MASTER

A STUDY OF SOLID METAL/CERAMIC REACTIONS

Progress Report

6/18/79 to 3/17/80

on

Contract No. DE-AC02-79ER10413

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

by

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February 26, 1980

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A STUDY OF SOLID METAL/CERAMIC REACTIONS

1. INTRODUCTION

Interactions that occur between metals and ceramics are becoming an important consideration in a number of high temperature technologies. Improvements in efficiency of energy generation which can result from higher operating temperatures are providing the impetus for the use of ceramic materials in increasingly severe environments. In most of these technologies, however, the ceramic must come into contact with a metal, and most likely this area of contact will be in compression. Within this contact area, then, oxygen will tend to be excluded, preventing the formation of oxide layers.

Ceramic-metal reactions under inert or reducing conditions received a good deal of attention about fifteen years ago in connection with the development of metal matrix composites, and much of this work has been summarized.^(1,2) More recently, the reactions between SiC,⁽³⁾ Si₃N₄,⁽⁴⁾ and complex superalloys have been studied. It has also been determined that ceramics containing free silicon, such as reaction bonded silicon carbide (Si/SiC), react more severely than SiC alone.⁽⁵⁾ Most of the above work 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 and apply phase equilibria concepts to them. By using a model superalloy containing just the elements Ni, Cr, and Al, the experiments and analyses presented below represent the beginning of an attempt to gain such a fundamental understanding for at least certain ceramic-metal reactions.

2. EXPERIMENTAL

2.1 Materials

Five silicon based ceramics have been studied. Most of the work to date has been performed on hot-pressed SiC manufactured by the Norton Company. Some experiments employed sintered silicon carbide⁽⁶⁾ fabricated in this laboratory.* Ceramics containing free silicon came from two sources; NC-435 from the Norton Company, and SilcompTM (7) Si/SiC composite material, again fabricated in this laboratory. The nitride base ceramic was hot-pressed Si_3N_4 , obtained from the Norton Company.

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 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.

*Supplied by the courtesy of C.A. Johnson, GE/CRD.
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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 mesh SiC paper and the ceramics on a 30 μ m diamond wheel; both were cleaned with acetone. The reaction couple consisted of a ceramic/metal/ceramic sandwich and was placed into the apparatus shown schematically in Fig. 1. Generally, two different ceramics were run against the same metal piece. Usually, a weight of 222 N was used, leading to a stress of 7 MN/m² at the interface. For the Si/SiC at higher temperatures, half this load was applied. The specimens were surrounded by a platinum wound tube furnace (not shown in Fig. 1), brought to temperature in about 30 minutes and left there for the required time. 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 separately, 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 showing such a section will be shown and discussed subsequently (Fig. 2).

3. RESULTS

3.1 Metallography and Microhardness

Metallographically, a reaction was detected in the model alloy, SiC, and Si/SiC at all temperatures investigated (700°C - 1150°C). For the case of Si₃N₄, the reaction was much less severe, and no reaction was

detected below 1000°C . For Si/SiC at temperatures above which a molten phase can exist (NiSi-Ni₃Si₂ eutectic at 964°C), the reaction was quite severe. This is illustrated in Fig. 2, where a load of 222 N was applied at 1150°C for 50 hours. Molten Si was extruded at the Si/SiC/metal side, and obviously a great deal of liquid phase interdiffusion took place. By contrast, the SiC/metal side showed a much lesser (but still severe) zone of reaction. This macrophotograph also illustrates that the apparatus shown in Fig. 1 is capable of applying a uniformly distributed load.

In the following paragraphs, the results using SiC will be discussed first, then Si/SiC, pure Si, and finally Si₃N₄. Phase identification and chemical composition will be mentioned only briefly; these subjects will be discussed in Section 3.3. It will be appreciated that the results and interpretations in this and the following sections are incomplete; experiments and analyses are continuing and many questions remain unanswered.

