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Employing reactive synthesis for metal to ceramic joining for high temperature applications

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Joining of dissimilar materials allows the properties of both materials to be exploited in a device or structure. The main reasons for the incorporation of dissimilar materials are to achieve function, improve efficiency and to reduce cost.

Silicon nitride is an engineering ceramic that has outstanding properties but has yet to find its full commercial potential. Silicon nitride is suitable for high temperature applications, however, its incorporation into devices or structures tends to be restricted due to a lack of suitable joining techniques.

This paper presents the results of joining between the high temperature and corrosion resistant iron-chromium-aluminium alloy (Fecralloy) with silicon nitride by a nickel aluminide (NiAl) interlayer. The formation of NiAl from its constituent elements (Ni-Al compact was used) by reactive synthesis is highly exothermic and this was utilised to cause partial melting of the Fecralloy interface and reactive wetting of the silicon nitride interface.

Joints with average shear strength of 94.3 MPa were fabricated under optimum processing conditions (900°C, 15 min, 45 MPa). Thermal cycling at 850°C in air showed that the joints could be used at this temperature.

The primary focus of this work was on the effects of process conditions upon the microstructure and mechanical properties of the joint. The reactive synthesis of NiAl was studied using differential thermal analysis (DTA), where the effects of varied heating rate were investigated. © *2004 Kluwer Academic Publishers*

1. Introduction

Engineering ceramics such as silicon nitride are of great commercial interest, especially for high-temperature applications [1]. This is due to their low cost, superior strength, high impedance to wear, good thermal properties, excellent corrosion and oxidation resistance [2].

Whilst silicon nitride has found certain applications mainly in the automotive industry (e.g., spark plugs and rocker arms) its full commercial potential is yet to be realised. A major obstacle to this is the lack of suitable metal to ceramic joining techniques, as the silicon nitride has to be incorporated into devices and structures. Riveting and bolting are not an option as silicon nitride, like most ceramics, is brittle. The use of adhesives is possible but mainly for room temperature applications. Due to the high processing temperatures, pressures and size/shape requirements diffusion bonding tends not be commercially viable. The popular commercial choice for producing metal to ceramic joints is by active metal brazing [3–5]. Joining of heat resistant alloys to silicon nitride using this method has been extensively studied and developed over the last decade [6–8].

However, not all combinations of metal and ceramic can be joined together and the main reasons for this and low strength in metal-ceramic joints can be summarised as;

(a) Formation of brittle phases at joint interface.
(b) Coefficient of thermal expansion (CTE) mismatch between metal and ceramic causing large interfacial residual stress build up, low strength and failure during thermal cycling.
(c) Lack of wetting at ceramic interface.

The major disadvantage of most metal to ceramic joining techniques tends to be the low operational temperature limit (maximum of 400°C) due to the melting temperature of the joining interlayer [9]. Thus, a need has been identified to develop and study a joining technique capable of producing metal to ceramic joints for high-temperature applications (above 500°C in air).

This paper reports the joining between two materials with a large CTE difference, the high-temperature and oxidation resistant iron-chromium-aluminium alloy ('Fecralloy') with silicon nitride. A powder metallurgy route was used; where reactive synthesis was employed to form a nickel aluminde, NiAl, interlayer.

NiAl was chosen as a viable material to join Fecralloy with silicon nitride due to its outstanding properties and exothermic formation via a powder metallurgy route. The major advantage of a powder metallurgy route is the ability to tailor the interlayer in terms of size and composition, so that it can join materials of different

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shapes and also the relative low cost. The disadvantages are that the properties of the formed product are greatly influenced by processing conditions and porosity, which therefore requires careful control.

The Ni-Al binary system [10] is composed of five ordered intermetallic phases. Single phase NiAl has very attractive properties, namely its high melting point (1683°C), excellent oxidation resistance, low density and good thermal conductivity.

The fabrication of NiAl from its constituent elemental powders has been carried out by numerous techniques [11–13]. Of most interest is reactive synthesis also termed as combustion synthesis or self-propagating high temperature (SHS) synthesis, where the mixed elemental powders are heated to a temperature where they react exothermically to form the intermetallic [14, 15]. The reaction usually occurs on the first formation of a liquid, normally a eutectic liquid at the interface between contacting particles. The formation of NiAl is an exothermic process and the reaction becomes self-sustaining [16]. At a particular temperature a spontaneous combustion reaction occurs and there are two basic modes of reaction, differing by their method of ignition.

In the propagating reaction mode, the powder reactants are ignited locally at one end of the sample using an external heat source and the combustion wave propagates through the sample converting it into product. The second method is thermal explosion, where the sample is heated at a constant heating rate in a furnace, until the reaction is iniated uniformly throughout the sample at the ignition temperature, T_{ig}. During the reaction the combustion temperature, T_{c}, reaches a very high temperature in a short period of time.

Extensive studies of the reaction using differential thermal analysis (DTA) have shown that the reaction can proceed at temperatures below the eutectic temperature of 640°C [17]. This was attributed to solid-state inter-diffusion that occurs between Al and Ni particles at temperatures below the eutectic temperature. Mainly Al-rich compounds are formed and these reactions are exothermic, heating the sample to the eutectic temperature and iniating the reaction.

Nardou *et al.* [18] reported that a pre-combustion stage exists for high heating rates of 20 K/min or above. This occurred at around 600°C and was due to the formation of NiAl layers, which effectively raised the temperature of the compact to the eutectic temperature. However, when the volume fraction of Al is large, such as in NiAl, the formation of these Al-rich intermetallic phases by solid-state reactions acts as a buffer that dilutes the exothermic reactions that normally cause melting.

The processing atmosphere plays an important role, mainly upon the final density. Vacuum is preferred as it reduces heat loss to the surroundings and maintains the combustion temperature for slightly longer times. Internal porosity is also evacuated leading to higher density. When inert gas such as argon is used, heat is carried away from the reacting compact by the atmosphere. Also, inert gas can be trapped inside the pores hindering further densification.

While there are no reports of successful metal-ceramic joining via a reactive synthesis route using NiAl as the joining interlayer, Matsuura *et al.* have joined NiAl to metal by various methods [19–21].

The primary aim was to produce integral Fecralloy to silicon nitride joints for higher temperature applications (above 500°C) by a simple and commercially viable technique. The focus of this work was to achieve joining and to study the effects of process conditions upon joint morphology and performance.

2. Experimental procedure

2.1. Materials and sample preparation

The materials to be joined were Fecralloy (72.3Fe, 22.0Cr, 5.0Al, 0.3Si, 0.02C, 0.2Mn, 0.1Y, 0.1Zr, chemical composition in wt%) and reaction bonded silicon nitride. They were supplied by Goodfellow Ltd UK in sheet form (100 mm × 100 mm × 5 mm). Using a low speed diamond wheel they were cut into samples measuring 10 mm × 10 mm × 5 mm. The joining surface was manually ground to a planar 1200 grit finish. Polishing to a 1 μm finish using 6 μm and then 1 μm diamond paste followed this. After polishing, the silicon nitride and Fecralloy substrates were cleaned ultrasonically and stored in acetone until use.

