ANALYTICAL AND EXPERIMENTAL EVALUATION OF JOINING
SILICON NITRIDE TO METAL AND SILICON CARBIDE TO METAL
FOR ADVANCED HEAT ENGINE APPLICATIONS

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ANALYTICAL AND EXPERIMENTAL EVALUATION OF JOINING SILICON NITRIDE TO METAL AND SILICON CARBIDE TO METAL FOR ADVANCED HEAT ENGINE APPLICATIONS

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ABSTRACT

This report summarizes the results of Phase I of Analytical and Experimental Evaluation of Joining Silicon Nitride to Metal and Silicon Carbide to Metal for Advanced Heat Engine Applications[†]. A general methodology was developed to optimize the joint geometry and material systems for 650 and 950°C applications. Failure criteria were derived to predict the fracture of the braze and ceramic. Extensive finite element analyses (FEA), using ABAQUS code, were performed to examine various joint geometries and to evaluate the affect of different interlayers on the residual stress state. Also, material systems composed of coating materials, interlayers, and braze alloys were developed for the program based on the chemical stability and strength of the joints during processing and service. Finally, the FEA results were compared with experiments using an idealized strength relationship. The results showed that the measured strength of the joint reached 30-90% of the strength predicted by FEA. Overall results demonstrated that FEA is an effective tool for designing the geometries of ceramic-metal joints and that joining by brazing is a relevant method for advanced heat engine applications.

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1 INTRODUCTION

In order to broaden the application area of advanced ceramic materials, it is necessary to have the technology to join ceramic and metallic components. The current ceramic heat engine program is an example of this type of effort. Perfection in ceramic forming and perfection in the production of reliable ceramic components are two of the key issues in the development of advanced heat engines. An additional key issue which will surface in the later stages of the engine development is the problem of joining a ceramic rotor to a metal shaft to transmit power. Besides the applications in advanced heat engines, which impose the most severe environments on ceramic-metal joints, there are many other application areas, such as cutting tools, electronic devices, and light bulbs, which require ceramic-metal joining technology.

The major problem in joining two dissimilar materials is the thermal mismatch, which causes a significant residual stress at the interface. Joining methods using a mechanical fit, diffusion bonding, glass frit sealing, or brazing generate complicated stress states in the ceramic parts, leading to catastrophic failure of the ceramic during processing or service. There were many studies to quantify the residual stress associated with joining dissimilar materials using finite element analysis (FEA). However, the studies reported were most often limited to two dimensions and elastic deformations. Also, no methodology to design the joint geometry using FEA has been reported.

In this program, brazing was chosen to join Si_3N_4 or SiC to structural alloys since this method provides superb tolerance for processing and excellent capability in stress accommodation. Brazed joints also perform well when subjected to dynamic motion with high loads. In order to handle the plastic deformation occurring in the joint, a general-purpose finite element program, ABAQUS, was used to guide the design of the joint geometry. ABAQUS is especially well suited for solid mechanics problems involving large elastoplastic deformations in three dimensions.

A general methodology was developed for the systematic and comprehensive study of ceramic-metal joints. The goal of Phase I of this work was to demonstrate analytical tools for use in designing ceramic-metal joints. This required the expression of the stress response of joints as a function of the mechanical and physical properties of the ceramic, metal, and other materials used in the joint. Various constitutive equations were derived for the joint materials as a function of temperature. Several joint geometries and interlayer materials were screened using the constitutive equations with the FEA technique.

The application temperatures of interest for Si_3N_4 to metal and SiC to metal joints were 650 and 950°C. Significant efforts were made to develop material systems which could perform at these temperatures. The efforts in material systems development were divided into three parts: (1) coating materials development, (2) interlayer development, and (3) brazing alloy development. Based on the screening study of coating materials, interlayer materials, and braze alloys, promising materials were tested as systems in terms of high-temperature performance and chemical stability during

processing and service. The final screening was done using the final joint geometry suggested by the FEA study.