3.1.1 SiC/Metal Reaction. A typical SiC/NiCrAl reaction, in this case at 1150°C , is shown in the montage microphotograph of Fig. 3. For clarity, the gap, presumably caused by a thermal expansion mismatch between the reacted SiC and the metal (see Fig. 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 containing a ternary CrNiSi sigma (σ) phase and mixed silicides, and a zone in the metal consisting of β NiAl and σ . Not evident from the photomicrograph is an area beyond the region where Si has diffused but not reacted. 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. The banded structure in the SiC is evident after a reaction time of only three hours at 1000°C .

A striking difference between sintered and hot-pressed SiC reacted with the NiCrAl alloy was observed and can be seen by comparing Fig. 3 with Fig. 4. The same phases are present in about the same amount, but

the banding in the sintered SiC is much coarser. The cause for this is not known. Chemically, the only difference between the two materials is 0.5 w/o B and C in the sintered material and about 8 w/o W (presumably introduced during milling the powder) in the hot-pressed material. Evidently, by some mechanism, this changes the nature of band formation but does not significantly affect the kinetics of the reaction.

The banded structure in the reacted SiC was considered interesting and unusual, and when x-ray diffraction analysis indicated the presence of graphite in the dark bands, the origin and nature of the structure became of even more interest. Previous analyses showed Ni_2Si present in the reacted SiC zone, and microprobe data indicated a high (~ 30 w/o) carbon content in the dark bands. The apparent presence of graphite in the SiC reaction zone was confirmed by heat treating a small section of reacted sintered SiC (100 hr - 1150°C) at 1000°C in air for three hours. If graphite were present, it would oxidize and leave voids behind. The series of SEM photographs shown in Fig. 5 confirm that voids indeed are present in the dark bands. The heat-etched light bands also displayed a perpendicular banded structure of unknown origin. EDS spectra from the indicated areas in Fig. 5 are shown in Fig. 6. It would appear that SiC undergoes a decomposition reaction in the presence of Ni and Cr, with the Si reacting to form silicides and the carbon remaining in place in the form of graphite. These structures will be discussed in terms of the governing phase equilibria in Section 3.3.

Turning now to reactions occurring at temperatures where no liquid formation occurs, at 900°C the same features are present but in different morphologies. The banded structure is still present in the SiC, but on the metal side the structure of the $\beta + \alpha$ Cr region has changed as shown in Figs. 7 and 8. This behavior will also be discussed in Section 3.3.

3.1.2 Si/SiC Metal Reaction. As indicated in connection with Fig. 2, at temperatures greater than 1000°C , a liquid phase forms and gross indentation into the metal occurs at 1100 and 1150°C . Tests just above

the liquidus temperature have not yet been conducted. At and below 900°C , however, the reaction morphology is quite similar but the reaction zone is larger than that for SiC, as may be seen by comparing Fig. 9 with Fig. 7. When pure CVD Si is used, the reaction zone is larger yet, but the same type of columnar structure is present at the end of the reaction zone, as shown in Fig. 10. It would seem, then, at temperatures less than about 900°C , the reaction that occurs when SiC or Si/SiC is brought into contact with a metal is similar, but more Si can diffuse from a Si/SiC material than that available from the decomposition reaction, $\text{SiC} \rightarrow \text{Si} + \text{C}$. As has been discussed, carbon plays a minor role in the reaction on the metal side of the ceramic/metal couple. The interdiffusion of Si and the metallic constituents for a Si/SiC material, NC 435 in this case, is illustrated in Fig. 11. The boundary of the Si depleted zone is quite sharp, and similar behavior is noted for Silcomp.

3.1.3 Si₃N₄/Metal Reaction. Si₃N₄ is much more stable when in contact with a metal at elevated temperature than SiC. In part this is due to the higher free energy of formation of Si₃N₄ (-38.7 Kcal/gm-atom N) compared to SiC (-26.1 Kcal/gm-atom C),⁽⁸⁾ and in part to the fact that the decomposition of Si₃N₄ depends on the nitrogen partial pressure while that of SiC is independent of gas pressure. A photomicrograph of the reaction between Si₃N₄ and NiCrAl is shown in Fig. 12. The reaction area in the metal, probably consisting of mixed oxides, nitrides, and silicides, is completely different from that of SiC (Fig. 3). In both the ceramic and metal the reaction at 1150°C occurs only in a few areas, as compared to the uniform reaction zone in SiC/NiCrAl. The extent of reaction at 1150°C into the ceramics is 0.32 mm in the SiC and a maximum of 0.1 mm in Si₃N₄, while at 1000°C no reaction is visible in the Si₃N₄ and just barely detectable in the metal.