The physical properties of the reaction bonded silicon nitride and Fecralloy are given in Table I.

The Ni-Al compact was made by dry mixing the Ni-Al powder mixture (1:1 molar ratio) for two hours in a Turbula$^{\mathrm{TM}}$ mixer. This was then cold pressed under a pressure of 900 MPA into a 10 mm × 2 mm compact.

2.2. High temperature vacuum furnace and joining procedure

Joining was carried out in a purpose built high temperature vacuum furnace, as illustrated in Fig. 1. A maximum of 1200°C was possible under vacuum (5×10^{-4} torr) and applied pressure up to 50 MPa.

The mild steel vacuum chamber is water cooled and mounted vertically on top of a mobile vacuum-pumping unit. It has a removable chamber lid, thus, allowing the sample holder to be placed inside the furnace unit. Correct alignment must be ensured when closing, as a moveable stainless steel ramp and bellow unit have been

TABLE I Properties of Fecralloy and silicon nitride (courtesy of Morgan-Matroc Ltd. and Goodfellow UK)

Property	RB silicon nitride	Fecralloy
Apparent porosity	15–23%	0
Density	2.4 $\mathrm{gcm^{-3}}$	7.2 $\mathrm{gcm^{-3}}$
Thermal conductivity at 20°C	10–16 $\mathrm{Wm^{-1}\,K^{-1}}$	16 $\mathrm{Wm^{-1}\,K^{-1}}$
Thermal expansivity, 20–1000°C	$3.3 \times 10^{-6}\ \mathrm{K^{-1}}$	11.1 $\mathrm{K^{-1}}$
Upper continuous use temperature	1200–1500°C	1100–1300°C
Compressive strength	550–650 MPa	Not given
Hardness (Vickers)	800–1000 $\mathrm{kgfmm^{-2}}$	Not given
Shear strength	190–240 MPa	Not given
Tensile modulus	170–220 GPa	330 GPa

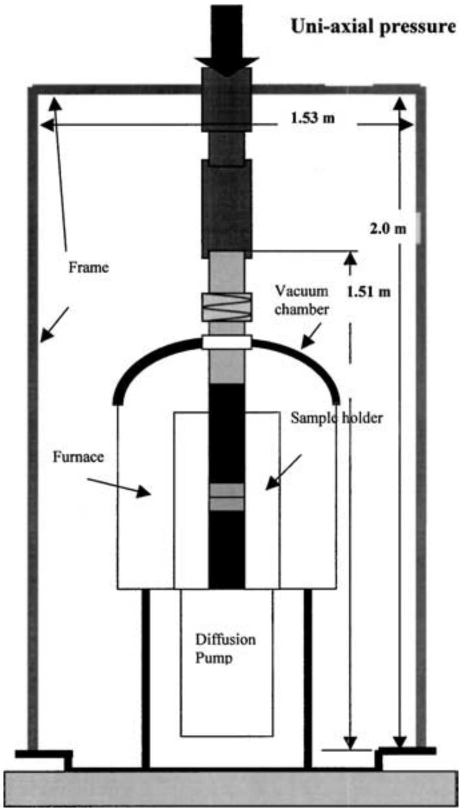


Figure 1 Schematic of high temperature vacuum furnace (not to scale).

machined and attached to the lid. Weights are placed on the upper ramp plate allowing pressure to be applied on the joining sample. The lower ramp is permanently fixed and protrudes into the furnace chamber upon which the sample holder rests.

The pumping unit is a fully valved system comprising of a Speedivac model 403 diffusion pump with a model 7L4 baffle valve. A Speedivac series 1SC150 rotary pump is used for roughing and backing purposes ("Speedivac" is manufactured by Edwards high vacuum ltd, Crawley, UK).

The joining process involved placing the Ni-Al compact between the polished sides of the Fecralloy and silicon nitride in a butt joint configuration. This configuration was then secured into the graphite sample holder, which was then placed into the vacuum furnace. Graphite was chosen as the sample holder material as it is easy to machine and is a good conductor of heat, allowing the butt joint configuration to be heated thermally. Pressure was applied and removed at room temperature.

Joining trials were carried out between 800–1000°C, 5–15 min dwell time and 0–45 MPa applied pressure.

2.3. Thermal analysis

DTA was used to observe the effects of varying heating rate upon the Ni-Al powder mixture. This was carried out under a nitrogen atmosphere (vacuum not possible) at varying heating rates of 5, 10, 15 and 20 K/min.

2.4. Joint analysis

In order to understand and improve metal-ceramic joining, it is very important to analyse and characterize the joining interface. Relationships or trends can be drawn from the interfacial microstructure with regards to processing parameters and joint integrity (mechanical performance). Hence, the requirement to transversely cross-section the joint. All the joined samples were cross-sectioned transversely using a low speed diamond wheel and polished to a 1 μm finish.

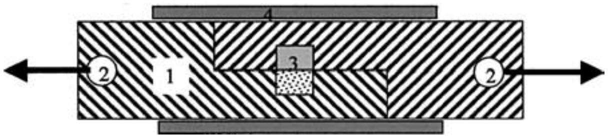


Figure 2 (1) Schematic of shear test jig, (2) direction of pulling pins, (3) joint sample, and (4) Instron holder.

Incident reflected light microscopy (Leitz) was the initial method of optical analysis and joint characterization.

A JEOL 840A Scanning Electron Microscope (SEM) was used to analyse the interfacial microstructure. Energy dispersive X-ray (EDX) analysis was used to identify the chemical composition of any formed phase/precipitate. Elemental mapping was used to visually demonstrate the elemental migration and presence of any reaction product layer. All image and analysis work was carried out using secondary electron imaging/analysis.

2.5. Mechanical testing

Two methods were employed to characterise the mechanical properties of the Fecralloy-silicon nitride joint. The first was shear strength testing to quantify joint strength. The second was thermal cycling to assess the effects of temperature upon the joints.

The shear test samples were machined down to 5 mm × 5 mm × 8 mm. In order to ensure greater accuracy three samples were tested for each joining condition.

A designed fixture was used such that sample movement was prevented during testing and that shear force was applied to the bond line and either side of bond line (see Fig. 2). This was carried out using an Instron tensile testing machine at a crosshead speed of 0.5 mm/min.

With thermal cycling the joined sample was placed in an air furnace and heated to 850°C with a dwell time of four hours (high heating and cooling rate, 50 K/min). Upon cooling the sample was inspected and if still intact the rigorous thermal cycling would be repeated until joint failure.

3. Results and discussion

Table II presents the results of the mechanical and thermal testing carried out on the joined samples.