Performance tests of the brazed joints were done with the final geometry and material systems using room-temperature and 650°C torsion tests. These testing results were compared to the FEA predictions of the residual stress. Attempts were made to link the experimental results with the FEA predictions based on several simplifying assumptions. Thermal and mechanical fatigue testing was also done with the final joint systems.

2 DESIGN AND ANALYSIS FOR CERAMIC-METAL JOINTS

2.1 FAILURE CRITERIA

The deformation mechanics for the brazing process of dissimilar materials is complex. It is a temperature dependent process; the braze alloy changes its state from liquid to solid at the beginning of the process, and experiences severe plastic deformation during the subsequent cooling stage.

Ceramics are brittle materials in comparison to metals. In addition, metals and ceramics have quite different thermal expansion coefficients. The differences in mechanical and thermal properties of these materials result in large thermal mismatch strains and, consequently, thermal residual stresses. In most cases, flaws in the ceramic near the interface and flaws in the braze due to imperfect bonding are believed to determine the strength of the joint.

Thermal stresses arising in ceramic-metal joints cause residual stress weakening of the joint structure. The thermal stresses are in equilibrium along the joining area; therefore, the global stress state decays exponentially away from the joint (St. Venant's principle). Fracture occurs within the distance of the characteristic dimension of the joint.

To date, investigations have not treated filler materials or special layers between two materials. In practice, there is a filler material for a braze joint. For this study, the influence of the filler material was considered. If the strength of the joint is bound by the flow stress of the filler material, the global tensile strength of various butt joints can be analyzed by using bound theorems¹. Shear failure of a ductile interface filler material can be understood with the aid of Green's slip line solution of direct shear². Therefore, the slip line solution was reexamined and compared with results from finite element analyses.

The most important part of the failure analysis and strength prediction of the braze joint is that of ceramic component failure. The strength of a ceramic is very sensitive to the distribution, orientations, and locations of initial flaws. Therefore, deterministic analysis of the ceramic's strength seems unrealistic.

In this study, four different approaches of predicting joint strength were investigated. The first was the application of the maximum principal stress criteria. This may be the most primitive and inaccurate approach. The second was the crack growth criteria for a particular mechanism of crack growth. However, there is great uncertainty concerning which crack growth mechanism to use. The third was the application of the J-integral near the edge of the braze. Lastly, a probabilistic fracture mechanics approach can be applied to the joint problem. However, there is difficulty in the probabilistic approach in that it is difficult to select an acceptable uncertainty level. In this report, the second and third approaches were used to make a strength criteria for ceramic failure.

Analysis of Braze Rupture - β Criterion

In the ceramic-metal joint, fracture of the braze alloy is one of the limiting factors to joint strength. Therefore, the mechanical properties of the braze have to be fully exploited by using a strength criterion of the joint in

the neighborhood of the braze. A simple β criterion was derived to determine the critical area and thickness of the braze joint for a butt joint geometry. This criterion has been established considering the state of strain in the braze during the thermal cycle of the brazing process and during loading. The strain components (z-direction is the thickness direction of the braze) can be approximated by

$$\gamma_{xz} = [(\alpha_m - \alpha_c)(T_s - T) - \epsilon^{EA}] \left(\frac{r}{t} \right) \quad \text{Eq. 2.1}$$

$$\epsilon_{rr} \equiv \epsilon_{\theta\theta} \equiv -\frac{\epsilon_{zz}}{2} \equiv \left(\frac{\alpha_m + \alpha_c}{2} - \alpha_b \right) (T_s - T) \quad \text{Eq. 2.2}$$

where α_m , α_b , and α_c are the thermal expansion coefficients of metal, braze, and ceramic. T_s is the solidification temperature of the braze alloy, and T is the operation temperature of the joint. 'r' is the distance from the centroid of the braze area, 't' is the thickness of the braze, and ϵ^{EA} is the elastic accommodation strain of the metal and ceramic. ϵ^{EA} can be approximated by