3.1.4 Microhardness Measurements. Some microhardness data have been obtained on reacted SiC/NiCrAl couples; more are planned for the other material combinations. Fig. 13 shows a SiC/NiCrAl reaction zone indicating

where the microhardness values were measured (Knoop indenter, 100 gram load), and Table I shows the average values (generally of about five readings). The low hardness in the dark bands in the SiC reaction zone is again indicative of a soft phase, such as graphite. In the transition zone (Area 1, 2, and 3), the relatively high values are suggestive of the presence of silicides and oxides. Typical microhardness values of such phases are Cr_3Si , 1005; Cr_3Si_2 , 1280; NiSi_2 , 1019; Al_2O_3 , 2100.^(9,10) Interestingly, the Ni_2Si detected in the SiC reaction zone has a relatively low microhardness of 440,⁽⁹⁾ again suggesting its presence in the dark bands. In the metal itself, a microhardness value of ~ 680 in the heat-treated σ region is not unreasonable and, as expected, is higher than the value of ~ 445 in the β phase.

3.2 Reaction Kinetics

As indicated earlier, the majority of the experimental work conducted to date has been on hot-pressed SiC, so it is only possible to analyze reaction kinetics in any detail for this material. From a total of 16 SiC/NiCrAl experiments at 1150°C, 1100°C, 1000°C, 900°C, 800°C, and 700°C at times ranging from 3 to 260 hours, straight lines of reaction depth in both metal and ceramic were plotted vs. $\text{sec}^{1/2}$. From the slopes of these lines, the Arrhenius plot shown in Fig. 14 was constructed. Within the accuracy of the data, a straight line seems to fit both the SiC and NiCrAl rate data over the entire range of temperatures. A least-square line was fitted to the data, and an activation energy of 22.3 Kcal mole⁻¹ was obtained. Assuming the 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 700°C, 800°C, and 900°C are shown in Fig. 14, as well as the rate for Si at 900°C. It was not possible to accurately measure the depth of metal penetration and/or Si depletion in the Si/SiC by metallographic means alone. For comparison, the reaction rates for for a Ni-base superalloy in contact with SiC⁽³⁾ are also shown in Fig. 14.

Considering first the reaction rates of SiC and Si/SiC, the activation energy at lower temperatures (700°C and 800°C) seem similar, with the Si/SiC forming larger reaction zones than SiC. This is consistent with metallographic observations and the fact that more Si is available from Si/SiC than from the decomposition of SiC. However, as the eutectic is approached, the rate increases significantly for the Si/SiC and more so for pure Si. In fact, because of the presence of Cr and Al in the Ni, a liquid phase may form below 900°C . This will be discussed later. As indicated earlier, more kinetic data need to be acquired for the Si/SiC/NiCrAl system between 800°C and 1000°C .

The fact that the Ni-base superalloy has a higher activation energy than the model NiCrAl alloy is encouraging from the viewpoint of minimizing ceramic-metal reactions. Observations to date indicate that Ni is the major element in causing reactions in the ceramic, 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 perhaps Ti has not as strong an affinity for Si as originally thought, or that at least it is possible to render the Ti relatively immobile.

