAlTi couples will be discussed, as well as some preliminary work on diffusion barriers. However, the bulk of the report consists of an appendix containing four papers, all of which will be or have been submitted for publication. These papers contain most of the work performed to date on this contract. Also listed in the appendix are the presentations made by the authors during the past year.

(1) R. L. Mehan and M. R. Jackson, "A Study of Solid Metal/Ceramic Reactions", Progress Report, Contract No. DE-AC02-79ER10413, February 26, 1980.

II. Experimental Results

A. Reaction-bonded Si_3N_4 vs sintered Si_3N_4 . The reaction of sintered Si_3N_4 with NiCrAl at 1150°C results in the formation of localized areas of attack, usually just one area consisting of about 20% of the total area of contact. Similar behavior has been noted by Bennett and Houlton⁽²⁾. The depths of attack in the ceramic is about 1/3 that observed with SiC, and in the metal the depth is difficult to detect because of the discontinuous nature of the reaction (See reference 1, Fig. 12). Furthermore, no metallographically detectable reaction occurs at 1000°C, indicating a much higher activation energy for the reaction. Indeed, Bennett and Houlton⁽²⁾ have suggested that the rate of attack of silicon nitride at 1000°C by Nimonic 75 followed a linear rather than parabolic rate law, indicating that the rate controlling process may not be diffusion controlled.

The additional work performed on Si_3N_4 during this year's work involved the use of reaction-bonded Si_3N_4 (RBSN). The material used was NC-350, manufactured by the Norton Company. Because RBSN can be fabricated to near final shape, in this respect it is a more practical material than the hot-pressed material which requires diamond grinding. Of course, RBSN does not possess the high strength of the hot-pressed material, and it is more porous. Because of the different microstructure of RBSN it was considered of interest to see if the reactivity with metals differed from the hot-pressed material. It was found, however, that the metallographic appearance of the reaction at 1150°C was identical for both materials. It appears that the porosity in the RBSN, although it affects its oxidation behavior, does not affect its reactivity with metals.

Although some microprobe work has been performed on reacted specimens involving Si_3N_4 , no phase identification studies have been carried out. This work needs to be performed, and it is proposed to do it during the coming year.

B. Effect of Ti Additions. Because Ti is such an interfacially active material, it was considered of interest to see if the SiC/metal reaction would be accelerated by the presence of Ti. Two melts were prepared with part of the aluminum replaced by Ti; in one case approximately equal weight percentages of Al and Ti was used, and in the other approximately 2 1/2 times more Ti was employed. Reactions were performed at temperatures of 1150°C and 1000°C.

At 1150°C there did seem to be an acceleration of the reaction, but the microstructure was very difficult to interpret because of the depth the SiC had penetrated into the metal couples. Consequently, the experiment was repeated at 1000°C. At this temperature, the reaction depth into the ceramic was exactly the same as when Ti was absent. Microprobe measurements of this couple are to be performed.

(2) M. J. Bennett and M. R. Houlton, J. Mater Sci, 14 184 (1979).

C. Effect of Sputtered Coatings. From past work⁽³⁾ it is known that thin sputtered ceramic coatings can profoundly affect the reaction between a metal and ceramic. In general, the higher the thermodynamic stability of the coating is with respect to the other components in the system, the greater the degree of protection. Based on past experience, Y_2O_3 ($\Delta F = -136,000$ cal/gm atom O_2) and Al_2O_3 ($\Delta F = -125,600$ cal/gm atom O_2) have provided some degree of protection in ceramic system. Consequently, several pieces of SiC and NiCrAl were sputter-coated with a 1.8 μm thick layer of Y_2O_3 in one case, and Al_2O_3 in the other. Reactivity experiments were performed with SiC, Si/SiC, and NiCrAl at 900°C and 1100°C for 100 hours in the case of Y_2O_3 , and 1000°C in the case of Al_2O_3 .

At 900 and 1000°C in the case of Y_2O_3 , the effect on the degree of reaction was profound. In no case was a reaction detected in the ceramic. At 900°C, a barely perceptible reaction was visible on the metal side of the Si/SiC-metal interface, and at 1000°C, the degree of reaction was only slightly larger. Bearing in mind that at 1000°C Si/SiC and NiCrAl react severely with no coating present, these results are very promising.

One observation made in the course of these experiments is interesting and puzzling. In the coating experiments, either the ceramic or the metal was coated, not both. The sandwich arrangement for both these experiments was SiC (Y_2O_3 coated)/NiCrAl (Y_2O_3 coated)/Si-SiC. In other words, at the SiC/NiCrAl interface the coating had been sputtered on the SiC, and at the Si-SiC/NiCrAl interface the coating was on the metal. It was observed, after test, that the Y_2O_3 coating on the SiC had turned milky and tended to spall off, but on the metal side the coating was not discolored and adhered tenaciously to the NiCrAl. Because the coefficients of thermal expansion are similar for the ceramics, and very dissimilar for the metal/coating combination, the opposite behavior would be expected. No explanation is available for this behavior.

Concerning Al_2O_3 coatings, only experiments at 1000°C were conducted, and the same coating arrangement was used as in the case of the Y_2O_3 . In the case of the Si/SiC, the coating broke through in two places, leading to a severe reaction similar to that in the absence of a coating. Alternately, it is possible that an Al_2O_3 coating is not able to prevent the diffusion of Si into the metal. On the SiC side, no reaction was evident, but again the coating became slightly milky but did not spall off.

III. Presentations, 1980 and 1981

1. R. L. Mehan

Paper presented at the 7th LBL/MMRD International Materials Symposium, Berkeley, California, July 13, 1980. Conference title: Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems.

2. M. R. Jackson

Paper presented at the 5th Annual Conference on Composites and Advanced Ceramic Materials, Merritt Island, Florida, January 21, 1981. Sponsored by the American Ceramic Society.

(3) R. L. Mehan and M. J. Noone, "Nickel Alloy Reinforced with α - Al_2O_3 Filaments". In K. G. Kreider, ed., Metallic Matrix Composites - Vol. 4 Academic Press, New York, 1974, p. 159.

IV. Appendices

1. M. R. Jackson, R. L. Mehan, A. M. Davis, and E. L. Hall, "Solid State SiC/Metal Reaction: I. General Considerations and Mechanisms" To be submitted for publication in Metallurgical Transactions.
2. E. L. Hall, A. M. Davis, M. R. Jackson, and R. L. Mehan, "Solid State SiC/Metal Reaction: II. Microstructural Analysis and Phase Identification" To be submitted for publication in Metallurgical Transactions.
3. M. R. Jackson and R. L. Mehan, "Reactions of Ni and Ni-Based Alloys with Si-Based Carbide Ceramics" To be submitted for publication by the American Ceramic Society.
4. R. L. Mehan and M.R. Jackson, "A Study of Solid Metal/Ceramic Reactions" To be published in the Proceedings of the Symposium on Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems at Berkeley, 7/28-8/1/80.

SOLID STATE SiC/METAL REACTION:

I. GENERAL CONSIDERATIONS AND MECHANISMS

by

M.R. Jackson, R.L. Mehan,

A.M. Davis, and E.L. Hall

ABSTRACT

The solid state reaction between silicon carbide and a model superalloy consisting of 70 a/o Ni, 20 a/o Cr, and 10 a/o Al was studied between 700°C and 1150°C for times ranging from "0" hours to 330 hours. Reaction couples consisting of SiC/Ni, SiC/Cr, and SiC/NiCr were also studied. The reactions were carried out in air with the materials, in the shape of discs, maintained in contact under a pressure of 7MPa. A reaction was detected with SiC and the model alloy at all temperatures studied, and the reaction was diffusion controlled with an activation energy of 43.6 kcal/mole. In the ceramic the reaction was dominated by the diffusion of Ni into the ceramic forming a banded structuring consisting of alternating layers of δ -Ni₂Si and a two phase mixture of graphite and δ . On the metal side, the reaction was very dependent on the presence of alloying elements, with pure Ni reacting to the greatest extent, followed by the binary NiCr alloy, and finally by NiCrAl. The growth and presence of the phases detected in these reactions is consistent with phase equilibria concepts.

1. Introduction

Silicon-based structural ceramics such as SiC and Si_3N_4 are under active consideration for structural use in hot machinery such as gas turbines. In these applications, ceramics and metals will be in contact with each other at temperatures of at least 1000°C . Because the ceramic and metal must be in intimate contact in order to prevent vibration induced stresses in the ceramic, oxygen will tend to be excluded at the interface. Under such reducing conditions, the protective oxide films will not form and the possibility exists for a chemical reaction between the metal and ceramic. This may lead to severe degradation of the strength of both materials in service.

Ceramic-metal reactions under inert or reducing conditions were the subject of intensive study some fifteen years ago in connection with the development of metal matrix composites, and much of this work has been summarized.^(1,2) It has been known since 1966, for example, that SiC filaments react in a reducing environment with Fe, Co, and Ni at temperatures as low as 700°C .⁽³⁾ More recently, Cornie et al. reported on the reactivity of SiC filaments with a number of nickel-based superalloys, as well as with an Fe-Cr-Al-Y alloy.⁽⁴⁾ All the alloys reacted to some extent with SiC during hot isostatic pressing in vacuum at 996°C , forming silicides in both metal and filament. The existence of these and similar reactions has been the primary barrier to the development of metal matrix composites using boron, SiC, or Al_2O_3 filaments in any metal matrix with a melting point higher than Al.

More recently, the reactions between SiC, Si_3N_4 , and reaction bonded SiC with complex superalloys have been studied^(5,6,7). The intent of these studies was to directly assess the degree of chemical interaction between these materials under conditions similar to those that could be encountered in hot machinery applications. However, most of this past work, including that performed with reinforcing filaments, was phenomenological in nature because of the complex chemistry of superalloys. No real attempt has been made to study the fundamental nature of such reactions, nor have phase equilibria concepts been applied to the reactions.

The present work was undertaken to apply such techniques to reactions between silicon-based ceramics and metal. In order to simplify the chemistry of the metal/ceramic reaction, and at the same time obtain results applicable to actual superalloys, a model superalloy consisting only of Ni, Cr, and Al was used in these studies. Several ceramics have been used, but the present paper will only consider hot pressed and sintered SiC in detail, although some results pertaining to reaction - bonded SiC will be discussed. More detailed discussions of the behavior of the reaction-bonded material, as well as Si_3N_4 , will be presented in future publications. This paper deals with the general nature of the reaction and phase relations; part II discusses the details of phase identification.

2. Experimental

2.1 Materials

The hot-pressed SiC was manufactured by the Norton Company, and the sintered material⁽⁸⁾ was fabricated in this laboratory (General Electric Corporate Research and Development Center). The reaction-bonded ceramics containing free silicon used in some of the study came from two sources; NC-435 from the Norton Company, and Silcomp^{TM(*)} fabricated in this laboratory.⁽⁹⁾ No difference in reactivity between the latter two materials was noted.