$$\epsilon^{EA} = \frac{4 \tau_y^B J_1}{2 A r_o} \left(\frac{1 - \nu_m}{E_m} + \frac{1 - \nu_c}{E_c} \right), \quad \text{Eq. 2.3}$$

where τ_y^B is the shear yield stress of the braze, J_1 is the first polar moment of inertia of the braze area, A , ν is Poisson's ratio, and r_o is the average radius of the braze area. The radius is measured from the centroid of the braze area. The subscript, m, c and b (or superscript B), indicate metal, ceramic and braze, respectively.

We can define a dimensionless number, β , which is an effective plastic strain normalized by the rupture strain, ϵ_e (ductility):

$$\beta = \frac{T_s - T}{\sqrt{3} \epsilon_e} \sqrt{\left(\alpha_m - \alpha_c - \frac{\epsilon^{EA}}{T_s - T} \right)^2 \left(\frac{r}{t} \right)^2 + 3(\alpha_m + \alpha_c - 2\alpha_b)^2} \quad \text{Eq. 2.4}$$

This equation indicates that when β becomes unity, the braze will rupture. Therefore, if r exceeds the critical value for which β becomes unity, the braze area beyond the critical value would behave as a crack. The total joint strength, in consequence, will be reduced for r greater than this value. For cyclical thermal loading, this equation has to be modified to account for damage accumulation.

As an example, for a butt joint between Inconel 600 and Si_3N_4 with a 0.004" thick braze layer (Ag-28Cu) and a 820°C brazing temperature, the

mismatch strain between the metal and ceramic, $(\alpha_m - \alpha_c)(T_S - T)$, is 0.8% and the elastic accommodation strain, $\epsilon^E A$, is 0.1%. With $\epsilon_c = 0.5$ and $\beta = 1$, the maximum braze diameter should not exceed 8 mm. The size of the braze can be increased if a compressive stress is induced in the braze during the cooling process.

The β criterion, Equation 2.4, was based on the braze surviving one brazing process thermal cycle. It was formulated assuming that the braze deforms in simple uniform shear throughout the thickness. The magnitude of the shear strain was assumed to vary along the lateral direction of the braze. However, if the braze terminates at the edge with a traction-free side surface, then the local deformation near the edge is under the condition of 'direct shear'. A study on the slip line field of direct shear in plain strain was reported previously². The slip line solution is shown in Figure 2.1, and the actual simple shear yield zone is surrounded by rigid dead zones (D). The shear yield zone is approximately three-quarters of the total braze thickness.

FEA has shown that the shear strain is localized along the boundaries of the dead zones, while the central region undergoes moderate simple shear. Results of the FEA are shown in Figure 2.2. This analysis indicates that shear rupture of the braze is more likely than predicted by the β criterion because of strain localization. Shear rupture along double localized layers has been observed experimentally. Another interesting feature of the finite element solution is that a normal stress concentration is induced near the edge of the braze by plastic deformation of the braze. However, the normal stress concentration is limited to a distance of approximately one-third of the braze thickness. One-half of the normal stress at the edge is applied as a compressive stress to the metal component, and the other half is applied as a tensile stress to the ceramic component.

Figure 2.1. Slip line solution for direct shear. Cross-hatched regions are rigid bodies subjected to the direct shear loading. D indicates shear dead zones. The shaded region represents deformed bulk braze material.

Figure 2.2. Position through the braze versus plastic shear strain for the model shown in Figure 2.1. $y = 0$ is the center line, and $y = 15$ is the outer surface.

Analysis of Ceramic Fracture - γ Criterion

As mentioned previously, strength prediction of a ceramic with insufficient information on the micro-flaw distribution is a difficult task. Four phenomenological failure criteria are used for ceramic fracture.