3.3 Microanalysis and Phase Relations

3.3.1 SiC and Si/SiC Metal Reaction. A typical electron probe microanalysis trace through the reaction zones of a ceramic-metal couple is seen in Fig. 15. The original couple interface was located at the boundary between the SiC reaction zone and the transition reaction zone. A feature of the SiC and Si/SiC couples that is not immediately apparent is the near total absence of Al in the ceramic region of the couple. In fact, as Fig. 15 shows, Al in the outer region of the metal is subjected to chemical potential gradients that lead to an uphill diffusion of Al. The outer region of the metal is nearly devoid of Al, while Al is concentrated in the metal reaction zone. This feature of the overall metal-ceramic reaction

aids analysis, since the major portion of the reaction is reduced in complexity from a quinary to a quaternary system: NiCrSiC. There are spikes of Al concentration in the transition reaction zone, but these are probably due to Al_2O_3 particles formed by diffusion of oxygen from the environment through the couple interface. As will be shown below, the dominance of Ni diffusion in reacting with the ceramics further reduces the complexity of analysis.

3.3.1.1 The Ceramic Reaction Zones. Consideration of the Si/SiC metal reaction will be taken first. The ceramic-metal interface can be treated as two couples on a local microstructure basis, one between Si and NiCrAl, the second between SiC and NiCrAl. A probable sequence of events occurring as the couples begin to heat to a reaction temperature of 1150°C is as follows: Interdiffusion is slow until the interface reaches about 965°C .⁽³⁾ At that point, the Ni-Si binary diagram (Fig. 16), indicates a liquid phase should form at the local NiCrAl-Si interfaces. Because Cr and Al both depress the liquidus of Ni, the liquid phase formation between NiCrAl and Si may actually occur at even lower temperatures. As seen in Fig. 16, Si concentrations less than about 38 a/o will result in totally solid state structures at 1150°C , while all Si concentrations greater than 38 a/o will consist of liquid or liquid-plus-solid reaction structures, except at 100 a/o Si. Thus, Si penetration from the liquid into the NiCrAl side will be primarily a solid state reaction, while penetration of the metallic elements into the Si/SiC side will be primarily a liquid state reaction. This may explain the microstructure shown in Fig. 11, where intimate Si-NiCrAl contact was established, and a wave of metal atoms washed through the Si network on the Si/SiC side. The couple in Fig. 11 saw a maximum exposure of 900°C . This indicates that the first liquid formation of 964°C shown in Fig. 16 may be depressed below 900°C because of the presence of Cr and Al.

While liquid phase formation dominates the reaction in the local NiCrAl-Si couples, little or no liquid phase formation is occurring between NiCrAl and SiC. This is noted in the more detailed analyses to follow, and also in the marked difference in attack for SiC and Si/SiC noted in Fig. 2. Large volumes of liquid-plus-solid "mush" have been squeezed from the interface with Si/SiC, like juice and pulp from a lemon, while little penetration is noted on the SiC side.

Returning to the details of the reaction for Si/SiC, a typical microstructure in the Si/SiC reaction zone is shown in Fig. 17a. Region A is SiC, region B is typically 59Ni, 35Si, 3.5Cr, 2.5Al (atom percent), and region C is typically 52.8Cr, 42.5C, 2.3Ni and 2.4Si. Region C is probably a Cr_3C_2 type carbide formed by interaction of the liquid wave moving through the Si network with the SiC particles. The Si network eventually receives sufficient Ni and Cr from dissolution of the metal that the solidus concentration is reached. As shown in Fig. 16, this should occur at 38 a/o Si, forming the θ phase. This phase has a range of compositions, reaching as low as 35 a/o Si. Region B can thus tentatively be identified as θ , with some Cr and Al substituting on either or both the Ni and Si sublattices. There is a possibility that a $\text{Si}+\text{SiC}+\delta$ (Ni_2Si) equilibrium exists in the NiCrSiAlC system, so that region B could possibly be δ . The weight percent of Si in Ni_2Si is 19.3, while in the 35 a/o Si composition of θ , it is 21.2 w/o Si. Final analysis will be done by x-ray diffraction, but the tentative analysis is θ . The predominant phase present in the Si/SiC reaction zone is θ , with a much smaller volume fraction of Cr_3C_2 being formed.