3.1. Interfacial microstructure

At 800°C (15 min, 45 MPa) weak joints were produced with large pores in the NiAl interlayer and detachment occurred under handling at the NiAl-silicon nitride interface, as shown in Fig. 3a. An increase in temperature to 900°C (15 min, 45 MPa) produced joints

TABLE II Summary of results

Temperature (°C)	Time (min)	Pressure (MPa)	Average shear strength (±5 MPa)	No. thermal cycles till failure
800	5	10	0	0
800	10	10	4.63	0
800	15	10	3.28	0
800	5	30	4.11	0
800	10	30	4.18	0
800	15	45	5.20	0
900	5	10	54.90	3
900	10	10	55.23	3
900	15	10	55.02	2
900	5	30	68.90	5
900	10	30	67.56	6
900	15	30	69.11	6
900	5	45	93.66	10
900	10	45	94.12	10
900	15	45	94.30	10
1000	5	10	34.16	2
1000	10	10	33.29	2
1000	15	10	34.33	2
1000	5	30	36.87	1
1000	10	30	31.29	1
1000	15	30	35.34	2
1000	15	45	38.21	2

that exhibited the highest shear strength. Dense and monophase NiAl was produced with good interfacial bonding and no visible reaction product layer, as shown in Fig. 3b. This demonstrates the importance of processing temperature and identified 900°C as the optimum processing temperature. The processing conditions are discussed in some depth in the next section.

The effects of pressure are shown in Fig. 3c, where the applied pressure is reduced to 30 MPa (900°C, 15 min). Joining is achieved with good interfacial bonding but medium sized pores are present in the interlayer. Pores are sites of stress concentration and from where crack initiation and propagation can occur, leading to joint failure.

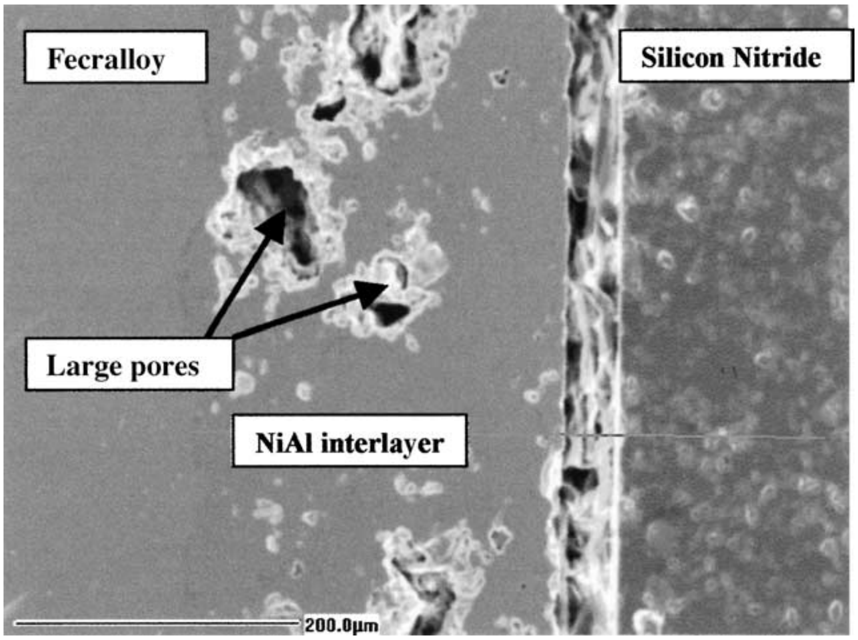
When the dwell time is reduced to 5 min (900°C, 45 MPa) as shown in Fig. 3d, joining was achieved with good interfacial bonding, however, numerous small pores were formed in the interlayer.

From this one can establish the effects and influence of process parameters on the microstructure and ultimately mechanical properties of the joint. The key factor for this joining system is the production of a dense and monophase NiAl interlayer.

The EDX elemental map (Fig. 3e) is typical of a good joint produced by this method. Due to the large amount of heat released during the exothermic formation of NiAl, partial melting of the Fecralloy interface occurs and hence the infiltration of small amounts of Fe and Cr into the interlayer. Temperatures of 1500–1800°C have been recorded by other authors [22] for periods ranging from 20 s to 5 min. This high temperature and applied pressure is sufficient to cause partial melting of the Fecralloy interface (melting temperature of Fecralloy is approximately 1400°C).

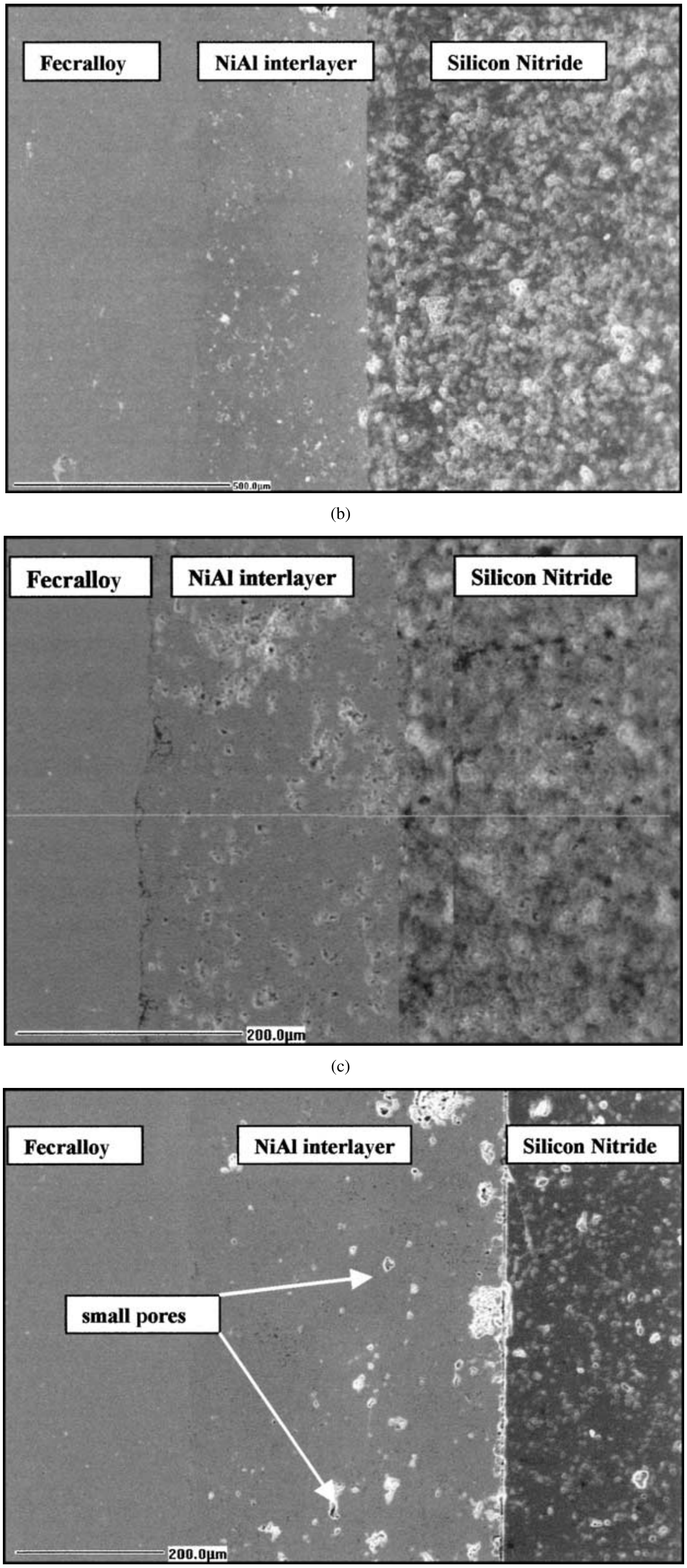
These conditions also assist in the wetting and dissolution of the silicon nitride interface by liquid Al. The dissolution of the silicon nitride interface is evident by the presence of Si and N in the NiAl interlayer. The liquid Al originates from the Ni-Al compact and is the driving force for the densification of the interlayer. This is discussed further in Section 3.3.