The first criterion is that of maximum principal stress. This is not an accurate criterion, because the crack growth mechanisms and the energy balance are not considered. Accurate estimation of maximum principal stress is impractical because preexisting flaws in the ceramic cause sharp stress concentrations. Therefore, this criteria has not been adapted here. However, for qualitative comparisons of stress states of different joint configurations, the distribution of maximum principal stress has been used.

The second criteria considered was a crack growth criteria with a particular choice of the most probable crack growth configurations. This assumes that a microcrack grows from the edge of the ceramic-braze interface. The energy release rate, or crack driving force, decreases initially as the crack grows, then increases after the crack has grown beyond a critical length. The initial decrease in the stress intensity factor is due to the local normal stress concentration near the edge caused by plastic shear deformation of the braze. The subsequent increase in the stress intensity factor is caused by long-range, compared to the braze thickness, shear stresses. These long-range shear stresses are caused by the thermal mismatch strain between the ceramic and metal and are transferred from the metal to the ceramic by the braze. This changing stress intensity factor implies that the fracture toughness of the ceramic should be greater than the minimum stress intensity factor of the critical crack length and that all of the initial flaw sizes should be smaller than the critical length.

Therefore, the criterion for safe brazing was derived as

$$\gamma_l < \gamma_t < 1, \quad \text{Eq. 2.5}$$

where

$$\gamma_l = \frac{4t\tau_0^2 g(\theta)f(\theta)}{K_{IC}^2} \quad \text{Eq. 2.6}$$

and

$$\gamma_t = \frac{4t\tau_0^2 g(\theta)^2}{K_{IC}^2}, \quad \text{Eq. 2.7}$$

where K_{IC} is the ceramic fracture toughness, 't' the braze thickness, τ_0 is the braze yield stress, and $g(\theta)$ and $f(\theta)$ are crack-angle dependent geometric factors.

Derivation of this result was obtained by examining the contribution of shear and normal point loading stresses to the stress intensity at the tip of the flaw:

$$K_I^p = \left(\frac{P}{\sqrt{l}} \right) f_I(\theta), \quad \text{for point loading, and} \quad \text{Eq. 2.8}$$

$$K_I^\tau = (\tau_0 \sqrt{l}) g_I(\theta), \quad \text{for distributed shear} \quad \text{Eq. 2.9}$$

where l is the crack length and $i = I$ or II , indicating the mode of the stress intensity factor. Then the total stress intensity factor can be written

$$K_i = \frac{P}{\sqrt{l}} f_i(\theta) + (\tau_0 \sqrt{l}) g_i(\theta). \quad \text{Eq. 2.10}$$

Provided that the crack initiates at a particular angle θ_0 , for which $K_{II} = 0$ and $P = \tau_0 l/2$ for equilibrium, the total stress intensity factor becomes

$$K_I = \tau_0 \sqrt{l} \left(\sqrt{l/l} f(\theta_0) + \sqrt{l/t} g(\theta_0) \right), \quad \text{Eq. 2.11}$$

where $f(\theta_0) = f_I(\theta_0)/2$ and $g(\theta_0) = g_I(\theta_0)$.

For initial flaws, $\partial K_I / \partial \bar{l} \leq 0$ prevents unstable crack growth and $\partial K_I / \partial \bar{l} = 0$ provides the minimum intensity factor, where $\bar{l} = l/t$. This condition gives

$$\bar{l} \leq f(\theta_0)/g(\theta_0) \quad \text{Eq. 2.12}$$

and

$$K_I^{\min} = 2 \tau_0 \sqrt{t f(\theta_0) g(\theta_0)}. \quad \text{Eq. 2.13}$$

The requirement that $K_I^{\min} < K_{IC}$ together with Equations 2.12 and 2.13 provide input for the criterion in Equation 2.5.