Immediately adjacent to the $\theta/\text{Cr}_3\text{C}_2/\text{SiC}$ structures, while still within the Si/SiC reaction zone, is the structure labeled "B" in Fig. 17b. The matrix is 33-36 a/o Si, and is likely to be δ (Ni_2Si) or θ , while the particles are most likely graphite, similar to structures discussed below in considering SiC-metal couples.

To summarize the high temperature Si/SiC-metal reactions on the Si/SiC side, the process is dominated by liquid phase formation above 900°C. 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 is mostly θ (35 a/o Si). Most of the Cr and Al are rejected from the liquid, being concentrated in new phases formed on the metal side of the couple. These will be discussed later.

Turning next to SiC reaction zones in SiC-metal couples, structures shown in Figs. 3-5 are typical. Alternating layers of the banded structure are high in C or high in Ni and Si. Even the layers high in C are still predominantly Ni and Si, as was seen in Fig. 15. The C concentration in the alternate layers decreases on approaching the metal side. Data for C are shown in Table II.

The dark bands consist of carbon in the form of graphite, identified by x-ray diffraction, and one or more silicides. The microanalysis indicates 4 a/o Cr, 1 a/o Al, 18 a/o Si, 37 a/o Ni, 40 a/o C adjacent to SiC, and 8 a/o Cr, 1 a/o Al, 25 a/o Si, 52 a/o Ni, 14 a/o C on the metal side. The particles in the dark band shown in Figs. 5 and 6 are thus graphite and θ and/or δ . The light band appears to be θ and/or δ with a Cr-rich phase, possibly Cr_3C_2 . The driving force for formation of the banded structure is not understood at this time. However, the structure does not disobey the phase rule; the carbon concentration decreases across the region, so that chemical potential gradients through the banded structure are monotonic. The banded structure is apparent after as little as three hours at 1000°C. The number of bands is essentially constant with time, with the thickness increasing with time. The thinner bands for the hot-pressed SiC (Fig. 3) must be influenced by the presence of W or the absence of B.

The Ni-Si-C ternary phase diagram has not been determined and reported in the literature. However, from the binary diagrams⁽¹¹⁾ and the structures observed in the ceramic reaction zones, it is possible to draw a

hypothetical diagram. This diagram is shown in Fig. 18, along with reaction paths discussed above for Si/SiC and SiC-metal couples. For couple A, between (Ni,Cr) and Si/SiC, the path goes from Si/SiC, through a region where a Si-rich liquid coexists with SiC, then through the $\theta + \text{SiC}$ region which is the major feature observed microstructurally, such as in Fig. 11. From there, a small region in the microstructure exists consisting of $\theta + \delta + \text{Cg}$, before crossing into the transition reaction zone on the metal side. (It should be noted that dotted lines in diffusion or reaction paths represent interfaces between their end points, and therefore do not represent any distance in the microstructure.) For couple B, between SiC and (Ni,Cr) the path begins at SiC, goes to the dark band consisting of δ , θ 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, since the system is really quinary. However, as seen in Fig. 15, Cr and Al do not play a major role on the ceramic side. The rejection of Al is nearly complete, and Cr is present primarily in isolated Cr_3C_2 particles. The banded structure also forms in Ni-SiC couples.

The striking differences in behavior seen in Fig. 2 are apparent in the phase diagram in Fig. 18. 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.

3.3.1.2 The Metal Reaction Zones. On the metal side, Al and Cr are much more critical to the phase relations governing the reaction. However, C plays little or no part in this region. Even the values of C concentration listed in Table II are probably much greater than actual.

*For examples of similar reaction phases in metal-metal systems, see References 12-14.

As seen in Fig. 15, 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. From available diagrams,⁽¹⁵⁾ this is apparently the ternary sigma (σ) phase frequently found in Ni-base superalloys. Some β (NiAl) with 29 a/o Al, 9 a/o Si and 8 a/o Cr is found interspersed in the σ phase. These types of structures are seen in Figs. 3 and 4.