The model superalloy was fabricated in this laboratory and had a composition of 70 a/o Ni, 20 a/o Cr, 10 a/o Al (75.8 w/o Ni, 19.2 w/o Cr, 5.0 w/o Al). In this model alloy, the complexity is lessened by the fact that only nickel and chromium are silicide formers. The rationale for this choice is as follows: In general, nickel-based superalloys are 0.95 to 0.98 volume fraction $\gamma + \gamma'$, where γ is the face centered cubic nickel solid solution and γ' is an ordered structure based on Ni_3Al . The remaining small volume fraction consists primarily of carbides and borides. One approach to developing a model composition, therefore, is to eliminate all phases except γ and γ' . The elements frequently employed for solid solution strengthening of γ are chromium, molybdenum, and tungsten at total

*TM - Trademark of the General Electric Company, USA.

levels of 14 to 30 atomic percent. To approximate the solid solution elements and to provide oxidation resistance, the model alloy contains 20 atomic percent chromium. The γ' phase in commercial materials is generally strengthened by partial substitution of aluminum by titanium, tantalum, and niobium. The total of aluminum and these other elements is in the range of 6 to 12 atomic percent; thus, the model alloy contains 10 atomic percent aluminum to approximate the composition of the γ' forming elements. Several experiments with Ni-Cr at a composition of 80 a/o Ni, 20 a/o Cr (81.8 w/o Ni, 18.2 w/o Cr) and with pure Ni and Cr were also performed in order to gain further insight into the pertinent phase relationships.

2.2 Reaction Couples

The ceramic specimens were machined into coupons 6.35 mm in diameter and 3.18 mm thick. The metal specimens had the same thickness but were 12.7 mm in diameter. Prior to assembly, the metal specimens were polished on 400 and 600 mesh SiC paper and the ceramics were used in the as-ground condition; both were cleaned with acetone prior to assembly in a reaction couple. The couple usually consisted of a ceramic/metal/ceramic sandwich and was placed into the apparatus shown schematically in Figure 1. In some cases the order was reversed (metal/ceramic/metal). Generally, two different ceramics were run against the same metal piece. The couple was loaded to 222 N, leading to a stress of 7 MPa at the interface. The specimens were surrounded by a platinum wound tube furnace (not shown in Fig. 1), brought to temperature in about 30 minutes and held there for the required time, ranging from "0" time to 330 hours. The furnace ends were covered with insulation, but an inert atmosphere was not used.

After a reaction run had been completed, the ceramic and metal pieces were removed, cut in two, examined metallographically, and then subjected to other analytical investigations. Initially, the ceramic and metal coupons were separated and sectioned individually, but it was found that during this process some pieces of the reaction product

were lost. The sectioning method adopted, at least in those cases where sufficient reaction occurred to cause the individual coupons to adhere to each other, was to encase the entire reaction "sandwich" in clear plastic and then section the mount. A macrophotograph (Fig. 2) showing such a section will be discussed subsequently .

3. Results

3.1 Nature of the Reaction

Metallographically, a reaction was detected in both the model alloy and SiC at all temperatures investigated (700°C - 1150°C). More severe reactions were detected with the reaction-bonded (Si-SiC) material. This is illustrated in Figure 2, where a load of 222N was applied at 1150°C for 50 hours. A molten Si-rich liquid was extruded at the Si-SiC/metal side, and obviously a great deal of liquid phase interdiffusion took place. By contrast, the hot pressed SiC/metal side showed a much smaller (but still severe) zone of reaction. This SiC/metal reaction will be the emphasis of this and the following paper. The macrophotograph in Figure 2 also illustrates that the apparatus shown in Figure 1 is capable of applying a uniformly distributed load.

A typical hot-pressed SiC/NiCrAl reaction, in this case at 1150°C , is shown in a montage microphotograph, Figure 3. For clarity, the gap, presumably caused by a thermal expansion mismatch between the reacted SiC and the metal (see Figure 2), has been removed. The reaction consists of three distinct zones: a banded structure in the SiC at the top of the photograph, a transition zone in the metal, and a metal reaction zone. Not evident from the photomicrograph is an area beyond the metal reaction zone where Si has diffused into the NiCrAl to a maximum concentration equal to the solubility limit. The original interface, determined by dimensional measurements and the use of fine quartz filament markers, is at the interface of the banded region and the transition zone. These metallographic features persist in decreasing quantities as the reaction temperature and

time are reduced. Figure 4 shows the reaction between SiC and the model NiCrAl alloy at 900°C. The same general features are seen to be present as at higher temperature, although the phase morphology in the metal reaction zone is different. Figures 5 and 6 show the results of typical electron probe microanalysis traces through the reaction zones of the ceramic-metal couples depicted in the previous two micrographs. The similarity of the two analyses is apparent, except at 900°C there is only a very small Si diffusion zone, while at 1150°C Si has diffused more than 200 μm into the metal after all metallographic evidence of a chemical reaction has vanished. This is likely due to greater solubility and diffusivity in NiCrAl at the higher temperature. For the reaction at 1150°C (Figures 3 and 5), a carbon analysis was performed and the results are shown in Table I. As may be seen, a carbon gradient is present in the banded structure of the SiC reaction zone and is vanishingly small in the metal reaction zone.

Based on the transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and X-ray diffraction (XRD) data presented in part II, the dark bands in the SiC reaction zone contain graphite, $\delta\text{-Ni}_2\text{Si}$, and a small amount of chromium silicon carbide ($\text{Cr}_{5-x}\text{Si}_{3-y}\text{C}_{x+y}$), while the light bands contain $\delta\text{-Ni}_2\text{Si}$ and trace amounts of $\text{Cr}_{5-x}\text{Si}_{3-y}\text{C}_{x+y}$. In both bands some white particles are observed, identified as WC. A W-rich fcc phase was also identified. Some unidentified phases are present in the bands and elsewhere in the reaction areas. The size and volume of these phases was generally too small to allow the analysis, an indication of the complexity of the mixed silicides that may form. It should be noted that even in the layers containing graphite, the predominant species are Ni and Si, as can be seen in Figure 5.

In the transition zone (arbitrarily named because it exists between a clearly defined ceramic and metal reaction area), an η' phase is predominant, with Al_2O_3 also present. The metal reaction zone which occurs between the transition reaction zone and the NiCrAl matrix, was shown by XRD, TEM and STEM to have a complicated structure containing several phases. At temperatures above 1000°C, a coarse columnar structure

develops (see Figure 3). This structure was characterized by XRD as γ -Ni, with interdendritic appearing regions of γ' -Ni₃(Al,Si) and η' -Cr₃Ni₂SiC. Small amounts of β -NiAl were also tentatively identified. STEM analysis confirmed the presence of γ + γ' , and also detected Cr₃Si and α -Cr. At lower temperatures, a different structure develops in the metal reaction zone (see Figure 4). This structure has not been analyzed in detail, but appears to contain a Ni-rich and Cr-rich phase. Similar columnar growth is observed in aluminized Ni-base alloys, where the Cr-rich phase corresponds to α -Cr.⁽¹⁰⁾

The details of the phase distribution in the metal reaction zone, and in the other reaction zones are discussed in Part II.

3.2 Effect of Sintered SiC

If sintered SiC is used in place of hot-pressed SiC, the nature of the ceramic reaction zone is similar but the banding in the SiC reaction zone is coarser, as shown in Figure 7. Microanalysis shows no difference in the compositions of various portions of the reaction zones, and the depths of penetration into the SiC and metal seem to be the same. The only difference detected chemically between these two types of SiC was the presence of WC in the hot pressed material found by XRD. The carbide was present in the form of small white particles, and was found in both the unreacted and reacted areas of the SiC. The WC was presumably introduced into the hot pressed SiC during manufacture, probably when milling the powder prior to hot pressing. XRD analysis showed that the WC particles are not present in the sintered SiC. In the reaction zone of the hot pressed material, particles are present, and associated with them is the W-rich phase. Although the exact mechanism is not clear, it seems that when the SiC dissociates into Si and C because of the inward diffusion of (primarily) Ni, the WC particles either prevent the growth in width of the graphite containing bands in the hot pressed SiC, or, more likely, serve as nuclei for more frequent initiation of these bands. Whatever the cause, the overall nature of the reaction is not altered in terms of extent and severity of chemical attack.

3.3 Effect of Alloy Chemistry

In order to gain additional understanding of the effect of the individual constituents in the overall SiC-model alloy reaction, reactivity experiments with Ni, Cr, and an alloy consisting of 80 a/o Ni and 20% a/o Cr were performed at several temperatures using only the hot pressed SiC; the results are discussed below.

3.3.1 SiC-Ni Reaction. With Ni alone at both 1000°C and 1150°C, the same banded structure observed in the model superalloy is formed in the SiC reaction zone. This is seen clearly in Figure 8, which is a micrograph of the SiC-Ni interface after a 100 hour exposure at 1000°C. The microprobe trace through this reacted area is shown in Figure 9. Comparing the Ni and Si values in the reacted SiC with those in Figure 5, it is seen that graphite and $\delta\text{-Ni}_2\text{Si}$ are present (verified by TEM and XRD analysis). In view of nickel's well known ability to act as a graphitizer, as well as not forming a carbide, perhaps this is not a surprising result. It seems clear that Ni is responsible for much of the reaction observed in the SiC by the model NiCrAl superalloy. However, the complete absence of the transition reaction zone and metal reaction zone in Figures 5 and 6 indicate that Cr and Al play a significant role in the overall reaction.

When Ni and SiC are reacted at 1150°C, the extent and severity of the reaction increases, but the basic chemical nature remains unchanged. This may be seen in the montage micrograph, Figure 10. The same banded structure with the metal content consisting of 60-70 a/o Ni and about 40-30 a/o Si, is observed adjacent to the SiC, followed by a porous region and then a reaction zone in the metal. The reaction products are primarily $\delta\text{-Ni}_2\text{Si}$ and graphite, based on microprobe measurements.

3.3.2 SiC-Cr Reaction. At 1000°C with a 100 hour reaction time, Cr and SiC react to a very small extent. Metallographically, a layer about 10 μm was found on the SiC and no detectable reaction was observed in the Cr. Microanalysis suggested the presence of a chromium carbide, and perhaps a chromium silicon carbide ($\text{Cr}_{5-x}\text{Si}_{3-y}\text{C}_{x+y}$). X-ray

diffraction identified Cr_3Si and several carbide phases including Cr_7C_3 , Cr_{23}C_6 and $\text{Cr}_{5-x}\text{Si}_{3-y}\text{C}_{x+y}$. Clearly, Cr by itself has much less effect on the severity of the reaction than elemental Ni.

3.3.3 SiC-NiCr Reaction. The reaction between a binary alloy consisting of 80 a/o Ni and 20 a/o Cr at 1150°C and 100 hours is shown in the micrograph of Figure 11. The corresponding microanalysis of the reaction zone is given in Figure 12. Although a small amount of Cr has diffused into the SiC reaction zone, the banded structure in the SiC reaction zone is still dominated by the presence of graphite and $\delta\text{-Ni}_2\text{Si}$, caused by the diffusion of Ni into the SiC. However, in the metal, microanalysis and x-ray diffraction of the reaction zone are consistent with the formation of $\eta'\text{-Cr}_3\text{Ni}_2\text{SiC}$. The η' phase was positively identified for reactions involving NiCrAl, so its presence as a product of the SiC-NiCr reaction is not unexpected. It is of interest to note the absence of the transition reaction zone found for the case of the SiC-NiCrAl reaction (Fig. 5), as well as the completely different nature of the metal reaction zone. For the case of the NiCrAl metal reaction zone, Ni, Cr, and Si are present in the approximate weight percent ratio of 10:1:0.8, while in the NiCr case the corresponding ratios are 4:5:1. Evidently, Al has a profound effect on the mechanism of the reaction of SiC and the NiCrAl model superalloy.