This criterion can also be written in a dimensional form as

$$\frac{lgI}{f_I} < t < \frac{K_{IC}^2}{4\tau_0^2 g_I f_I}. \quad \text{Eq. 2.14}$$

As shown in this inequality, an acceptable braze thickness is bound by the flaw size and ceramic toughness. Therefore, if $K_{IC}^2/(4\tau_0^2 g_1 f_1) < |g_1/f_1|$, the brazing process will cause fracture of the ceramic component for any thickness. An asymptotic geometric function for $f_1(\theta)$ can be obtained in the closed form, using a conservation integral (M-integral), as

$$f_1(\theta) = \cos \psi \sqrt{\frac{\sin^2 \phi}{\phi + \sin \phi} + \frac{\cos^2 \phi}{\phi - \cos \phi} - \frac{\sin^2 \theta}{\theta + \sin \theta} - \frac{\cos^2 \theta}{\theta - \cos \theta}} \quad \text{Eq. 2.15}$$

where ϕ is the ceramic corner angle and $\tan \psi = K_{II}^P/K_I^P$. In general, $f_1(\theta)$ and $g_1(\theta)$ have to be determined for finite geometry specimens, by FEA or other numerical methods, such as the boundary integral method. Closed form geometric functions for $f_1(\theta)$ and $g_1(\theta)$ are not known.

The above criterion is applicable if a failure begins from the edge of the interface. However, experiments show that in many cases failure starts from some distance away from the edge. As mentioned previously, tractions induced on the ceramic surface by a thermal strain mismatch are in equilibrium. Therefore, the global stress state decays exponentially with distance from the joint. If the structure is elastic everywhere, then a stress singularity occurs at the interface edge for certain ranges of interface corner angles. If the interface is able to slide with flow stress τ_0 , the stress concentration near the interface is reduced and the peak stress is pushed away from the interface.

If the braze does not flow plastically, but flows by purely elastic deformation, the stress concentration near the critical area, in terms of the principal shear stress, is approximately

$$\tau \approx \frac{2\mu_1\mu_2}{\mu_1 + \mu_2} (\alpha_1 - \alpha_2) \Delta T \left(\frac{L}{r}\right)^m F^*(\alpha^*, \beta^*), \quad \text{Re}(m) > 0, \quad \text{Eq. 2.16}$$

where μ_1, μ_2 and α_1, α_2 are the shear modulus and thermal expansion coefficient for material 1 and 2, respectively, F^* is a dimensionless function of Dundurs parameters³ (α^*, β^*), and L is a characteristic length for the braze interface. As r approaches 0, the stress concentration increases rapidly. This may cause the initiation of crack growth in the ceramic part.

If we introduce a braze layer that has the flow shear stress τ_0 , the J-integral around the stress concentration area may be expressed as

$$J = \tau_0 L (\alpha_1 - \alpha_2) \Delta T h^*(\alpha^*, \beta^*, \text{geometry}), \quad \text{Eq. 2.17}$$

where h^* is a function of sample geometry and material properties, is bounded by unity, and is calculated by numerical techniques.

The J integral can be regarded as a measure of the strength of a stress concentration. Therefore, one design strategy is to keep J as small as possible. That means τ_0 , L , $(\alpha_1 - \alpha_2)$, ΔT , and h^* have to be small. Therefore, the following inequality should be valid to prevent cracking:

$$\frac{K_{IC}^2(1-\nu^2)}{EJ} > 1 \quad \text{Eq. 2.18}$$

or replacing J with Equation 2.17:

$$\frac{K_{IC}^2(1-\nu^2)}{E\tau_0 L(\alpha_1 - \alpha_2)\Delta T} > h^*(\alpha^*, \beta^*, \text{ geometry}) \quad \text{Eq. 2.19}$$

for $\gamma_0 t \leq L(\alpha_1 - \alpha_2)\Delta T \leq \gamma_f t$, where $\gamma_0 = \tau_0/2$, and γ_f and t are the shear failure strain and braze thickness, respectively. K_{IC} , ν , and E are toughness, Poisson's ratio, and Young's modulus of ceramic, respectively. In general, we must satisfy

$$\frac{K_{IC}^2(1-\nu^2)}{E\tau_0 L(\alpha_1 - \alpha_2)\Delta T} > \frac{K_{IC}^2(1-\nu^2)}{E\tau_0 \gamma_f t} > h^*(\alpha^*, \beta^*, \text{ geometry}). \quad \text{Eq. 2.20}$$