Interfacial melting is also reported by Matsuura *et al.* [21] where molten Ni and Al was poured onto a steel block forming a good joint upon cooling. It was found that the depth of melted steel increased with the thickness of the NiAl layer and also by heating the steel block.



(a)

Figure 3 (a) Micrograph of failed Fecralloy-silicon nitride joint (800°C, 15 min, 45 MPa). (b) Micrograph of Fecralloy-silicon nitride joint (900°C, 15 min, 45 MPa). (c) Micrograph of Fecralloy-silicon nitride joint (900°C, 15 min, 30 MPa). (d) Micrograph of Fecralloy-silicon nitride joint (900°C, 5 min, 45 MPa). (e) EDX elemental map of Fecralloy-silicon nitride joint (900°C, 15 min, 30 MPa). (*Continued*)

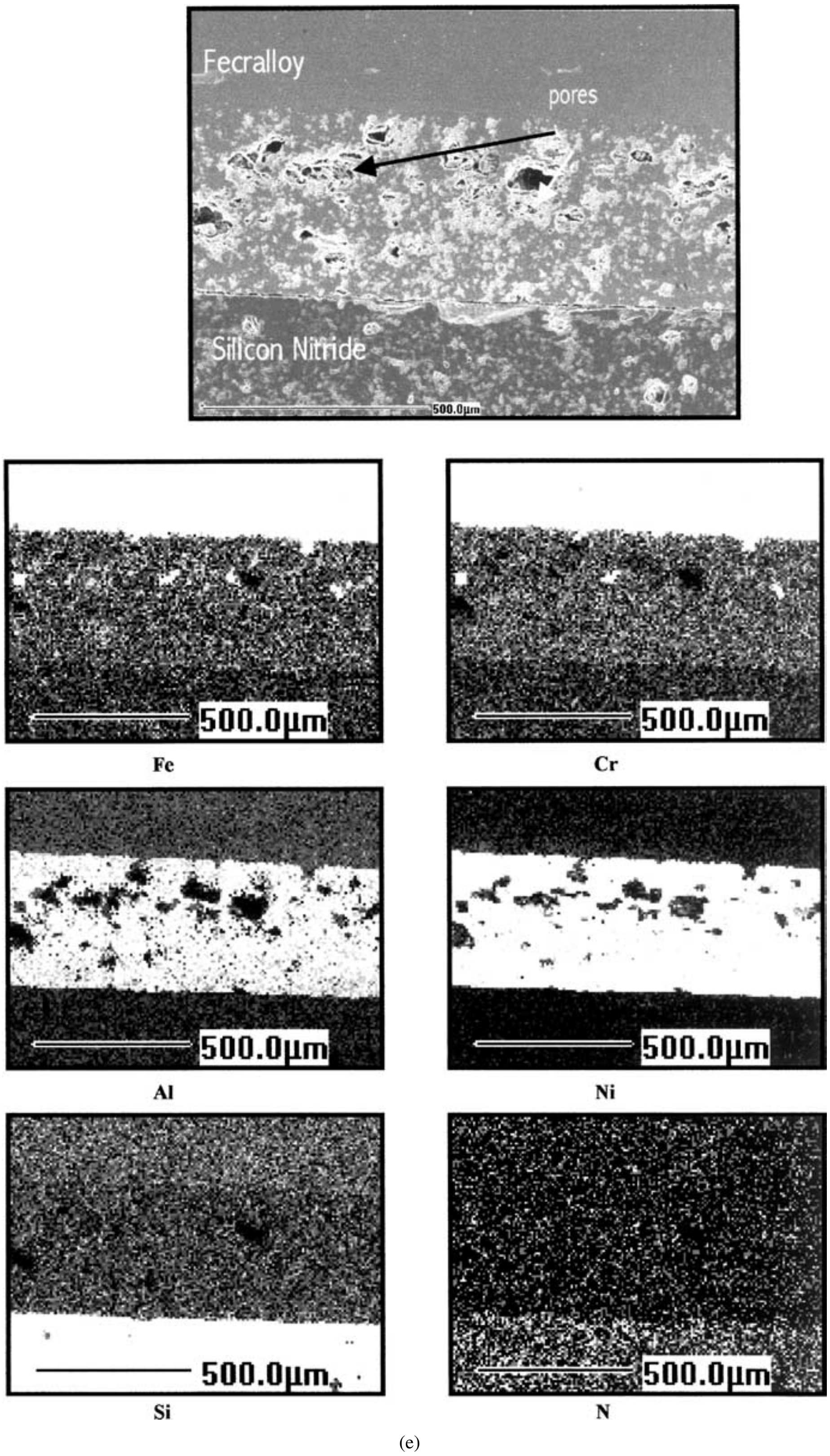


(b)

(c)

(d)

Figure 3 (*Continued*).



Fe Cr

Al Ni

Si N

(e)

Figure 3 (*Continued*).

There was initial concern that the presence of small amounts of Fe, Cr, Si and N might have a detrimental effect upon the NiAl interlayer. However, work by Miracle *et al.* [12] showed that the properties of NiAl, such as room temperature ductility, fracture toughness and yield strength were dramatically improved by microalloying with elements such as Fe, Ga or Mo.

3.2. Processing conditions

The key to successful joining is the production of a dense monophase NiAl interlayer by reaction synthesis. It is therefore important to optimise all process conditions to produce the interlayer during the joining process. Process conditions that influence the reaction between the constituent powders will alter the amount of transient liquid, length of time the liquid is present and its distribution. The various process factors affect the final microstructure and mechanical properties of the interlayer and these can mostly be explained in terms of their effects on the liquid phase and reaction synthesis.

Process variables are not independent from each other and the most important factors are discussed outlining their effects upon the interlayer and joining.

3.2.1. Temperature

The main function of temperature is to initiate the self-propagating synthesis mode in the Ni-Al compact at the ignition temperature (T_{ig}). At this temperature the exothermic formation of NiAl is initiated and temperatures above this increase the rates of diffusion and wetting and increase the solid solubility in the liquid phase. Rapid densification is favoured by these factors, however, the time-temperature combination is the most important influence on the rate of densification. This has to be identified and controlled as according to the classical sintering theory, the optimal sintering time decreases with increased sintering temperature due to greater diffusion and transient liquid content [23].