3.4 Reaction Kinetics

To date, only the kinetics of the reaction between SiC and the model superalloy have been studied systematically. On the assumption that the reaction is diffusion controlled, and hence the reaction zone thickness follows a parabolic growth law, the thicknesses of the SiC reaction zone and metal reaction zone (including the transition zone) have been plotted at various temperatures as a function of the square root of time in Figures 13 and 14, respectively. As may be seen by the linear relationships, the

reaction does seem to be diffusion controlled. By plotting the logarithm of the rate of reaction thickness, in $\text{cm sec}^{-1/2}$, vs the reciprocal of the absolute temperature, the activation energy for the process can be calculated. The Arrhenius plot is shown in Figure 15, and the slope was found to be 21.8 kcal/mole. Because the diffusion coefficient is proportional to $x^2 t^{-1}$ rather than $xt^{-1/2}$, the activation energy for diffusion is twice that calculated from the square root of time plot, or 43.6 kcal/mole.

Also shown in Figure 15 is the square root-time plot of the reaction between SiC and an actual superalloy, Rene' 77.* The reaction rates are similar, lending credence to the use of a simple alloy to model a superalloy. It also may be noted that these reaction rates are similar to those reported by Cornie, et al. for reactions involving SiC filaments and a number of different metal compositions.⁽⁴⁾ These activation energies are similar to those found for $M_2\text{Si}$ silicides formed by reacting elemental Si and M (M = Ni, Co, Pd, Pt, and Mg), which are of the order of 35 kcal/mole at lower temperatures (100°C - 700°C)⁽¹¹⁾.

4. Discussion

4.1 SiC-Ni Reaction

Although most of the experimental work reported dealt with SiC/NiCrAl, the reactions can best be understood by first considering the SiC/Ni couples. The variation of chemistry from the SiC terminal across the reaction zone to the Ni terminal can be plotted on a ternary phase diagram for the simplest case. The binary diagrams Ni-C, Ni-Si and Si-C are well-characterized,⁽¹²⁻¹⁴⁾ but the ternary Ni-Si-C system has not been treated. A pseudo-ternary diagram hypothesized previously by two of the present authors,⁽¹⁵⁾ based on reaction studies performed at that time, is a reasonable representation, but may contain some errors.

A diagram for Ni-Si-C that is consistent with the reaction path observed for SiC/Ni couples is shown in Figure 16, along with the reaction path. It is unclear whether a θ

* Rene'77: 14.5 Cr, 15.3 Co, 3.4 Ti, 4.3 Al, 4.2 Mo, 0.5 Fe, .07C, .016B, .04M Zr, balance Ni (weight percents).

Ni_3Si_2 + graphite (C_G) phase field exists, and the diagram has been drawn without such a field. At high temperatures the θ phase extends to the Ni_2Si composition, but at lower temperatures δ - Ni_2Si and θ are two distinct phases. The weight percents of Si in δ and θ are very close, however, and may not be distinguishable for the fine, complex microstructure such as shown in Figures 8 and 10. X-ray diffraction indicates δ - Ni_2Si , with a rare determination of small amounts of the θ phase. However, it is possible that at reaction temperatures θ was present, but was converted to δ while the couples were cooling from the reaction temperatures.

The diagram of Figure 16 thus shows two-phase equilibria between δ and SiC, between δ and C_G , and between δ and Ni. The reaction path drawn on the diagram is simply a plot of the chemical composition across the reaction zone. The path begins at the SiC terminal, adjacent to which is a layer of δ - Ni_2Si . In a ternary system, three phases coexist only when the composition of each of the phases is invariant. In a reaction couple, then, a three-phase equilibrium can exist only at an interface, since there can be no chemical potential difference to act as a driving force for diffusional growth.⁽¹⁶⁾ In the reaction path of Figure 16, the three phase field $\text{SiC} + \text{C}_G + \delta$ is crossed with a dashed line to indicate it represents no physical distance in the actual couple, but is the interface between SiC and the $\delta + \text{C}_G$ layer.

The microstructural and microchemical analyses of Figures 8-10 show that the structure below that first $\delta + \text{C}_G$ layer consists of alternating layers of δ - Ni_2Si and $\delta + \text{C}_G$. This is plotted in Figure 16, where the reaction path nearly follows tie-lines in the two-phase field of $\delta + \text{C}_G$. The path first enters the δ phase field (the clear white layers of Figure 10), then to $\delta + \text{C}_G$, and back to δ . Each succeeding layer of $\delta + \text{C}_G$ is shown to be lower in carbon content (i.e., a lower volume fraction of C_G). This has not been verified directly for SiC/Ni couples, since microprobe analysis for C was done by difference (100% - %Si - %Ni) for most reaction couples. However, a direct microanalysis of carbon was made for an SiC/NiCrAl couple, and it showed a decrease in carbon content in the $\delta + \text{C}_G$ layers from the SiC side to the metal side.

As seen in Figure 10, the layered structure ends with a broad layer of the clear δ - Ni_2Si adjacent to the Ni terminal of the couple. This is shown in the reaction path of Figure 16, as the last layer is in the single-phase δ - Ni_2Si field. The path leaves the δ field and crosses the Ni+ δ field along a tie-line, since δ and Ni coexist in the microstructure only at an interface.

This completes the description of the SiC/Ni reaction path at 1150°C. The path shown is thermodynamically allowable since the chemical potential for each element varies monotonically from one terminal to the other. As noted earlier, less reaction occurs at lower temperature, but the microstructural features are identical and can be understood from the same reaction path.

4.2 SiC-NiCr Reaction

The next degree of complexity of reaction was observed for the SiC/NiCr couples. The path could be plotted in a quaternary phase equilibria space, but the microstructure in Figure 11 and the microanalytical data in Figure 12 suggest that this may not be necessary. A layered structure, similar to that for SiC/Ni, is the dominant feature on the SiC side of the reaction, while a region of η' - $\text{Cr}_3\text{Ni}_2\text{SiC}$ appears between the layers and the NiCr terminal. The NiCr terminal contains 20 at/o Cr for a Ni/Cr ratio of 4. In the layered zone of the reaction, however, the Ni/Cr ratio is generally greater than 50. At the original SiC/NiCr interface, Ni diffuses across to react and form the alternating layers of δ and of $\delta+\text{C}_G$. Almost no Cr crosses the interface, so that a concentration of Cr builds up on the metal side of the interface due to the departure of Ni. As Si and C diffuse into the metal side, their reaction with the concentrated Cr and the remaining Ni forms η' carbide.

The reaction path for the bulk of the couple is again as shown in Figure 16, with the variation of high Ni and Si to low Ni and Si as the structure progresses from δ to $\delta+\text{C}_G$. The small amount of Cr present in this region is probably in the form of $\text{Cr}_{5-x}\text{Si}_{3-y}\text{C}_{x+y}$,

as was observed in the more detailed study of SiC/NiCrAl couples. In effect, the diagram of Figure 16 would need to include this phase in a three phase field being traversed in the alternating layers, but the volume fraction of $\text{Cr}_{5-x}\text{Si}_{3-y}\text{C}_{x+y}$ is quite small. The major difference, of course, occurs in the concentrated Cr zone. The reaction path leaves the δ and $\delta+\text{C}_G$ layers, possibly along a tie-line in the two-phase field between δ and η' field, along a tie line to single phase NiCr solid solution, ending at the Ni 20 a/o Cr composition.

Although Ni and Cr move through the reaction path in quite different fashion, the Si and C fluxes in the opposite direction are apparently nearly equal. For example, the reaction of Ni and SiC would have mass balance if the reaction were:

On an atomic basis, there would be three times as much δ formed as graphite, due to the addition of two Ni atoms for each Si atom. Because of density differences, this would require 80 v/o δ and 20 v/o C_G if mass balance is maintained. A rough estimate of the microstructures indicates the graphite-free δ regions are ~50 v/o of the structure, so that the fraction of the $\delta+\text{C}_G$ layer that is graphite, on average, will be 40%. This will vary along the reaction path, since the carbon content of the $\delta+\text{C}_G$ layer decreases with increasing distance from the SiC terminal. In the η' carbide zone, Si and C masses are balanced naturally by the carbide formula, $\text{Cr}_3\text{Ni}_2\text{SiC}$. In the Ni or NiCr terminal, Si leads C diffusion because of the greater solubility of Si in the γ lattice.

An important point to note is that the presence of Cr in the Ni matrix acts to retard the reaction kinetics. The interjection of the η' carbide zone between the Ni-rich terminal and the growing layered structure effectively reduces the Ni source strength. In SiC/Ni, the Ni_2Si zone presents a 67 a/o Ni source for layer growth, while in SiC/NiCr, the η' carbide zone presents a 29 a/o Ni source. Because Cr is only a minor actor in the SiC side of the reaction, its concentration on the metal side reduces the rate of reaction. As discussed below, the presence of Al in the Ni rich terminal has a similar influence.

4.3 SiC-NiCrAl Reaction

As with SiC/NiCr, reaction paths for SiC/NiCrAl could be plotted in all their complexity on a quinary representation of the equilibrium phase diagram. Microchemical analyses such as shown in Figure 5, however, indicate that Al is nearly totally excluded from the SiC side of the reaction, being concentrated in the transition reaction zone as isolated Al_2O_3 particles, and in the metal reaction zone as a more homogeneous structure. More Cr is present in the SiC reaction zone than was the case for SiC/NiCr couples. However, the Ni/Cr ratio is generally greater than 20 in the SiC reaction zone, compared to 3.5 in the initial metal terminal. Again, the initial portion of the reaction path in Figure 16 is characteristic of the layered structure of SiC/NiCrAl couples. Some small amount of $\text{Cr}_{5-x}\text{Si}_{3-y}\text{C}_{x+y}$ was observed in the layers, but the alternation of δ and $\delta+\text{C}_G$ is the dominant feature. Beyond the layers is the η' carbide zone resulting from the concentration of Cr. As noted above, there are isolated particles of Al_2O_3 , but otherwise Al is excluded from the η' carbide zone. Essentially, the reaction path passes from the δ - Ni_2Si single-phase field along a tie line to the η' carbide single-phase field, behaving as though Al were absent and the couple were between NiCr and SiC.

At this point in the couple, an Al-rich metal reaction zone is interjected between η' and the NiCrAl terminal. The original couple interface was at the layered structure/ η' interface. Therefore, the Al concentration in the metal reaction zone is due in part to outward diffusion of Ni and Cr, but in larger part to actual rejection of Al by the growth of the η' zone. As transmission electron microscopic and x-ray diffraction observations presented in the subsequent paper indicate, the structure in the metal reaction zone is extremely fine and complex. Details of the structure vary considerably with temperature as seen in Figures 3 and 4. An accurate quinary description, if one existed, would be useful to describe these structures since they involve all five elements.

As with Cr, the addition of Al greatly reduces the reaction rate of Ni alloys with SiC. For example, at 1150°C/100 h only 70% as much reaction occurs in Ni20Cr as in Ni, and only 45% as much reaction occurs in Ni20Cr10Al as in Ni. As shown in Figure 15, a Ni-base superalloy with all its elemental additions shows lower reaction rates than does NiCrAl with SiC. As the alloy becomes more complex, the number of reaction products increases. The form the microstructure takes on reaction appears to present a barrier to rapid reaction by slowing the diffusive processes and by reducing the driving forces for reaction.

SUMMARY

Reaction of SiC with Ni-base alloys occurs readily over the temperature range of 700-1150°C. Kinetics of growth in thickness of reaction products on either side of the original metal/ceramic interface follow a parabolic relation with time for a Ni 20 a/o Cr 10 a/o Al alloy, and the activation energy for the process was found to be 43.6k cal/mole.