The structure formed below the σ layer varies with temperature. At elevated temperatures, a coarse columnar structure of β (dark phase) and σ (light phase) develops, as seen in Figs. 3, 4 and 8. Within the β Ni(Al,Si) phase are fine, white particles. These particles have not been extracted for analysis but are expected to be α Cr. They are similar to α Cr particles observed in β structures in aluminized Ni-base alloys.⁽¹⁶⁾ At lower temperatures, a different structure develops below the σ layer, as seen in Figs. 7 and 9. This structure has not been microanalyzed as yet, but appears to consist of β with high Al+Si concentration (dark phase), β of low Al+Si concentration (light phase) and α Cr (white phase). This columnar growth of $\beta + \alpha$ structures is observed in aluminizing Ni-base alloys, as seen in Fig. 19, and also in the interdiffusion of Si and NiCrAl (Fig. 10).

Recapitulating the sequence of microstructure from the $\delta+\theta+Cg$ structures on the ceramic side of the couples, a σ layer forms adjacent to the ceramic. This layer may contain isolated β Ni(Al,Si) regions. At high temperatures, a columnar $\beta + \alpha$ layer forms. At the extreme boundary of the $\beta + \alpha$ or $\beta + \sigma$ structures, there is about 6 a/o Si in solution in the Ni₂₀Cr₁₀Al metal terminal of the couple. The distance to which Si further penetrates into the metal is very dependent on time and temperature.

3.3.2 Si₃N₄ Metal Reaction. Very little analytical work has been performed on the Si₃N₄ couples, primarily because of the fine structures formed, the limited reaction distances and the non-uniformity of the couples,

as seen in Fig. 12. A profile through an 1150°C couple is seen in Fig. 20. From the Si_3N_4 side, the first reaction phase formed was a Cr_xN_y phase, where x and y cannot be defined accurately. The phase is approximately 40 a/o Cr, 55 a/o N, balance Ni, Si and Al. Below the nitride phase, a layer of σ was seen (the flat portion of the curves in Fig. 20). Below the σ is a β layer of approximate composition 65 a/o Ni, 3 a/o Cr, 33 a/o (Al + Si) with Si decreasing from about 20 a/o and Al increasing from about 13 a/o while moving toward the metal terminal. As seen in Fig. 20, the data collection was stopped prematurely. Presumably, however, the Si concentration fell to a low level just beyond the data presented, since the microstructure shown in Fig. 12 shows about 150 μm of reaction zones.

4. DISCUSSION AND FUTURE WORK

A model superalloy containing only three elements was chosen for this study to reduce the complexity of the metal-ceramic reaction. It is obvious that although the complexity may have been reduced, a great deal of work still needs to be done to understand this "simple" system. Additional analytical techniques, such as Auger and STEM analyses, need to be conducted on the reaction areas, and alloys need to be synthesized in order to understand the postulated phase relations.

One point that is evident as a result of the research conducted to date is that a very real problem exists when Si/SiC, SiC, and (to a lesser extent) Si_3N_4 is brought into close contact with a nickel-base alloy in a piece of hot machinery. Particularly with the reaction bonded Si/SiC material, it seems that liquid phases may be present at 900°C and perhaps lower, and this would prevent its use without protective barriers.

To date, as has been seen, not a great deal of work has been performed with Si_3N_4 . The reasons for this have been detailed in this report; less severe reactions and non-uniformity of the reaction. Although some additional

work is planned on the analysis of the reaction, not a great deal of further work will be performed with the hot-pressed material. This is a complex material containing densification aids which complicate the study and the composition is still being varied.

The same remarks, however, do not apply to reaction bonded silicon nitride (RBSN). This material can be formed into final shape without expensive machining and has excellent high temperature properties. Although it has a lower strength and some problems with oxidation, in view of the relative inertness Si_3N_4 exhibits with nickel-base alloys, some reactivity experiments using RBSN are in order.

Other future work that is planned is to examine the effect of Ti on the reaction. This element has a high affinity for Si, although as pointed out in Section 3.2, in an alloy it might not be as severe as anticipated. Nevertheless, to validate this point alloys containing 10 atomic percent Al + Ti (rather than just 10 a/o Al) will be fabricated and reactivity experiments will be conducted with this alloy and SiC, Si/SiC, and Si_3N_4 .