Our results highlight the effects temperature has on the NiAl interlayer and on joining. At 800°C (5 min, 30 MPa) weak joints are formed with an average shear strength of 4.11 MPa. This is due to large pores and incomplete densification of the NiAl. An increase in temperature to 900°C (5 min, 30 MPa) results in joints with an average shear strength of 68.90 MPa, where a dense NiAl interlayer is formed with little or no porosity. Increased temperature to 1000°C causes a decrease in the average shear strength and this believed to be due to the build up of residual thermal stresses primarily at the interlayer-ceramic interface. Hence, 900°C has been identified as the optimal processing temperature for producing joints of high shear strength.

3.2.2. Time

Our results show that dwell time at temperature and pressure has a direct effect upon shear strength. An increase in dwell time from 5 to 15 min (900°C, 45 MPa) not only eliminates porosity in the NiAl interlayer but also increases the average joint shear strength. This is explained by considering the effects dwell time has on the interlayer densification.

The time needed to attain a densified structure depends on several processing factors, the most important of which is the volume fraction of solid present and the process temperature (time-temperature combination).

It is believed that while the bulk of the interlayer is formed by self-propagating reactive synthesis, there are some areas of incomplete densification and porosity. Although not detected by XRD, this could be due to their small concentration. Thus, increased temperature and dwell time are beneficial as pore elimination and complete densification occurs by classical sintering.

While the optimal dwell time was identified as 15 min, prolonged time would most likely be detrimental to the interlayer as pore growth and microstructural coarsening become favourable. The formation of brittle interfacial phases also becomes possible. Such a detrimental time was not identified during the course of this work.

3.2.3. Pressure

Compaction of the Ni-Al powder is very important and aids the reactive synthesis process. Matsuura *et al.* [20] conclusively showed that increased pressure on the green Ni-Al compact was beneficial in reducing porosity and producing a densified structure. A pressure of almost 1 GPa was suggested as optimum for the reactive synthesis process, where the green density was 70% of the theoretical density of NiAl. Subsequently a compaction pressure of almost 1 GPa was used during the course of this work.

The effects of pressure during the joining process were investigated upon the interlayer and average joint shear strength. From the micrographs shown in Fig. 3a–d and the graph showing average shear strength versus bonding pressure (Fig. 4), it is clear that increased pressure is beneficial in reducing porosity and increasing shear strength. The increased pressure ensures good particle-particle contact and aids the break up of surface oxides present at the particle surface. This assists the self-propagating reaction synthesis and the applied pressure also help the liquid phase to propagate through the compact.

With the application of an external pressure, the rearrangement processes plays a greater role in densification. In the rearrangement stage the rate of densification increases with capillary force. Increased pressure generally increases the capillary force and this aids the densification process. Large particle size is known to have low capillary forces as they have an inverse relationship, but as pressure increases the particle size effects become smaller.

Increased pressure also forms joints with higher shear strengths. This is due to the intimate contact between the interlayer and metal/ceramic interface. Pressure aids the break up of the detrimental surface oxides and oxynitrides on the silicon nitride interface, helping the wetting process. It is the molten Al that wets the ceramic interface and Eusthapoulous *et al.* [24] showed that the non-wetting to wetting transition of an Al drop on silicon nitride occurs at about 1100°C.

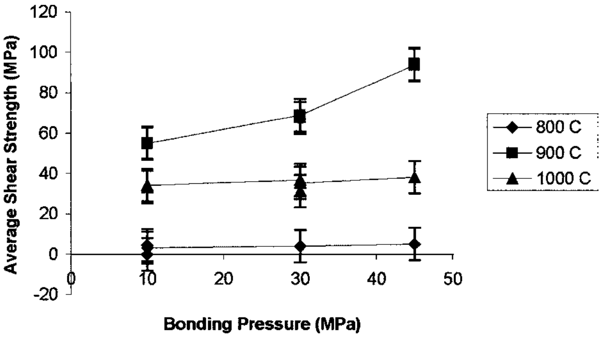


Figure 4 Graph showing relationship between bonding pressure and temperature on average shear strength of joint.

Process temperatures lower than these were used, but the T_c reaches temperatures well above this and aids the reactive wetting process.

3.3. Thermal behaviour

3.3.1. Effect of heating rate

Using the Perkin-Elmer 7 DTA, the effects of heating rate between 5–20 K/min were investigated on the 1:1 molar Ni-Al as-compacted powder. Fig. 5 shows the DTA plots. The peak maximum temperature, T_p, corresponds to the temperature at which the rate of transformation of the viscous liquid into a crystal becomes a maximum. In all the DTA plots a large exotherm is evident at approximately 500–600°C demonstrating the onset of reactive synthesis. The first eutectic temperature in the Ni-Al binary system is at 640°C and Al melts at 660°C and so our results show that exothermic peaks prior to liquid formation. The reactions are initiated in the solid state (solid-solid) and are followed by solid-liquid interactions. The NiAl formation can be divided into several steps, the first of which is solid-state inter-diffusion that causes the formation of $NiAl_3$ and Ni_2Al_3 at 520°C. In all samples heated up to the T_{ig}, small amounts of $NiAl_3$ and Ni_2Al_3 were detected, but the major XRD peaks were of Ni and Al.