The dominant structural feature formed in the SiC is a banded structure. Alternate bands are first δ -Ni₂Si+C_G (graphite) followed by δ -Ni₂Si. Depending on composition of the substrate, other phases may be present in minor amounts within the banded structure, but the δ and C_G phases dominated, independent of the metal composition. Reaction products on the metal side were very dependent on metal composition. In pure Ni, a thick δ layer formed. When NiCr reacted with SiC, Cr was concentrated on the metal side, being nearly excluded from reaction in the SiC. With Si and C diffusing from the ceramic, the Cr concentration resulted in formation of η' -Cr₃Ni₂SiC. With Al present in the metal, it was also excluded from the SiC side, but was included in the η' carbide layer only as isolated Al₂O₃ particles. Rejection of Al by the growth of η' carbide resulted in a concentration of Al in a zone containing γ , γ' , β -NiAl, and several other phases, depending on reaction temperature.

Reaction was most rapid for pure Ni. Reaction depth was decreased when Cr was present, and was further decreased when Al was present as well. Compared to complex superalloys, with Ti, Mo, W, Co, C, B and Zr, reaction was more rapid for the model NiCrAl alloy. Additional complexity of the metal composition apparently causes more complex reaction products, but this in turn leads to less overall reaction.

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TABLE I
CARBON CONCENTRATION IN SiC/METAL REACTION ZONE*

Microstructural Feature	Wt. % C
A. SiC	35
B. SiC Reaction Zone	
1st Dark Layer	31
2nd Light "	1.8
3rd Dark "	26
4th Light "	2.2
5th Dark "	30
6th Light "	Not Determined
7th Dark "	28
8th Light "	Not Determined
9th Dark "	10
10th Light "	Not Determined
11th Dark "	9
C. Transition Zone	
(a) Adjacent to SiC Reaction Zone	4.5
(b) Center of Zone	4.0
(c) Adjacent to Metal	3.0
D. Metal Reaction Zone	~1.0

*Using diamond standard. Absolute accuracy estimated to be about 25%.

Fig. 1. Schematic diagram of experimental apparatus.

Fig. 3. Reaction zones in hot-pressed SiC and NiCrAl alloy after 100 hours at 1150°C. SiC is at top of figure.

Fig. 2. Macrograph of Si-SiC, SiC, and NiCrAl alloy after 50 hours at 1150°C.

Fig. 4. Reaction zones in hot-pressed SiC and NiCrAl alloy after 220 hours at 900°C. SiC is at top of figure.

Fig. 5. Electron microprobe chemical analyses for Ni, Cr, Si, and Al in SiC/NiCrAl couple treated 100 hours at 1150°C.

Fig. 6. Electron microprobe chemical analyses for Ni, Cr, Si and Al in a SiC/NiCrAl couple treated 220 hours at 900°C.

Fig. 7. Reaction zones in sintered SiC and NiCrAl after 100 hours at 1150°C. SiC is at top of figure.

Fig. 8. Reaction zones in hot-pressed SiC and Ni after 100 hours at 1000°C. SiC is at top of figure.

Fig. 9. Electron microprobe chemical analyses for Ni and Si in a SiC/Ni couple treated 100 hours at 1000°C.

Fig. 10. Reaction zones in hot-pressed SiC and Ni after 100 hours at 1150°C.

Fig. 11. Reaction zones in hot-pressed SiC and NiCr after 100 hours at 1150°C.

Fig. 12. Electron microprobe chemical analyses for Ni, Cr, and Si in a SiC/NiCr couple treated 100 hours at 1150°C.

Fig. 13. Reaction depth in SiC vs square root of time for various times and temperatures.

Fig. 14. Reaction depth of NiCrAl vs square root of time for various times and temperatures.

Fig. 15. Reaction rates in SiC and NiCrAl alloy vs reciprocal absolute temperature. Reaction rates for SiC/superalloy from reference 5. The activation energy shown is twice the value obtained from this square root of time plot.

Fig. 16. Hypothetical phase diagram at 1150°C for Ni-Si-C on which is superimposed the path followed by reaction of Ni with SiC.

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SOLID STATE SiC/METAL REACTION:

II. MICROSTRUCTURAL ANALYSIS AND PHASE IDENTIFICATION

by

E. L. Hall, A. M. Davis, M. R. Jackson, and R.L. Mehan

ABSTRACT

The analytical procedures and results upon which the phase analysis and reaction path data of part I of this paper were developed are presented in this section. Techniques used include x-ray diffraction, transmission electron microscopy, and x-ray spectroscopy in a scanning transmission electron microscope. Detailed analyses of the phases discussed briefly in part I are presented, including phase identification, composition, and structure.

1. Introduction.

In part I of this paper, the topic of reactions between silicon-based ceramics and metals at elevated temperatures was introduced, and previous research in this area was described. It was proposed to study the fundamental nature of such reactions by using a model superalloy containing only Ni, Cr, and Al, and by reacting this model superalloy with various silicon-based ceramics, primarily SiC. In part I, the reaction between both hot-pressed and sintered SiC and the model superalloy was discussed in detail; in addition, reaction couples of SiC with pure Ni, pure Cr, and NiCr were used to elucidate the role that the various constituents of the model superalloy played in the development of the reaction products. It was shown that distinct zones occurred in both the metal and the SiC during the high-temperature reaction. The phases present in each zone were described, and the kinetics of the reaction zone formation were explored. Finally, the principles of phase equilibria were used to chart the probable reaction paths during the experiments and to explain the resulting microstructure.

The details of the phase identification and the microstructure of each zone will be discussed in the present paper. The microstructural analysis was performed using X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray spectroscopy in a scanning transmission electron microscope (STEM). These techniques will be described, and the crystallography, chemistry and distribution of the phases present in each zone will be presented.

It should be pointed out that the three analytical methods used in this investigation, electron probe microanalysis (discussed in part I), XRD, and TEM/STEM yield complementary but distinctly different information, and the task of the analyst is to integrate these results. Microanalysis yields chemistry versus position from various microstructural regions at relatively low resolution. XRD provides a macroscopic and detailed identification of the crystallography of the phases present, and can be used to provide

extensive information from a large number of couples; TEM/STEM shows the phase distribution, crystallography, and chemistry in a small region in each zone, and thus furnishes intensive data from selected samples.

2. Experimental

2.1 Materials and Reaction Procedure

The characteristics of the alloys and ceramics used were described in part I. The formation of the couples, the apparatus used, and the reaction procedure were also discussed. After each reaction run was completed, the ceramic/metal couple was removed, encased in epoxy, and sectioned into two pieces along the compression axis. The two halves were then metallographically polished and subjected to light microscopy and electron microprobe analysis. After completion of these nondestructive studies, the samples were available for phase identification by XRD or TEM/STEM.

2.2 X-ray Diffraction Analysis Procedures

Phases and particles were removed from each reaction zone in the polished specimens using fine-tipped dissecting probes, and the extricated material analyzed by the Debye-Scherrer technique. After the polished specimens were examined, selective etching⁽¹⁾ was employed to separate phases in the various reaction zones, and to extract phases that might have been undetected previously. Three different etches were used in this investigation, namely:

1. 20% H_3PO_4 in H_2O (electrolytic)
2. 7% HCl in methanol (electrolytic)
3. 5% bromine in methanol (chemical)

In cases where more than one etch was used in a single zone, the specimen was repolished between etches to insure that no residual effects of the preceding etchant would remain.

Deep etching allowed the various components of each reaction zone to be separated and analyzed using XRD. Prior to dissection, the etched samples were examined in the scanning electron microscope (SEM) in order to reveal the distribution and morphology of each extracted phase.

2.3 Transmission Electron Microscopy/Scanning Transmission Electron Microscopy Procedures

In preparation for examination using TEM/STEM, the samples were demounted from the epoxy and sectioned parallel to the reaction zone interfaces (normal to the compression direction). In this way a planar section containing only one type of zone could be produced. To isolate the zones present on the metal side of the original metal/ceramic interface, the metal coupon was cut using a diamond wafering blade and metallographically polished to isolate a chosen reaction zone. The reaction zones in the ceramic coupon were isolated by either cleavage or wafering with a diamond blade, followed by metallographic polishing to a thickness of ~25 μm . Final preparation of the metal reaction zone samples was accomplished by electropolishing in a solution of 20% perchloric acid in methanol at -40°C and 25V. The ceramic reaction zone samples were prepared by ion milling using a beam of argon ions accelerated through a potential 6kV.

Transmission electron microscopy was performed on a JEOL JSEM 200 TEM/STEM operating at 200kV. Bright-field imaging in conjunction with selected-area electron diffraction was used to crystallographically identify the phases present in each reaction zone. In addition, the microscope was equipped with STEM capabilities, so that a fine probe of electrons could be focused on phases or particles in the structure, and energy dispersive X-ray spectroscopy used to determine the chemistry of the features of interest.

Quantitation of the X-ray information in STEM can be accomplished by use of a simple empirical relation,⁽²⁾ namely:

$$\frac{C_A}{C_B} = K_{AB} \frac{I_A}{I_B} \quad (1)$$

where I_A and I_B are the X-ray intensities from elements A and B, respectively, C_A and C_B are weight fractions, and K_{AB} is a proportionality constant that does not vary with thickness, orientation, or changes in stoichiometry. This constant can be determined by use of a standard containing elements A and B, or may be calculated from fundamental principles. Using Equation (1) and the additional expression:

$$C_A + C_B + C_{\text{Remainder}} = 1 \quad (2)$$

the weight fraction of any element can be calculated from the X-ray intensities.

Equation (1) applies rigorously only to situations where absorption and fluorescence of x-rays are negligible, the so-called "thin film approximation." It has been shown that in many cases, particularly involving light elements in a heavy element matrix, an additional term must be added to Equation (1) to take into account absorption.⁽³⁾ However, this procedure requires an accurate assessment of sample thickness. Since this value was not readily available in the present study, the effects of absorption were neglected, so that the phase compositions determined have an error of approximately $\pm 10\%$ in the worst case.

3. Results and Discussion.

The techniques of XRD and TEM/STEM were applied to phase identification in a variety of different metal/ceramic reaction couples. In the present work, XRD was used to study the following reaction couples: sintered SiC/NiCrAl; hot-pressed SiC/NiCrAl; hot-pressed SiC/NiCr; hot-pressed SiC/Ni at two different reaction temperatures; and hot-pressed SiC/Cr. The samples examined by TEM/STEM were: sintered SiC/NiCrAl and hot-pressed SiC/Ni. In almost all cases, analyses were performed on specimens reacted at high temperatures ($>1000^\circ\text{C}$), where a larger degree of reaction product was available for analysis. Because microanalysis and metallography indicated the presence of the same phases at lower temperatures, this is not considered a serious deficiency. The results of

these investigations will be presented in this section. The SiC/NiCrAl reaction couple will be described in detail since this is the system that received the most study and represents the most general case. In addition, differences between sintered and hot-pressed SiC will be discussed. The XRD analysis of the SiC/NiCr and SiC/Cr couples, and the XRD and TEM/STEM results on SiC/Ni will also be presented, since these findings play an important role in the elucidation of the reaction paths described in part I.

3.1 Sintered SiC/NiCrAl

Much of the TEM/STEM work was initially performed on the sintered SiC material because of the larger bands in the ceramic reaction layer which facilitated analysis. For this reason, and the fact the basic chemistry is the same, this system will be discussed first.

A light micrograph showing the result of the reaction between sintered SiC and the model NiCrAl superalloy for 100 hours at 1150°C was shown in Figure 7, part I, with Figure 5 of part I illustrating an electron microprobe trace across a reaction couple, in this case hot-pressed SiC/NiCrAl. As discussed in part I, three distinct reaction zones are evident: a banded zone in the SiC, a transition zone in the metal, and a metal reaction zone. The phase composition of each of these zones, as well as that of the SiC and NiCrAl matrices, will be considered separately.