To ensure that the ceramic will not fracture upon cooling and in order to have a large effective torque transmitting area of the braze joint, the following is suggested based on the γ criteria:

- γ_f and t should be optimized for the β and γ criteria.
- E and τ_0 should be minimized.
- K_{IC} should be maximized.
- $h^*(\alpha^*, \beta^*, \text{ geometry})$ should be minimized.

The major geometry variables are (t/L) , curvature, and shape factors. It is clear that numerical optimization schemes to reduce $h^*(\alpha^*, \beta^*, \text{ geometry})$ should be examined, and these are discussed in the following sections.

A fourth approach to ceramic failure involves the implementation of probabilistic fracture mechanics. The probability of failure of the ceramic component evolves from the nonuniform distribution of flaws or stress concentrations, their size, and their orientation within the ceramic structure.

This approach has not been studied in Phase I, but will be investigated in Phase II.

2.2 CONSTITUTIVE MODELING OF JOINT MATERIALS

In order to express the response of the joint as a function of materials properties and temperature, constitutive equations were developed for the joint materials with the assumptions discussed below. Based on these constitutive equations, various joint geometries and material systems were examined using FEA.

Strain Response of Joints

The rotational strain, γ , of a member loaded in torsion is given by:

$$\gamma = \frac{\tau}{G} \quad \text{Eq. 2.21}$$

and the shear stress, τ , is given by:

$$\tau = \frac{Tc}{J} \quad \text{Eq. 2.22}$$

where G is the shear modulus (a proportionality constant between τ and γ), T is the torque, c is the distance from the center of the member to the point of interest, and J is the polar moment of inertia, $1/2 \pi r^4$. c is usually set equal to the radius r .

The angle of twist of one end of the joint with respect to the other end, ϕ , is given in radians by:

$$\phi = \frac{TL}{JG} = \frac{\gamma L}{c} \quad \text{Eq. 2.23}$$

where L is the length of the member.

Once the failure stress of the joint, τ , has been predicted by FEA the failure strain of the joint can also be predicted. The mechanical tests of the brazed joints resulted in linear plots of T versus ϕ :

$$T = k\phi \quad \text{Eq. 2.24}$$

where k is a constant of proportionality. Solving Equation 2.23 for T we get:

$$T = \frac{J G}{L} \frac{\gamma_f L}{c} \quad \text{Eq. 2.25}$$

Comparing Equation 2.24 and 2.25 we see that:

$$k = \frac{J G}{L} \quad \text{Eq. 2.26}$$

Since the FEA predicts the failure stress of the joints, Equation 2.25 was rearranged into a relationship between failure stress, τ_f , and failure strain, γ_f :

$$\gamma_f = \tau_f \frac{J}{k L} \quad \text{Eq. 2.27}$$

Basic Assumptions for Constitutive Equations

The materials used in the ceramic-metal braze joint are the following:

Ceramic	PY6
Interlayer Material	Mo (low α) or Ni (low yield stress, σ_y)
Braze	Au-18Ni or Au-5Pd-2Ni
Structural Alloy	Incoloy 909

The uniaxial stress and strain relations of all the materials were considered to be temperature-dependent, but rate-independent, with power law hardening constitutive relations. Therefore, the stress can be described as follows:

$$\text{in the elastic range} \quad \sigma = E(T)\epsilon \quad \text{Eq. 2.28}$$

$$\text{in the plastic range} \quad \sigma = f(T)\epsilon^n \quad \text{Eq. 2.29}$$

where σ is true stress, ϵ is true strain, $E(T)$ is Young's modulus as a function of temperature, n is strain hardening coefficient, and $f(T)$ is a strength coefficient as a function of temperature.