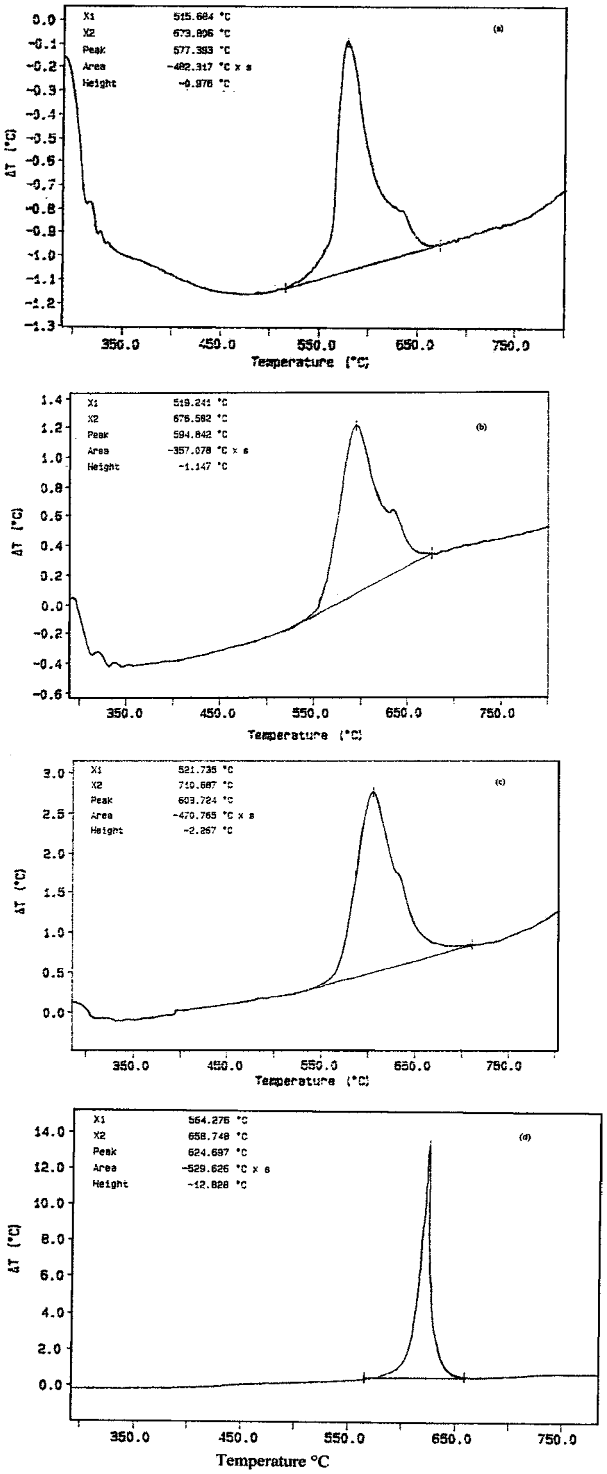


Figure 5 DTA plots of Ni-Al (molar 1:1) at heating rates: (a) 5 K/min, (b) 10 K/min, (c) 15 K/min, and (d) 20 K/min.

These reactions are exothermic which subsequently heat the compact to the eutectic temperature of 640–660°C triggering further reactions and melting of Al. The liquid consumes the elemental powders and interdiffusion of Ni and Al is rapid in the liquid phase and the compound generates sufficient heat that further assists the reaction. Under ideal conditions the liquid becomes self-propagating through the compact. The solid-solid reactions liberate heat and the heat release rate is kinetically controlled. The transient liquid provides a capillary force on the interlayer that leads to densification. Due to the rapid spreading and reaction of the liquid, pore formation is common. Vacuum degassing to remove any impurities is not necessary as the high temperature reached during reactive synthesis achieves this.

As to the influence of heating rate, our results show that the T_{ig} increases with heating rate, as shown in the graph of Fig. 6. This demonstrates that the reaction mechanism results from a competition between thermal effects (heating rate) and kinetic effects (activation energy). At lower heating rates the solid-solid diffusion process prevails with the formation of Ni_2Al_3 and $NiAl_3$ products. These can act as a physical barrier to liquid spreading and the heat generation rate will be small compared to heat loss rate, the reaction will stop at this intermediate stage. Higher heating rate kinetically disallows the formation of $NiAl_3$ and the heat generation rate is larger than the heat loss rate, so enough liquid phase is produced for the reaction to proceed with the formation of monophase and homogenous NiAl.

In the reaction synthesis of NiAl using a low heating rate, numerous papers have characterised the behaviour in to several steps [25]. The solid–solid reactions lead to the formation of a dense layer of $NiAl_3$ and Ni_2Al_3. These prevent the reaction from further proceeding and so the system cannot produce enough heat to reach the eutectic temperature. Once the furnace reaches the eutectic temperature of 640°C the eutectic liquid forms and spreads allowing more Ni and Al to react. With increased furnace temperature the $NiAl_3$ and Ni_2Al_3 phases react with the remaining Ni and Al forming NiAl. From all of this it is clear that the synthesis of NiAl is very sensitive to numerous factors, the most important of which are the heating rate and particle size. It was therefore deemed important for us to characterize our as-compacted Ni-Al mixture in order to produce a dense NiAl interlayer and successful metal-ceramic joining.

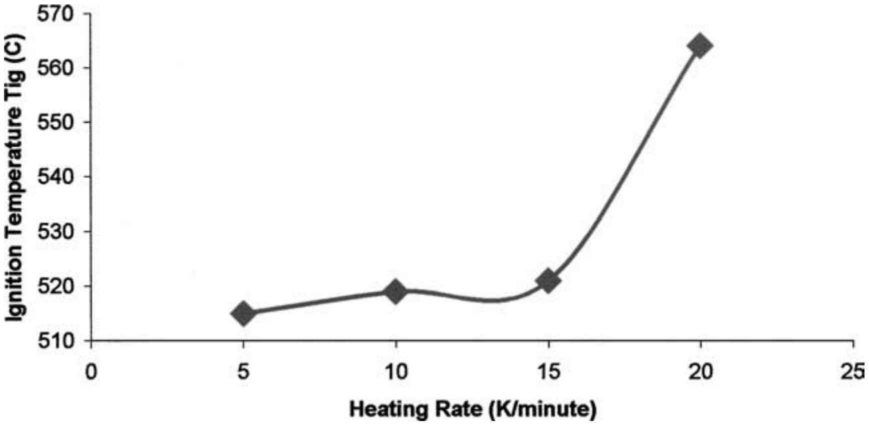


Figure 6 Graph showing variation of Ignition temperature, T_{ig}, with heating rate.

XRD was used to characterise and analyse the reaction product after all the DTA heating rate trials. In all cases monophase NiAl was formed in the same quantity. This is surprising as the ΔT value (from y-axis DTA plots) is found to increase with heating rate. Therefore, the difference in ΔT must relate to the extent of formation of the product through liquid-phase reactions. For the samples heated at a lower rate significant amounts of the product form through solid-state reactions. When this occurs the amount of free Al is decreased which leads to a lower exothermicity of the liquid phase reaction and hence a lower ΔT, as observed experimentally. With higher heating rates the opposite is true where most of the product is formed through liquid-phase reactions giving rise to a higher ΔT. The ΔT value is a function of composition, heating rate and particle size [23].

The interlayer formed using a lower heating rate (5 K/min) and a higher heating rate (30 K/min) all attempting to join Fecralloy with silicon nitride (900°C, 15 min, 45 MPa) are shown in Fig. 7a and b. The higher heating rate results in the formation of monophase NiAl, which is confirmed by the XRD plot (Fig. 7a) and this contains large pores. The lower heating rate produces an interlayer that is very porous and powder like in nature. The XRD plot (Fig. 7b) confirms the presence of unreacted Ni, in addition to NiAl. In terms of reaction kinetics an increase in heating rate increases the activation energy and accelerate the self-propagating reaction. However, too high a heating rate leads to a loss of process control and one of the results is the formation of large pores as was demonstrated. An intermediate heating rate of 15 K/min was chosen as the optimum and resulted in good joining with limited interlayer porosity, as shown in Fig. 3b.

While DTA results accurately characterised the behaviour of the Ni-Al as-compacted powder, joining trials using varied heating rates had to be carried out. This is because additional factors such as applied pressure, heat loss and process conditions all have an effect upon the reaction bonding process, which the DTA trials cannot take account of. This was found to be the case with a heating rate of 5 K/min. The DTA results show this heating rate to be sufficient to produce NiAl by a self-propagating mode. However, under joining conditions the self-propagating mode did not prevail rather solid-solid reactions. This is believed to be due to greater heat loss under joining conditions that prevented the self-propagating mode to occur.

It has been shown that heating rate is an important parameter for the reaction synthesis of NiAl by the self-propagating mode in order to produce sound Fecralloy-silicon nitride.