The SiC matrix was shown by XRD and TEM/STEM to be of the β -SiC form with the heavily faulted structure typical of β -SiC. No evidence of any second-phase particles or regions was detected.

The banded reaction zone shown in Figure 7, part I, to form in the SiC consists of two distinct types of regions, one of which exhibits dark contrast and one of which is light in the optical microscope. It was found that a dark band always occurred at the interface between the SiC and the banded reaction zone. The electron microprobe trace (Figure 5, part I) shows that the dark bands are relatively depleted of Ni and Si compared with the

light bands, and that slightly enhanced levels of Cr exist in the dark bands. The microstructure of the dark bands was found to consist of δ -Ni₂Si and graphite, and the distribution of these two phases is shown in Figure 1. In this TEM micrograph, the graphite, which has a fibrous morphology, is light compared with the dark Ni₂Si due to preferential thinning of the graphite. Light microscopy and SEM performed on etched samples indicated that the graphite grains are equiaxed, and that the δ -Ni₂Si forms a semicontinuous network structure around the graphite. The small amount of Cr shown to be present in the dark bands from the electron microprobe trace occurs as Cr_{5-x}Si_{3-y}C_{x+y}. This latter compound is found in the δ -Ni₂Si/graphite network as a discrete phase, with a grain size on the order of 1-2 μ m. X-ray spectroscopy in STEM indicates that some Ni is soluble in this phase. Cr_{5-x}Si_{3-y}C_{x+y} + graphite were observed by XRD in the residue remaining after a 7% HCl/methanol etch was used to selectively dissolve the δ -Ni₂Si of the dark bands.

The light bands in the banded reaction zone consist nearly exclusively of δ -Ni₂Si (Figure 2). The δ -Ni₂Si in these light bands was observed by XRD to be coarser grained than the δ in the dark bands. A trace of Cr_{5-x}Si_{3-y}C_{x+y} was also detected in these regions by XRD, but due to the macroscopic nature of the method, this may be from unintentionally included remnants of the dark bands.

On the metal side of the original metal/ceramic interface, the region described as the transition reaction zone occurs nearest to the original interface. This zone consists primarily of a matrix of fcc η' -Cr₃Ni₂SiC. The lattice parameter (a_0) of this phase was calculated to be $10.625 \text{ \AA} \pm 0.001$. In this matrix, discrete layers of α -Al₂O₃ are found, accounting for the Al-rich regions shown on the electron microprobe scan of this zone. The distribution of these two phases is shown in Figure 3, which is an SEM micrograph of a sample which has been etched in bromine/methanol. The α -Al₂O₃ is present in the cavities in the η' matrix. The α -Al₂O₃ is distributed in the form of small particles, 0.05 - 0.2 μ m in diameter, and these particles are shown in Figure 4.

The metal reaction zone, situated between the transition reaction zone and the NiCrAl matrix, proved to have the most complex microstructure. Figure 5 shows an overall view of this region, taken using SEM, after the sample had been etched in HCl/methanol. It can be seen that the zone has a dendritic-appearing structure, with a fine equiaxed grain distribution between the dendrite arms. The dendrites consist of the γ -Ni matrix with a uniform dispersion of γ' -Ni₃Al precipitates present in the γ -Ni. The γ - γ' structure is shown by TEM in Figure 6. The γ' phase generally exists in the γ matrix as a coherent ordered precipitate. In Figure 6, the γ' appears as a fine modulation of the matrix intensity, and was sufficiently finely-dispersed that imaging discrete particles was not possible. The overall composition of the γ - γ' matrix, obtained from X-ray spectrometry in STEM, was 82 w/o Ni, 6 w/o Cr, and 7 w/o Al, significantly less Cr than in the model superalloy. In addition, 6 w/o Si was dissolved in the γ - γ' phases. Approximately 5 w/o Si is soluble in γ -Ni at room temperature, and it is also possible for Si to substitute for Al in the γ' structure.⁽⁴⁾ The chemistry of the γ - γ' phases did not change with position in the metal reaction zone.

The dendritic structure also was characterized by XRD using a bromine/methanol selective etching. This technique dissolved the dendrite interstices and the γ -Ni. The residue from the γ dendrites was identified as γ' and η' . No η' was seen in TEM of this structure. The cell dimension of the γ' (ordered cubic) was calculated to be $3.557 \text{ \AA} \pm 0.003$ as opposed to a value of $3.563 \text{ \AA} \pm 0.001$ calculated for the extremely fine-grained γ' extracted from the NiCrAl alloy reaction couple terminal. The difference in cell sizes of the γ' would again imply a substitution of Si for some of the Al in the Ni₃Al lattice.

Both XRD of extracted residue and TEM/STEM were performed on the interdendritic structure. When 20% H₃PO₄/H₂O selective etching was used to determine phases present in the metal reaction zone, the dendrites were attacked, as seen in Figure 7. The interdendritic residue has been tentatively characterized by XRD as β -NiAl plus

an unidentified phase, neither of which were seen in TEM. Additional phases were found when intensively studied using TEM/STEM, and the phase composition of the interdendritic regions in the metal reaction zone was found to be a function of distance from the zone interfaces. Near the transition-reaction zone/metal reaction zone interface, a structure similar to that of the dark bands in the banded reaction zone was observed. As shown in Figure 8, this structure consists of equiaxed grains of Cr_3Si , which display light contrast, separated by a semicontinuous network structure of $\delta\text{-Ni}_2\text{Si}$. The $\delta\text{-Ni}_2\text{Si}$ in this case shows dark contrast because of the preferential thinning of the Cr_3Si . The $\delta\text{-Ni}_2\text{Si}$ grains are heavily faulted on parallel planes, and the effect of this can be observed in the electron diffraction pattern from this phase (Figure 8, inset). X-ray spectroscopy in STEM reveals that a small amount of Al substitutes for Si in the $\delta\text{-Ni}_2\text{Si}$. Neither Cr_3Si nor $\delta\text{-Ni}_2\text{Si}$ was observed in the metal reaction zone by XRD, and hence the TEM micrographs taken from extremely limited electron transparent area on the sample may overestimate the volume fraction of these phases present in the metal reaction zone.

In the middle of the metal reaction zone, much less Cr_3Si is found, and this phase appears to occur primarily between secondary $\gamma\text{-}\gamma'$ dendrite arms (Figure 9). The $\delta\text{-Ni}_2\text{Si}$ occurs as a discrete phase with a very fine grain size (Figure 10), similar to the structure of the light bands in the banded reaction zone. However, this phase remains much more heavily faulted in the metal reaction zone, perhaps due to the presence of Al in the structure. Interspersed in the regions of $\delta\text{-Ni}_2\text{Si}$ are discrete, equiaxed grains of $\alpha\text{-Cr}$, as shown in Figure 9. The complexity of phase combinations and the fine scale of the structure may account for the "unidentified phase" found by XRD. However, it may represent a previously unobserved phase.

Finally, near the interface of the metal reaction zone and the model superalloy matrix, the Cr_3Si phase is not found, and the structure consists of regions of $\gamma\text{-}\gamma'$ matrix and $\delta\text{-Ni}_2\text{Si}$. In the $\delta\text{-Ni}_2\text{Si}$, the occurrence of grains of $\alpha\text{-Cr}$ has increased (Figure 11).

The microstructure of the model superalloy matrix is shown in Figure 12. The structure consists of γ matrix with a uniform distribution of spherical γ' particles which are 0.05-0.1 μm in diameter. The inset in Figure 12 shows a dark-field view of the structure formed by using an excited γ' reflection, so that the γ matrix appears dark and the γ' particles are bright. In this region, the overall γ - γ' composition is identical to the nominal composition of the model superalloy.

3.2 Hot-pressed SiC/NiCrAl

A light micrograph illustrating the result of the reaction of hot-pressed SiC with the model superalloy was shown in part I (Figure 3). It is clear that the primary difference on a macroscopic level between the results using sintered versus hot-pressed SiC lies in the morphology of the bands in the banded reaction zone. Microstructural analysis using XRD of the hot-pressed SiC revealed that the unreacted region consisted of both α -SiC, which is hexagonal with a multiplicity of polytypes, and β -SiC. In addition, approximately 8 w/o of tungsten was present in the form of WC. The tungsten carbide occurs as discrete particles, and presumably was introduced into the hot-pressed SiC during manufacture, probably during milling of the powder prior to hot pressing.

The tungsten was also found in the banded reaction zone. At the SiC/banded reaction zone interface, a large amount of WC was present, but this compound was not observed by XRD in the banded zone itself, although it was observed metallographically. Instead a fcc phase, isostructural with the η' carbide found in the transition zone ($a_0 = 10.625\text{\AA}$), was detected in the banded reaction zone of the hot pressed silicon carbide. The calculated lattice parameter of this new phase, $a_0 = 10.796\text{\AA} \pm 0.006$, shows a considerable expansion of the cell over that of η' carbide, indicative of a heavier element such as W substituting in the lattice, and this compound might be of the type $\text{Ni}_5\text{W}_6\text{C}^{(5)}$. In addition, the grain size of this phase tends to be finer than that of the η' - $\text{Cr}_3\text{Ni}_2\text{SiC}$. The remainder of the phases in the bands, as well as the phases found in the transition

reaction zone and metal reaction zone, were identical to that previously discussed for the case of sintered SiC/NiCrAl.

A summary of the phases detected for the SiC/NiCrAl reaction by XRD and STEM analysis is shown in Table I. The results clearly indicate that it is possible to detect a phase by one technique and not by another due, in part, to their sampling of large and small areas, respectively. For the identification of phases in reactions such as discussed here, it is necessary to perform both types of analysis, in addition to the chemical microanalysis discussed in part I.

3.3 Hot-pressed SiC/NiCr

The light micrograph corresponding to a reaction between hot-pressed SiC and a binary Ni-Cr alloy at 1150°C for 100 hours was presented in part I as Figure 11. The associated electron microprobe trace across the reaction couple was given as Figure 12. It can be seen that only two reaction zones exist in this sample: a banded-type of zone on the SiC side of the original interface, and a metal reaction zone on the NiCr side. XRD was used to study the phase composition of these zones. Because of the fine scale of the banding in the SiC reaction zone, it was not possible to separate the light and dark bands, but the phases present overall in this zone include δ -Ni₂Si, graphite, and WC. A trace amount of Cr_{5-x}Si_{3-y}C_{x+y} was also found. The similarity of the structure as shown by light microscopy, of the microprobe trace, and of the phase composition of this zone with that found in the NiCrAl couples is a strong indication that the identical structure has developed. However, although Al does not play a role in the development of the structure of this zone, the extent of the zone is clearly increased by the absence of Al.

The narrow metal reaction zone in Figure 3, part I was shown by XRD to consist of single phase η' -Cr₃Ni₂SiC, in agreement with the microprobe analysis. In addition, XRD revealed the presence of a narrow layer of η' carbide and coarse-grained δ -Ni₂Si at the metal reaction zone/metal interface. Therefore Al also plays a strong role in the

development of the reaction zones and their phase composition on the metal side of the original ceramic/metal interface; however, in contrast with the situation in the ceramic, the extent of the zones in the metal is decreased by the absence of Al.