The assumptions made on the temperature dependence were

- Strain hardening coefficient, n , is temperature independent.

- Young's modulus, $E(T)$, is a linear function of temperature.

$$E(T) = E_1 T + E_0, \quad \text{Eq. 2.30}$$

- $f(T)$ is a linear function, or piecewise linear function of temperature,

$$f(T) = AT + B, \quad \text{Eq. 2.31}$$

- Ultimate tensile strength and yield strength are linear functions of temperature and are equal to zero at the melting temperature.

The hardening coefficient 'n' can be calculated as

$$n = \frac{\ln(\sigma_{TS}/\sigma_y)}{\ln(\epsilon_{TS}/\epsilon_0)}, \quad \text{Eq. 2.32}$$

where σ_{TS} and ϵ_{TS} are ultimate strength and corresponding strain, and yield strain, ϵ_0 , equals σ_y/E .

Physical Properties for Joint Materials.

The properties of the structural alloys, Ni, and the Au-18Ni braze are listed in Table 2.1. The properties of other joint materials were discussed separately.

Table 2.1. Material properties for materials used in the joint.

Material	T (°C)	σ_y (MPa)	E (GPa)	σ_{TS} (MPa)	ϵ_f	Poisson's Ratio	CIE (x $10^{-6}/^\circ\text{C}$)
Incoloy 909	20	1034	158.585	1276	0.15		6.5
	650	862	155.174	1034	0.25		10.0
Inconel 718	20	1033	179			0.27	14.1
Ni	20	58.6075	214	400	0.65		13.4
	800	26.43	173.46				16.5
Au-18Ni	20	582	38.98	715	0.048		17.5

Molybdenum. The material data for Mo are listed in Table 2.2. Because of the strong nonlinearity of the yield stress with respect to temperature, $f(T)$ was taken as piecewise linear function of temperature in four different sections. The sections were from 20°C to 200°C, from 200°C to 300°C, from 300°C to 800°C, and from 800°C to 1000°C. $f(T)$ was expressed as the following:

$$\begin{aligned} f(T) &= A_1T + B_1 && \text{for } 20^\circ\text{C} \geq T \geq 200^\circ\text{C} \\ f(T) &= A_2T + B_2 && \text{for } 200^\circ\text{C} \geq T \geq 300^\circ\text{C} \\ f(T) &= A_3T + B_3 && \text{for } 300^\circ\text{C} \geq T \geq 800^\circ\text{C} \\ f(T) &= A_4T + B_4 && \text{for } 800^\circ\text{C} \geq T \geq 1000^\circ\text{C} \end{aligned}$$

Table 2.2. Material properties for Mo.

T(°C)	σ_y (MPa)	E (GPa)	σ_{TS} (MPa)	ϵ_f
20	560.60	328.17	665.00	0.01
200	124.11	319.48		
300	206.85	309.68		
800	68.95	294.00		
1000	55.16	269.50		

PY6 Silicon Nitride. The ceramic was regarded as an elastic material. Young's modulus as a function of temperature was obtained using general rules of temperature dependence. Unless there is a phase transformation in the temperature range of interest, the temperature dependent Young's modulus can be represented as

$$E(T) = E^* \left(1 - a \frac{T + 273}{T_m + 273} \right), \quad \text{Eq. 2.33}$$

where E^* is the 'extrapolated' Young's modulus at absolute zero degree Kelvin and T_m is the melting temperature of the material in degrees Celsius. The empirical constant "a" is 0.33 for covalent bonding ceramics and 0.47 for metals.