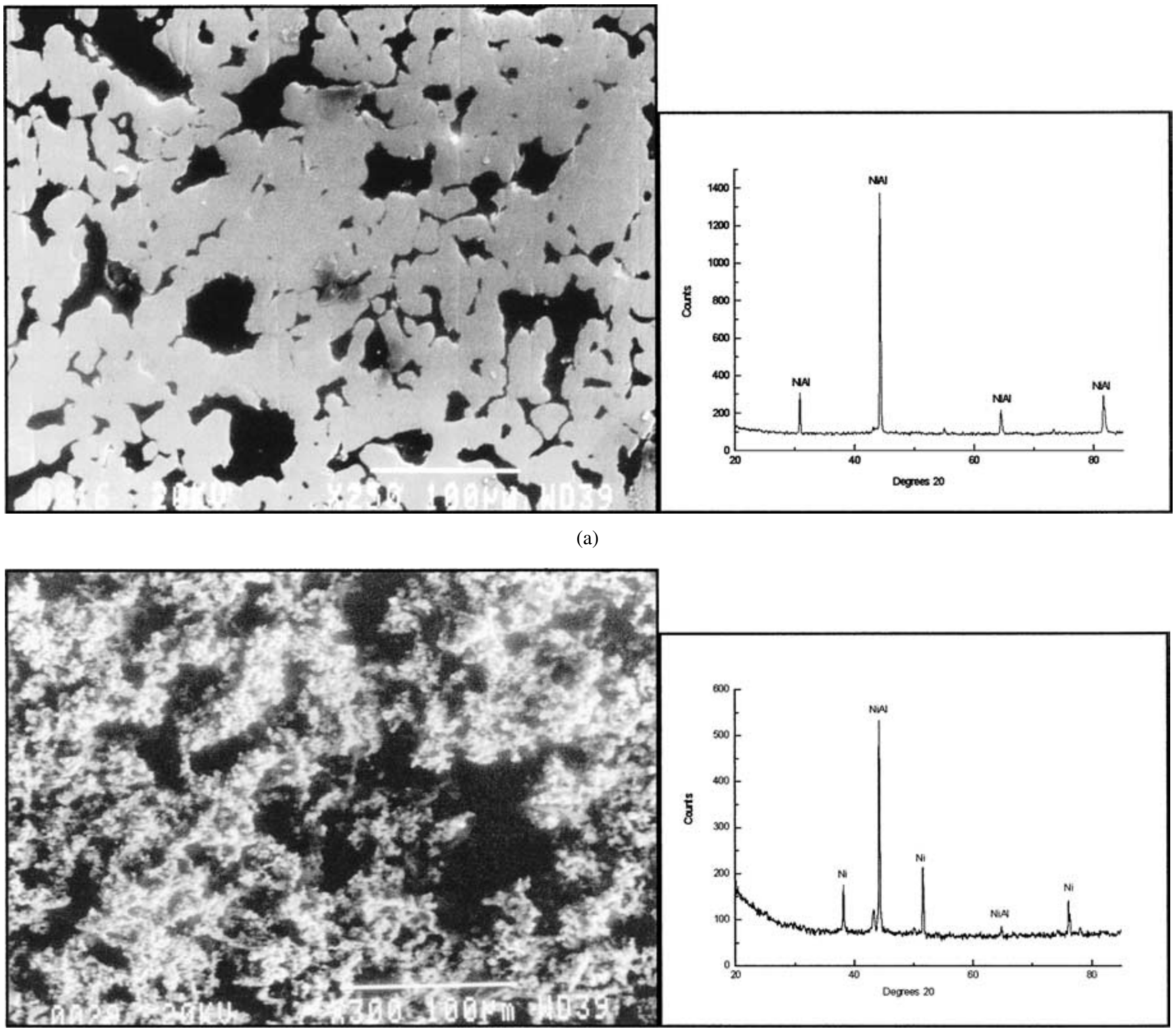
3.4. Mechanical testing

3.4.1. Shear testing

Table II presents the data for the average shear strength of the joined samples. Shear strength ranged from 4.63–94.30 MPa and are modest compared to those of metal-metal and ceramic-ceramic joining. Metal-ceramic joints tend to have inherently low shear strength results. The two main reasons for this are the residual thermal stress due to the CTE mismatch (Fecralloy = 11.1 and silicon nitride = 3.3×10^{-6} K^{-1}) and formation of brittle phases at the joint interface. The shear strength values compare well to other metal-silicon nitride joints. Using an active metal braze, Lee [26] presented shear strength values of 46.1–70.4 MPa for Inconnel 718-silicon nitride joints. Work by Vegater [27] produced Zirconia-silicon nitride joints using a Ni interlayer that has maximum shear strength of 57 MPa.

The modest shear strength values obtained in this work can be attributed to the mentioned reasons along with the presence of interfacial defects such as cracks and pores. Processing conditions do affect the shear strength of the joint and the results reveal the following trends.

1. At a given joining time and pressure, the shear strength increases with joining temperature, reaching a maximum and then decreasing with further temperature increase.
2. At a given joining temperature and pressure, the shear strength increases with joining time. This work did not establish the optimum time after which shear strength decreases.
3. At a given joining time and temperature, the shear strength increases with pressure. This work did not establish the maximum pressure after which shear strength decreases.



(a)

(b)

Figure 7 (a) Micrograph of interlayer formed at 30 K/min with corresponding XRD plot confirming formation of monophase NiAl. (b) Micrograph showing interlayer formed at 5 K/min and corresponding XRD plot showing that unreacted Ni particles remain.

These results establish that the optimum process conditions to produce a Fecralloy-silicon nitride joint with the highest shear strength is 900°C, 45 MPa and 15 min.

Zhang *et al.* [28] investigated the influence of CTE mismatch on bond strength for a metal-ceramic joint. Finite element analysis was used to simulate the stress distribution along the joint, where alumina was joined to 304 stainless steel using a Ni-Cr interlayer (1150–1250°C, 180 min). Their work showed that the residual stress is tensile in nature on the ceramic side and this gradually changes in to compressive stress on the ceramic side. Accordingly, the thermal stress is more detrimental for the ceramic. The tensile stresses in the ceramic side were found to be maximum in the vicinity of the interface, the shear stresses also being found to be maximum near to this location. The presence of shear stress at the ceramic side near to the joint interface may in combination with the tensile stress induce fracture along the ceramic interface. Ceramics tend to have poor fracture toughness and cannot provide enough energy to prevent crack progression. Their work showed that a compliant interlayer does reduce the residual stress and improve joint strength. This was found to be dependent upon interlayer thickness and ductility, where a thicker interlayer reduced the residual stress. This can be related to our joining results, where the NiAl interlayer was of considerable thickness and moderate ductility.

Optical analysis of the fractured shear test samples found that two-fracture types exist. In the first type, as shown in Fig. 8, the crack propagates along the interlayer-ceramic region separately the two. This type of fracture was associated with joints of low/moderate shear strength. This suggests that this is a weak zone and that adhesion between the interlayer-ceramic is poor.