3.4 Hot-pressed SiC/Ni

The reaction of hot-pressed SiC with pure Ni at 1000°C for 100 hours was shown in Figure 8, part I, with the electron microprobe trace shown in Figure 9, part I. One reaction zone is evident - a banded zone on the SiC side of the original interface. Once again, the light bands in this region were shown to contain δ -Ni₂Si, and the dark bands consisted of graphite and δ -Ni₂Si. WC particles were present in both bands. Figure 13 is a TEM micrograph of the structure of the dark bands. The primary difference between Figs. 1 and 13 is the scale of the microstructure, with the graphite grains being much smaller in Figure 13. A narrow layer of coarse-grained δ -Ni₂Si plus lesser amounts of NiO, WC and an unidentified phase were detected by XRD adjacent to the metal. At a reaction temperature of 1150°C, the narrow layer adjacent to the metal contained only coarse-grained δ -Ni₂Si.

No other reaction zones were found in this simple couple. A comparison of these results with those of the previous section stresses the importance of Cr in the formation of these reaction zones.

3.5 Hot-pressed SiC/Cr

At 1000°C for 100 hours, hot-pressed SiC and pure Cr show very little tendency to react. A very narrow reaction zone, ~10 μ m in width, was observed on the SiC side of the original interface. This zone contained primarily Cr₃Si, with the tentative identification of some chromium carbides such as Cr₇C₃, Cr₂₃C₆, and Cr_{5-x}Si_{3-y}C_{x+y} being present.

4. Conclusions

Based on the work presented in parts I and II of this study, the following conclusions may be drawn:

1. SiC reacts with nickel and nickel-base alloys under reducing conditions at temperatures of 700°C and above.
2. The reaction is quite complex even in relatively simple alloy systems, such as NiCrAl. At least 14 individual phases have been identified, and more are known to be present.
3. Phase identification in such solid state reactions requires a variety of analytical techniques, each of which complements the other.
4. The formation of many and complex phases reduces the severity and extent of the SiC/metal reaction. Reaction was most rapid with pure nickel, and least for the ternary NiCrAl alloy.
5. Phase equilibria concepts may aid in the understanding of the gross features of such reactions, but work is needed to understand the detailed mechanisms of the formation of the fine-scale structures observed.

ACKNOWLEDGMENTS

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TABLE I

SUMMARY OF PHASES FOUND BY XRD AND TEM/STEM ANALYSIS
IN THE REACTION PRODUCT OF SiC/NiCrAl SOLID STATE REACTIONS

MICROSTRUCTURAL FEATURE					
BANDED REGION IN SiC		TRANSITION ZONE IN METAL		REACTION ZONE IN METAL	
XRD	TEM/STEM	XRD	TEM/STEM	XRD	TEM/STEM
Graphite	Graphite	η' -Cr ₃ Ni ₂ SiC	η' -Cr ₃ Ni ₂ SiC	γ -Ni	γ -Ni
δ -Ni ₂ Si	δ -Ni ₂ Si	α -Al ₂ O ₃	α -Al ₂ O ₃	γ' -Ni ₃ Al	γ' -Ni ₃ Al
Cr _{5-x} Si _{3-y} C _{x+y}	Cr _{5-x} Si _{3-y} C _{x-y}	Cr ₃ C ₂ ⁺		η' -Cr ₃ Ni ₂ SiC	Cr ₃ Si
WC *		AlN ⁺		β -NiAl	δ -Ni ₂ Si
Ni ₅ W ₆ C-type phase*					α -Cr

* Hot pressed SiC only. Not analyzed by TEM/STEM

⁺ Extremely minor phase

0.5 μm

Fig. 1. Transmission electron micrograph of the structure of the dark bands in the banded reaction zone in SiC, consisting of $\delta\text{-Ni}_2\text{Si}$ (dark) and graphite (light).

0.2 μm

Fig. 2. Transmission electron micrograph of the structure of the light bands in the banded reaction zone in SiC, consisting of $\delta\text{-Ni}_2\text{Si}$.

20 μm

Fig. 3. Scanning electron micrograph of the transition reaction zone after etching in bromine/methanol.

0.5 μm

Fig. 4. Transmission electron micrograph of $\alpha\text{-Al}_2\text{O}_3$ particles in transition reaction zone.

Fig. 5. Scanning electron micrograph of the metal reaction zone after etching in HCl/methanol.

Fig. 6. Transmission electron micrograph of γ -Ni matrix with fine γ' -Ni₃Al particles present, taken from metal reaction zone.

Fig. 7. Scanning electron micrograph of the metal reaction zone after etching in bromine/methanol.

Fig. 8. Transmission electron micrograph of interdendritic region in the metal reaction zone consisting of Cr₃Si (light) and δ -Ni₂Si (dark). Inset: Electron diffraction pattern from δ -Ni₂Si which shows streaking characteristic of a faulted structure.

Fig. 9. Transmission electron micrograph of structure in the metal reaction zone consisting of Cr_3Si and $\gamma-\gamma'$ matrix.

Fig. 10. Transmission electron micrograph of region of $\delta\text{-Ni}_2\text{Si}$ in the middle of the metal reaction zone. Small grain of $\alpha\text{-Cr}$ also shown.

Fig. 11. Transmission electron micrograph of region $\delta\text{-Ni}_2\text{Si}$ in the metal reaction zone near the interface with the unreacted model superalloy. Grains of $\alpha\text{-Cr}$ are indicated.

Fig. 12. Transmission electron micrograph of model superalloy matrix ($\gamma\text{-Ni}$) with spherical $\gamma'\text{-Ni}_3\text{Al}$ particles present. Inset: Dark-field image formed using γ' reflection so that γ' particles appear bright and γ matrix appears dark.

Fig. 13. Transmission electron micrograph of dark band in banded reaction zone of Ni/SiC reaction couple, showing δ -Ni₂Si (dark) and graphite (light) present. The large single grain is WC.

REACTIONS OF Ni AND Ni-BASED ALLOYS WITH Si-BASED CARBIDE CERAMICS

by

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ABSTRACT

The reactions between ceramics containing free silicon and Ni-based alloys were studied over the temperature range between 1150°C and 700°C. The metal and ceramic specimens were heated in air under a compressive load of 200 N, and a reaction was detected at all temperatures. The reaction was analyzed utilizing microprobe, XRD, and STEM techniques.

INTRODUCTION

Reaction-bonded silicon carbide ceramics containing free silicon (Si-SiC) are being considered for structural application in hot machinery components because they can be easily formed to near final shape and because of their ability to operate in a high temperature oxygen-containing environment. In all probability, initial use of such structural ceramics in hot machinery will be in conjunction with metals; an all-ceramic machine lies far in the future.

In such designs, the hottest sections would be ceramic, with predominantly compressive loading, while the metal supporting the tensile stresses would be at a lower temperature. The ceramic/metal interface would be in compression with a service temperature likely to be in excess of 850°C, possibly as high as 1100-1150°C. Oxygen would be excluded at the interface by the compressive load. The temperatures and tensile stresses in the metal dictate that very strong, high temperature materials be chosen with $\gamma'(\text{Ni}_3\text{Al})$ -strengthened Ni-base alloys being prime candidates.

Reactions between Si-base ceramics and Ni-base metals have been studied for several systems. Complex reaction structures were observed for Ni-base superalloy reactions with SiC (1), Si_3N_4 (2) and Si-SiC (3). Studies involving filament/matrix reactions in metal matrix composites are also pertinent, since inert or reducing conditions are present during fabrication and service similar to those expected in the applications discussed above (4, 5). In all these studies, a phenomenological approach was taken because of the complexity of each system. Some phase identification was performed, but because of the 8-10 element space needed to describe the superalloys, little could be established relative to phase equilibria. Recently, studies have begun using simplified model alloys (of Ni, Cr and Al to represent the principal elements in the superalloys) to determine the mechanisms and the phase equilibria governing the reactions with SiC (6, 7). The present experiments and analyses attempt to extend this approach to Ni-alloy reactions with Si-SiC ceramics.

EXPERIMENTAL METHODS

Ceramic discs (6.4 mm dia. x 3.2 mm) were prepared of NC-435 Si-SiC obtained from the Norton Company and of a Si-SiC composite material (8) fabricated in this laboratory.* In regard to chemical reactivity, no difference was detected between these two materials, and no further distinction will be made between them. The discs were used in the as-ground condition and were cleaned in acetone. Metal discs (12.7 mm dia. x 3.2 mm) of a Ni, 20 a/oCr, 10 a/oAl alloy were polished on 400 mesh SiC paper and were also cleaned in acetone. The metal composition was chosen to represent the >95% of Ni alloy volume consisting of γ and γ' , neglecting effects of carbides and borides. Limited experiments were performed with Ni, Cr and Ni-20 a/oCr.

Sandwiches of ceramic/metal/ceramic were placed in the apparatus shown schematically in Figure 1, and a compressive stress of 7MN/m^2 (3.5MN/m^2 at higher temperatures) was applied to the metal/ceramic interfaces. The couple was surrounded

* SilcompTM-Trademark of the General Electric Company

by a Pt-wound furnace which equilibrated the system at the reaction temperature in approximately 30 minutes. The furnace ends were covered with insulation, but no inert atmosphere was used. Temperatures studied were between 700 and 1150°C, for exposure times up to 100 hrs. The pieces were removed after reaction, encased in clear plastic and sectioned for metallography and other analytic investigations.

RESULTS

In the following presentation of results, the behavior above and below 1000°C will be discussed separately. A eutectic exists in the Ni-Si system at ~950°C, so above (approximately) this temperature liquid phases will exist, while below this temperature the reaction is predominantly solid state.

Reactions above 1000°C: For 1100 and 1150°C exposures, electron microprobe analyses have been performed. Although this yields information only about the composition of the structures, sometimes containing more than one phase in the region analyzed, previous x-ray diffraction and scanning transmission electron microscopic analysis (6, 7) of reactions with SiC have aided in phase identification.

The severity of reaction at 1150°C, of the Si-SiC ceramic with the NiCrAl model superalloy can be seen in Figure 2, compared to the corresponding less severe reaction with SiC. The structure appears to show a liquid formation and extrusion of this liquid from the ceramic/metal interface by the compressive loading. Microanalysis indicates this extruded area to be Si rich. In addition, high concentrations of Ni are present in the Si-SiC ceramic to approximately the depth of the coarse porosity. Higher magnification structures of the reaction products under the Si-SiC sample are seen in Figure 3. Probing the Si-SiC side of the reaction couple indicates large amounts of Ni (up to ~60 at.%) penetrating the Si matrix. The chemical profile for Ni, Si and Cr is shown in Figure 4, with Si/SiC at the right and NiCrAl at the left. Very little Cr penetration into the Si/SiC occurred, and no Al was present. The clear band shown in Figure 3 is the high Cr region in

Figure 4. This region is again free of Al. Within this band are isolated particles with ~10 a/oCr, 7 a/oSi and 20 a/oAl. These particles have not yet been identified but the clear band appears to be η' -carbide, $\text{Cr}_3\text{Ni}_2\text{SiC}$, based on analyses of carbon by difference. This η' phase has been previously identified in reactions involving SiC/NiCrAl (6, 7). The very long region of uniform composition below the η' carbide layer is 7-12 a/oCr, 6-8 a/oSi, and 17-23 a/oAl and appears to be equivalent to the isolated particles. As seen in Figure 3b, this zone is made up of several phases arranged in a dendritic appearing pattern. The angularity of the η' layer suggests the appearance of faceted growth from a liquid. The phases present in this relatively uniform composition zone are currently being studied. At the end of this zone, the structure appears to be $\gamma+\gamma'$ with an overall composition of 20 a/oCr, 6 a/oSi and 9.5 a/oAl, with the Si content falling to zero over an extended diffusion zone.