In view of the extent and severity of the Si/SiC-metal reaction discussed above, and the persistence of both SiC and Si/SiC reactions as low as 700°C , it is considered both timely and necessary to begin work to minimize these reactions by the use of barrier coatings. Such work can be initiated before a complete understanding of the fundamental mechanisms involved in ceramic-metal reactions is attained. As shown in this report, such a barrier coating will be a necessity if Si/SiC and SiC structural ceramics are to be used in contact with nickel-based alloys above about 700°C .

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TABLE I
MICROHARDNESS VALUES FOR VARIOUS PHASES IN SiC/NiCrAl REACTION ZONE
(KNOOP - 100 GRAM LOAD)

Material/Phase (See Fig. 13)	Microhardness
SiC	2820 $\pm$ 57
SiC Reaction Zone	
White Banded Areas	847 $\pm$ 32
Dark " "	398 $\pm$ 28
Metal Reaction Zone	
Area 1	1152 $\pm$ 86
" 2	1133 $\pm$ 50
" 3	1290
" 4	445 $\pm$ 29
" 5	679 $\pm$ 46
Unreacted Matrix	358 $\pm$ 14

TABLE II
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. 2. Macrophotograph of Si/SiC, SiC, and NiCrAl alloy after 50 hours at 1150°C.

0.1 mm

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

0.1 mm

Fig. 4. Reaction zones in sintered SiC and NiCrAl alloy after 100 hours at 1150°C.

OVERALL VIEW

LIGHT BAND

DARK BAND

LIGHT BAND

DARK BAND

LIGHT BAND

Fig. 5. SEM photographs of reaction sintered SiC after (a) 124 hours at 1150°C in contact with NiCrAl alloy, and (b) 3-hour heat treatment in air at 1000°C.

A

B

C

D

Fig. 6. Semi-quantitative EDS spectra from indicated areas in Fig. 5.

20 μm

Fig. 7. Reaction zones in hot-pressed SiC and NiCrAl alloy after 220 hours at 900°C.

1150 °C

25 μm

900 °C

25 μm

Fig. 8. Photomicrographs illustrating the difference in α -Cr distribution at 1150°C (small white areas) and 900°C (stringers) in $\beta + \gamma'$ reaction zone.

40 μm

Fig. 9. Reaction zone in NiCrAl alloy after 100 hours at 900°C in contact with Si/SiC.

0.1 mm

Fig. 10. Reaction zone in NiCrAl alloy after 100 hours at 900°C in contact with pure Si.

0.5 mm

Fig. 11. Reaction zone in NiCrAl alloy and Si/SiC (NC 435) after 100 hours at 900°C.

Fig. 12. Reaction zone in Si_3N_4 and NiCrAl alloy after 100 hours at 1150°C .

50 μm

Fig. 13. Reaction zone in NiCrAl after contact with SiC at 1150°C showing areas where micro-hardness values were obtained.

Fig. 14. Reaction rates in SiC, Si/SiC, Si, and NiCrAl alloy as a function of reciprocal absolute temperature. Reaction rates for SiC/superalloy from Reference 3.

Fig. 15. Electron microprobe chemical analyses for Ni, Cr, Si and Al in a SiC-NiCrAl couple treated 50 hours at 1150°C.

Fig. 16. Ni-Si binary phase diagram, after Hansen. (11)

a

40 μm

b

0.1 mm

Fig. 17. Microstructure in (a) Si/SiC reaction zone and (b) across the Si/SiC metal couple after 100 hours at 1100°C.

Fig. 18. A hypothetical (Ni,Cr)-Si-C 1150°C isothermal section with maps of the ceramic portion of the Si/SiC(A) and SiC(B)-metal reaction paths.

20 μm

Fig. 19. Microstructure of pack aluminized Ni-base alloy IN-738, after Jackson and Rairden(16).

Fig. 20. Electron microprobe chemical analyses for Ni, Cr, Si and Al in a Si₃N₄-NiCrAl couple treated 50 hours at 1150°C.