In the second type of fracture the crack initiates and propagates in the ceramic only, close to the joint interface (Fig. 9). This type of fracture behaviour was associated with joints that exhibited high shear strength, where adhesion between interlayer-ceramic was good usually due to greater applied pressure. This confirms the predicted behaviour put forth by Zhang *et al.* [28] where the residual stress is high in the ceramic near to the interface and from where crack propagation is most likely.

In the joining of dissimilar materials residual stresses are inevitable due to CTE mismatch. This problem cannot be eliminated but has to be addressed. The use of lower processing temperatures, short dwell time and an

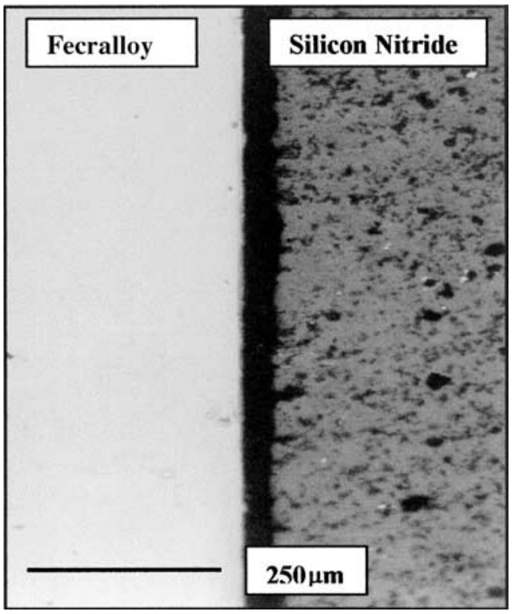


Figure 8 Micrograph showing failure due to first type of failure mode during shear test (detachment).

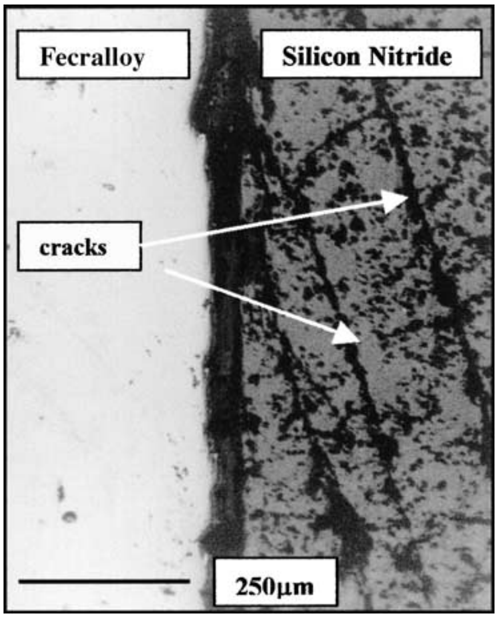


Figure 9 Micrograph showing shear test failure due to second type of failure (cracking in ceramic).

interlayer improve the shear strength by reducing the residual stress.

3.4.2. Thermal cycling

On reviewing literature related to metal-ceramic joining, one finds that joint strength is measured by various techniques but no thermal cycling is carried out. This is an important parameter that should be used in conjunction with strength measurement to characterise the mechanical properties of the metal-ceramic joint. In this work materials known for their high temperature oxidation resistance were used and while they would not be effected by oxidation, the effects of thermal cycling were looked at.

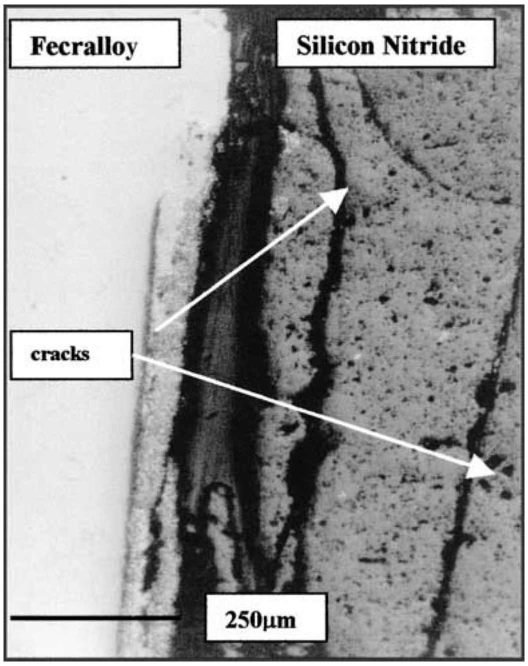


Figure 10 Micrograph showing joint failure after thermal cycling, where cracking is in the ceramic only.

The thermal cycling results given in Table II are encouraging, with some joints withstanding 10 thermal cycles until failure. This is due to good interfacial bonding and reduced residual thermal stress. These results can be directly related to the shear strength results. Joints that exhibit high shear strength are also able to withstand a greater number of thermal cycles till failure.

With the joints exhibiting higher shear strength, there is good interfacial bonding and it is the good high-temperature ductility of the interlayer that is responsible for withstanding the thermal cycling. The interlayer elastically/plastically deforms in order to counteract the residual stress caused by the CTE mismatch. Failure was always due to crack propagation always in the ceramic close to the joint interface. The crack initiated from the pores present and then propagated till failure, as shown by the micrograph of Fig. 10. These are regions from where stress concentrates and when the stress in a pore reaches a critical value, a crack forms and propagates. There are no large energy absorbing process in ceramics such as those that operate in ductile metals during deformation and so a crack propagates till failure. Pores decrease the cross-sectional area over which a load is applied and hence lowers the stress a material can support.

Reaction bonded silicon nitride is inherently 15–20% porous and so it's mechanical properties will be lower compared to sintered silicon nitride where porosity is almost non-existent.

For the low/moderate strength joints, failure was usually due to the detachment of the interlayer from the ceramic. This is due to poor interfacial bonding where the interface is unable to withstand the residual stresses that take effect with the thermal cycling.

4. Conclusions

Joining between Fecralloy and silicon nitride was achieved by use of a NiAl interlayer. The heat released from the exothermic formation of NiAl from its elemental constituents (1:1 molar ratio of Ni and Al) was important. This allowed moderate processing conditions to be employed, eliminating high process temperatures and long dwell times commonly associated with metal to ceramic joining. These conditions can be detrimental to joining resulting in excessive residual stress and formation of brittle interfacial phases.

Due to the large amount of heat generated from the reactive synthesis of NiAl, partial melting of the Fecralloy interface occurred causing infiltration of mostly Fe, Cr and Al into the NiAl interlayer. Liquid Al from the Ni-Al compact caused wetting and dissolution of the silicon nitride interface and hence the diffusion of Si and N into the interlayer.

The mechanical performance of the joined samples was encouraging, as shear strength of up to 94.30 MPa was attained with the joint withstanding numerous thermal cycles in air at 850°C. This showed that the joints could be used for higher temperature applications (above 500°C).

Optimising the process variables so that a fully dense and monophase NiAl interlayer with no porosity was produced by reactive synthesis was found to be paramount for successful joining.

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