At an 1100°C reaction temperature, similar structures are observed (Figure 5). Rather than performing a microanalysis step profile, point probing was performed to insure that individual phases were analyzed. Far from the reaction interface, the structure remained Si-SiC. However, for a large distance from the interface with the metal, Ni was present in very high concentration. In the structure shown in Figure 5a, the area of the ceramic/metal interface is evident. The original structure of Si-SiC still remains the SiC portion of the ceramic composite (Figure 5b), but the Si matrix has been transformed to a silicide phase, 35 a/oSi, 58 a/oNi, 4 a/oCr, 3 a/oAl. Without knowing which sublattice Al and Cr occupy, it is most likely to be Ni_3Si_2 , but possibly includes an Ni_2Si intermetallic. The lighter areas shown inside the silicide in Figure 5b are a Cr-rich carbide. From microprobe analysis these phases are probably Cr_7C_3 , but x-ray diffraction analysis remains to be performed to verify this. Between this region retaining SiC and the crack running through the reaction zone in Figure 5a is a different structure, shown in detail in Figure 5c. The light matrix appears to be the η' carbide, while the fine dark particles are graphite. From previous work (6, 7), it has been established by x-ray

diffraction that the products of the decomposition reaction, $\text{SiC} \rightarrow \text{Si} + \text{C}$, are indeed Si and free graphite. Formation of the η' carbide is accompanied by the decomposition of SiC. Since the η' carbide contains nearly equal amounts of Si and C, and since graphite remains, mass balance requires that more Si diffuses and reacts in the adjoining metal side of the couple than does carbon.

On the metal side immediately adjacent to the gap shown in Figure 5a, the light matrix again appears to be η' carbide. The darker phase is of variable chemistry; the Cr content is 2.5-5 a/o and Ni is 60-62 a/o. However, Si varies between 11 and 20 a/o and Al between 13-20 a/o. The sum of Al and Si is consistently between 33.5 and 36.4 a/o. From the limited phase equilibrium data available in the literature (9), this could be analogous to the Σ phase observed in the NiAlSi system, which is reported to consist of a narrower composition range of 17-19 a/oAl and 16-18 a/oSi. However, it could alternatively be a $\text{Cr}_3\text{Si} + \beta\text{NiAl} + 6\text{Ni}_2\text{Si}$ structure similar to that formed at lower temperature (see later discussion). Beyond this region is a region of $\gamma + \gamma'$ containing as much 11 a/oSi. This extends for a long distance before Si is absent. The structure is dendritic in appearance, and an additional, very fine unidentified phase is seen.

Reaction Below 1000°C: Reaction couples at 900°C have been studied in detail by microprobe, x-ray diffraction and scanning transmission microscopy analyses, and the kinetics of the reaction have been studied from 700°C to 1000°C. Kinetically, the reaction has a similar apparent activation energy (~44 kcal/mole) to that for SiC/NiCrAl reactions at low temperatures (Figure 6), but in the region of 900°C and above reaction rates accelerated. Reactions on the ceramic side are greater in depth than those on the metal side. For SiC/NiCrAl, reaction depths were approximately equal in metal and ceramic for NiCrAl, but greater depths were seen in the metal side when the metal was NiCr, and greater depths still when it was Ni (6, 7). For Si-SiC, the reaction on the ceramic side was more pronounced than the metal side and was nearly equal for Ni, NiCr

and NiCrAl. This can be seen in Figure 7 for Si-SiC/NiCrAl (Figure 7a) and Si-SiC/Ni (Figure 7b) for an exposure of 900°C/100 h. Ceramic reaction depth is noted by the layer of porosity.

Phases on the ceramic side are similar to those seen at higher temperature. The Si matrix is transformed by reaction with Ni to Ni_3Si_2 . X-ray diffraction analysis suggests $\text{Ni}_{16}\text{Cr}_6\text{Si}_7$ may also be present, while scanning transmission electron microscopy showed Ni_3Si_2 alone. A single electron diffraction pattern could be indexed alternately as $\delta\text{-Ni}_2\text{Si}_3$, but all other patterns were clearly Ni_3Si_2 .

Details of the 900°C metal side reaction are seen in Figure 8. Electron microprobe analysis indicates the region at the top of the figure is Ni_3Si_2 . Below is a layer of $\delta\text{-Ni}_2\text{Si}$ containing darker particles of Ni_3Si_2 . In the remainder of the reaction zone three different layers exist, each containing a columnar arrangement of phases. These are similar in appearance to structures formed in aluminizing Ni alloys (10). The first has not been analyzed completely, but it is probable that the matrix is $\delta\text{-Ni}_2\text{Si}$ and the particles are $\beta\text{-NiAl}$. The second columnar zone contains a bright phase and the darker phase continuing from the layer above. This structure is shown in more detail in the section transverse to the columnar orientation in Figure 9. Scanning transmission electron microscopic analysis indicates the light phase is Cr_3Si , the dark phase is $\beta\text{-NiAl}$ and the fine particles are $\delta\text{-Ni}_2\text{Si}$. The Cr_3Si and $\beta\text{-NiAl}$ phases are the two obvious fibrous phases in the middle columnar structure of Figure 8. It is not clear whether the $\delta\text{-Ni}_2\text{Si}$ is fibrous or in isolated particles since its dimensions are too small to be seen in the optical micrograph.

DISCUSSION

The general features of Si-SiC/NiCrAl model superalloy reactions of the present study are similar to those for SiC/NiCrAl reactions (6, 7): Ni is the major species moving from the metal into the ceramic, while both Si and C move into the metal, with Si

penetration being far greater. The motion of Ni leaves Cr and Al in greater concentration in the metal reaction zone. The details of the Al and Cr concentration vary with temperature.

Although the general features are similar for SiC and Si-SiC reactions with NiCrAl, the specifics are quite different, at least at temperatures above 1000°C. This can be seen in Figure 10, a schematic representation of the reaction path at 1150°C for SiC/Ni (6). All phase fields crossed by the reaction path are solid state fields, so only solid state interdiffusion occurs. For any of the Si-SiC compositions possible, reaction paths with Ni or a Ni alloy must pass through at least one phase field which contains a liquid, so that reaction rates are much greater. From the Ni-Si phase diagram (11), shown in Figure 11, liquid phases are expected to ~950°C. Both Al and Cr depress the Ni solidification temperature, so that a liquid phase may exist for short times in reactions of Si-SiC/NiCrAl at temperatures even lower than 950°C. This is consistent with the observed change in reaction rate near 900°C shown in Figure 6.

In Figure 11 it is seen that a liquid phase exists at temperatures above ~950°C, with the composition range skewed slightly toward Si-rich materials. At the Si-SiC/NiCrAl interface, diffusion of Ni into the Si matrix quickly forms a liquid phase which then accelerates further liquification. The layer of porosity associated with the depth of reaction in the Si-SiC is apparently a solidification structure similar to micro-shrinkage in castings. The SiC skeleton is strong enough to support a compressive load, even in the presence of a liquid. The liquid phase forming initially in the metal side has no such skeleton, and is extruded by the compressive load as seen in Figure 2.

Below ~950°C, the reaction between Si-SiC and NiCrAl is somewhat similar to that observed in the SiC/NiCrAl system (6, 7). Because of the presence of free Si, however, reaction depths are greater.

CONCLUSIONS

This study has shown that when reaction-bonded Si-SiC ceramics are brought into close contact with Ni-base alloys at temperatures above $\sim 700^{\circ}\text{C}$, severe diffusion-controlled reactions occur both in the ceramic and metal. The presence of such reactions suggests that close attention be placed on ceramic/metal attachments currently being contemplated for hot machinery components, and that serious considerations be devoted to diffusion barrier coatings at these interfaces.

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Fig. 1. Schematic diagram of experimental apparatus.

Fig. 2. Macrograph of Si-SiC, SiC, and NiCrAl alloy after 1150C/50 h.

Fig. 3. Photomicrographs of Si-SiC/NiCrAl reaction after 1150C/50 h.

Fig. 4. Electron probe microchemical profile for Ni, Cr and Si across the reaction zone of Si-SiC/NiCrAl after 1150C/50 h.

5a

5b

5c

Fig. 5. Photomicrographs of Si-SiC/NiCrAl reaction after 1100C/100 h: a) overall structure, b) details in Si reaction, and c) details in Si-SiC reaction near metal interface.

Fig. 6. Reaction rates vs reciprocal absolute temperature for Si-SiC and SiC reacting with NiCrAl.

Fig. 8. Photomicrograph of the Si-SiC/NiCrAl reaction after 900°C/50 h.

7a

7b

Fig. 7. Photomicrographs of reactions after 900°C/100 h: a) Si-SiC/NiCrAl, and b) Si-SiC/Ni.

Fig. 9. Scanning electron micrograph of surface transverse to and through the columnar region (see Figure 8) of the Si-SiC/NiCrAl reaction after 900°C/50 h.

Fig. 10. Schematic representation of the reaction path for SiC/NiCrAl, after Ref. 6.

Fig. 11. The constitutional diagram for Ni-Si, after Ref. 11.

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A STUDY OF SOLID METAL/CERAMIC REACTIONS

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INTRODUCTION

In advanced energy systems, ceramics may allow higher operating temperatures for greater efficiency. However, compressive contacts at joints with metals are required by the poor tensile behavior of ceramics. Compression at these interfaces excludes oxygen, and oxides do not form. Reactions under inert or reducing conditions (as in metal matrix composites) have been studied,(1,2) as have reactions of complex superalloys with SiC,(3) Si/SiC(4) and SiN₄.(5) The reactions were complex, dictating a phenomenological study with no treatment of their basic nature or the phase equilibria. With a model alloy containing only Ni, Cr and Al, the present experiments and analyses are an attempt to gain a more basic understanding of metal/ceramic reactions.

EXPERIMENTAL

Materials. Most of the work described here has been performed on hot-pressed SiC manufactured by the Norton Company. Some experiments employed sintered SiC(6) fabricated in this laboratory.* Ceramics containing free Si were NC-435 from the Norton Company, and a Si/SiC composite material(7) fabricated in this laboratory.† The model superalloy made in this laboratory had a composition of 70 a/o Ni, 20 a/o Cr, 10 a/o Al (75.8 w/o Ni, 19.2 w/o Cr, 5.0 w/o Al); only Ni and Cr form silicides. In general, Ni alloys are 95% γ + δ by

*Supplied by the courtesy of C. A. Johnson, GE/CRD.

†SilicompTM - Trademark of the General Electric Company.

volume (remainder carbides and borides), where γ is the Ni solid solution and γ' is Ni_3Al . The model alloy is $\gamma + \gamma'$ only. The 14-30 a/o of solid solution elements (Cr, Mo, W) in superalloys are represented by 20 a/o Cr, while the 6-12 a/o of formers (Al, Ta, Ti, Nb) are represented by 10 a/o Al in the model alloy.

Reaction Couples. Metal discs (12.7 mm dia. x 3.2 mm) were polished on 400 mesh SiC paper and ceramic discs (6.4 mm dia. x 3.2 mm) on a 30 μm diamond wheel, and were cleaned in acetone. A ceramic/metal/ceramic sandwich was placed in the apparatus shown schematically in Fig. 1. Generally, two different ceramics were included in the sandwich. Nominal stress applied at the metal/ceramic interface was 7MN/m (3.5 MN/m for Si/SiC at high temperatures). A Pt-wound tube furnace surrounding the couple (not shown in Fig. 1) brought the couple to temperature in about 30 minutes. During the desired exposure at temperature, the furnace ends were covered with insulation, but no inert atmosphere was used. After reaction the ceramic and metal pieces were removed, encased in clear plastic, cut in two, examined metallographically, and then subjected to other analytical investigations.

Figure 1. Schematic of experimental apparatus.

RESULTS

Metallography

A reaction was detected in the model alloy, SiC, and Si/SiC at all temperatures investigated (700C - 1150C). For Si/SiC at temperatures above which a molten phase can exist, 964C(8), the reaction was quite severe. This is illustrated in Fig. 2, where a uniformly distributed load of 222 N was applied at 1150C for 50 hours. Molten Si was extruded at the Si/SiC/metal side, and obviously a great deal of liquid phase interdiffusion occurred. By contrast, the SiC/metal side showed a less severe zone of reaction.

Figure 2. Metal/ceramic reaction, 1150C/50h.

SiC/Metal Reaction. A typical SiC/NiCrAl reaction at 1150C is shown in the montage microphotograph of Fig. 3. The gap in Fig. 2, presumably due to thermal expansion mismatch, has been removed for clarity. The reaction consists of three distinct zones: a banded structure in the SiC at the top of the photograph, a transition zone in the metal containing (Cr_3Ni_2SiC) , and a zone in the metal consisting of Cr rich and NiSiAl phases. Diffusion of Si into the alloy occurs below this zone. From dimensional measurements and the use of fine quartz filament markers, the original interface is at the interface of the banded region and the transition zone. These zones persist in decreasing quantities as the reaction temperature and time are reduced. The banded structure in the SiC is evident after a reaction time of only three hours at 1000C.

A striking difference is seen in reactions for sintered and for hot-pressed SiC in Figs. 3a and 3b: Banding in the sintered SiC is much coarser. Chemically, there is 0.5 w/o B and C in the sintered

(a)

(b)

Figure 3. Reaction of a) hot pressed, and b) sintered SiC with NiCrAl, 1150C/50h.

material and about 8 w/o W (presumably introduced during milling the powder) in the hot-pressed material. Actual W-rich particles can be seen in the bands in the hot pressed SiC (Fig. 4). By some mechanism, this changes the nature of band formation but does not significantly affect the kinetics of the reaction. For temperatures where no liquid formation occurs, such as at 900C, the banded structure is still present in the SiC, but the reaction zone on the metal side has changed as shown in Fig. 5.

Figure 4. White W-rich particles in hot pressed SiC reaction zone.

20 μm

Figure 5. Hot pressed SiC reacted at 900C.

Si/SiC Metal Reaction. As noted in Fig. 2, at temperatures greater than 1000C, a liquid phase forms, and gross indentation into the metal occurs at 1100 and 1150C. Tests just above the liquidus temperature have not yet been conducted. At and below 900C, however, the reaction morphology is quite similar but the reaction zone is larger than that for SiC, as may be seen by comparing Figs. 5 and 6. For pure CVD Si, the reaction zone is larger yet, but a similar columnar structure is present at the end of the reaction zone. Below 900C, reactions for SiC or Si/SiC contacting the metal are similar, but more Si is available in Si/SiC than solely from the decomposition reaction, $\text{SiC} \rightarrow \text{Si} + \text{C}$.

40 μm

Figure 6. Si/SiC reacted at 900C.

Reaction Kinetics. From a total of 16 hot-pressed SiC/NiCrAl experiments at 1150C to 700C and times of 3 to 260 hours, straight lines of reaction depth in both metal and ceramic were plotted vs. $\sqrt{t}$. From the slopes of the lines, an Arrhenius plot (Fig. 7) was constructed. Within the accuracy of the data, a least-squares straight line fits both SiC and NiCrAl data over the entire range of temperatures, with an activation energy of 22.3 Kcal/mole. Assuming reaction rates for Si/SiC and Si are similarly diffusion controlled, single points for the reaction rates (depth/time) for metal penetration by Si/SiC couples at 700C, 800C, and 900C are shown in Fig. 7, and for Si at 900C. An accurate measure of the depth of metal penetration and/or Si depletion in the Si/SiC was not possible by metallography alone. For comparison, reaction rates for a Ni-base superalloy with SiC(3) are also shown in Fig. 7.

Figure 7. SiC/NiCrAl reaction kinetics.

Comparing reaction rates of SiC and Si/SiC, the activation energies at lower temperatures (700C and 800C) are similar, but Si/SiC shows more reaction. This is consistent with metallography. More Si is available from Si/SiC than from the decomposition of SiC. However, as the eutectic temperature is approached, the rate increases significantly for the Si/SiC and more so for pure Si. More

kinetic data are needed for the Si/SiC/NiCrAl system between 800C and 1000C.

The major element reacting with the ceramic is Ni, and apparently in a superalloy its activity is reduced, at least at lower temperatures. This lends encouragement to the interlayer concept in reducing or eliminating such reactions. The lower SiC/superalloy reaction rates also indicate that Ti has less affinity for Si than expected or that it is relatively immobile.

Microanalysis and Phase Relations

A typical electron probe microanalysis of a ceramic-metal couple is seen in Fig. 8. The original interface was between SiC reaction and transition reaction zones. In SiC and Si/SiC couples there is a near total absence of Al in the ceramic region, and Al in the outer region of the metal diffuses uphill due to the chemical potential gradient. The outer region of the metal is nearly devoid of Al, while Al is concentrated in the metal reaction zone. This feature reduces the complexity of most of the reaction to the NiCrSiC system. Spikes of Al concentration in the transition reaction zone are due to Al_2O_3 particles.

Figure 8. SiC/NiCrAl reaction profile, 1150C.

The Ceramic Reaction Zones. The Si/SiC/metal interface can be treated as two couples on a local microstructure basis, Si/NiCrAl, and SiC/NiCrAl. A probable sequence occurring on heating to 1150C is as follows. Interdiffusion is slow until the interface reaches about 964C,(8) when liquid should form at the local NiCrAl-Si interfaces. Since Cr and Al also depress the liquidus of Ni, liquid may form earlier. Concentrations less than about 38 a/o Si will result in only solid structures at 1150C, while greater Si concentrations will be liquid or liquid-plus-solid reaction structures, except at pure Si. While liquid formation dominates the local NiCrAl-Si

couples above 900C, little or no liquid phase formation occurs for NiCrAl-SiC, as seen in the marked difference in attack for SiC and Si/SiC in Fig. 2. The liquid is mostly Ni and Si, with small amounts of Cr and very little Al. The dissolution of the metal allows Ni to diffuse through the liquid + solid structure to the advancing front. The solid structure formed (35 a/o Si) is mostly Θ or Δ -Ni₂Si. Lesser amounts of Cr₃C are formed by dissolution of adjacent SiC grains. Most of the Cr and Al are rejected from the liquid, and concentrated in new phases in the metal side. Immediately adjacent to the Θ /Cr C₂/SiC structures, but still in the Si/SiC reaction zone, is a structure with a matrix of 33-36 a/o Si, likely to be Δ or Θ , and particles which are most likely graphite, similar to structures discussed below for SiC/metal couples.

Turning to reaction zones in SiC-metal couples, banded structures shown in Figs. 3 and 8 are typical. The dark bands consist of carbon in the form of graphite particles, identified by x-ray and electron diffraction, Δ Ni₂Si and ξ ,⁷ identified by STEM and diffraction. The light bands are mostly Δ with ξ . Although the driving force forming the bands is not understood, the structure obeys the phase rule: the carbon concentration decreases from 31 w/o in the first dark band (SiC side) to 9 w/o in the last dark band, so that chemical potential gradients through the banded structure are monotonic. The number of bands is constant, but thickness increases with time; bands are seen at short exposures (3h at 1000C).

The Ni-SiC ternary phase diagram has not been determined and reported in the literature. However, one can be hypothesized from the binary diagrams(8) and the structures observed in the ceramic reaction zones. This diagram is shown in Fig. 9, along with reaction paths discussed above. For couple A, between (Ni,Cr) and Si/SiC, the path goes from Si/SiC, through a region where a Si-rich liquid co-exists with SiC, then through the Θ or Δ + SiC region which is the major feature observed microstructurally. From there a small region exists consisting of Θ + Δ + Cg, next to the transition reaction zone on the metal side. (Dotted lines in reaction paths represent interfaces between compositions at the dotted line end points, and are interfaces in the microstructure.) For couple B, between SiC and (Ni,Cr) the path begins at SiC, goes to the dark band consisting of Δ and Cg, then migrates back and forth between a band that is free of Cg and alternately one that contains Cg.* Each progressive band contains less Cg before the path eventually crosses into the transition reaction zone in the metal side. Of course the reaction paths are more complex than this, but as seen in Fig. 8, Cr and Al play minor roles on the ceramic side. The rejection of Al is nearly complete, and Cr is present primarily in Cr,Si carbides. The

⁷ ξ is the complex carbide Cr_{5-x}Si_{3-y}C_{x+y}.

*Similar reaction paths are seen in metal-metal systems(9).

Figure 9. Ceramic reaction zone paths.

banded structure also forms in Ni-SiC couples where only Δ and graphite are likely to form.

The striking differences in behavior seen in Fig. 2 are apparent in the phase diagram in Fig. 9. The reaction path for SiC-metal is predominantly or totally solid state. The reaction path for Si/SiC-metal passes through a $L + SiC$ phase field that allows dissolution of metal atoms and much more rapid interaction.

The Metal Reaction Zones. On the metal side, Al and Cr are much more critical to the phase relations governing the reaction, while C plays a minor part. As seen in Fig. 8, Cr and Al are concentrated in transition and metal reaction zones, respectively. Uphill diffusion of Cr occurs from the metal through the reaction zone and into the transition reaction zone, while for Al, uphill diffusion occurs from both the metal and the transition reaction zone into the metal reaction zone. The transition zone is largely 50 a/o Cr, 16-17 a/o Si and 33-34 a/o Ni (C not included). From available diagrams,(10) and STEM and x-ray diffraction, this is predominantly the carbide phase. A Ni,Al rich phase with 29 a/o Al, 9 a/o Si and 8 a/o Cr is found interspersed in γ . Typical structures are seen in Fig. 3.

The structure formed below the layer varies with temperature. At elevated temperatures, a coarse columnar structure of a Ni,Si,Al phase and Cr_3Si (light phase) develops, as seen in Fig. 3. Within

the Ni,Al,Si phase are fine, white particles. These particles are > Cr, similar to > Cr particles observed in NiAl structures in aluminized Ni-base alloys.(11) At lower temperatures, a different structure develops below the layer, as seen in Figs. 5 and 6. This structure has not been analyzed in detail, but appears to be a Ni,Si,Al rich phase, a lower Al+Si concentration (light phase) and > Cr (white phase). Similar columnar growth is observed in aluminized Ni-base alloys. The structures of the Ni,Si,Al phases appear to be predominantly Ni_3Si_2 , with some Ni_2Si .

DISCUSSION

A model superalloy containing only three elements was chosen to simplify the metal-ceramic reaction. The complexity was reduced, but much work remains to understand this "simple" system. Additional analysis is needed in the reaction areas, and alloys need to be synthesized to verify the postulated phase relations.

A very real problem exists when Si/SiC or SiC is in close contact with a Ni-base alloy in hot machinery. With the Si/SiC material, liquid phases may be present at 900C and perhaps lower. With the extent and severity of the Si/SiC-metal reaction and the persistence of both SiC and Si/SiC reactions as low as 700C, work is needed to minimize these reactions by the use of barrier coatings. Such work can be initiated before understanding the fundamental mechanisms in these reactions. Such barrier coatings will be a necessity if Si/SiC and SiC structural ceramics are to be used in contact with Ni-based alloys above about 700C.

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