Table 2.3 lists Young's moduli and strength coefficients as a function of temperature for the joint materials. For PY6 Si_3N_4 , the material constants were derived using $T_m = 1900^\circ\text{C}$ and $E = 296.5$ GPa at 20°C . The material property data shown in the table was expressed in a form suitable for the ABAQUS finite element program. These constitutive data were implemented

with the ABAQUS finite element program. J_2 flow theory (Pranor-Reuss equations) with an isotropic hardening law was used. The materials were assumed to be rate-independent. Because of the heating process during manufacturing of the joint, it was assumed that the effect of heat generation due to plastic work on constitutive models was negligible.

Table 2.3. Material constants for the ABAQUS finite element model.

Constant	Incoloy 909	Ni interlayer	Mo interlayer	Au-18Ni braz	Au-5Pd-2Ni braz	PY6 Si ₃ N ₄
E_1 (GPa/°C)	- 0.005415	- 0.05197	- 0.05987	- 0.02433	-0.001008	- 0.04712
E_0 (GPa)	158.7	215.0	329.4	56.68	28.41	297.4
n	0.0575	0.235	0.099	0.129	0.1304	
A_1 (MPa/°C)	- 0.3478	- 0.2282	- 4.333	- 1.256	- 0.2093	
B_1 (MPa)	1338.0	391.0	1137.0	1236.0	241.2	
A_2 (MPa/°C)			1.571			
B_2 (MPa)			238.5			
A_3 (GPa/°C)			- 0.5387			
B_3 (MPa)			588.7			
A_4 (GPa/°C)			- 0.1472			
B_4 (MPa)			277.5			

2.3 OPTIMIZATION OF JOINT GEOMETRY

Several studies have concentrated on either measuring⁴ or predicting⁵⁻⁷ the thermal stresses generated during cooling of the joint from the brazing temperature as a function of joint materials and geometry. The purpose of this study was to determine the optimum geometry of the braze layer to minimize the residual tensile stresses in the ceramic shaft. The initial geometry of the joint is shown in Figure 2.3a. The ceramic shaft had a diameter of 14 mm. The metal shaft was either solid or hollow. The braze was 0.05 mm thick and had an area of 154 mm². The length of each component was taken to be 30 mm to allow for interface effects to sufficiently decay.

The joining process was performed by heating the components until the braze melted, then cooling the joint to 20°C. Relevant mechanical properties of the materials used were described in the previous section. The ceramic was assumed to be linearly elastic. Metal and braze materials were assumed to be elastic-perfectly plastic, and to obey a von Mises yield condition.

Several joint geometries were studied; these are shown in Figure 2.3 and consist of flat, parabolic, conical, and cylindrical geometries. Each of the joint geometries was investigated with material system A, shown in Table 2.4.

Table 2.4. Material properties of material system A.

Property	Ceramic (Sintered AY6)	Braze (Cusil ABA)	Metal (Inconel 718)
Young's Modulus (GPa)	296	83	179
Poisson's Ratio	0.0	0.36	0.27
Yield Stress (MPa)	---	271	1033
CTE ($10^{-6}/^{\circ}\text{C}$)	3.7	18.5	14.1
Brazing temperature ($^{\circ}\text{C}$)	---	780	---

Since the joints are axisymmetric, only half of the model is shown. The dimensions of the metal shaft and the braze were chosen so that the braze area was 154 mm^2 and the limit torque of the metal shaft was not less than what the braze layer could support.

The numerical analysis was done using ABAQUS with 8-node, parametric axisymmetric finite elements with reduced integration. Element 'CAx8R' was used for the ceramic, and the hybrid element 'CAx8RH' was used for the metal and braze materials.

Figure 2.3. Joint geometries investigated for the optimization study.

The finite element modeling was performed to ensure that the differences in stress states among different models were due to their geometry differences and not to modeling differences. This implies that finite element modeling errors should be approximately the same for all models. An h-convergence study was performed to ensure that acceptable results were generated by each of the finite element models used in this study. The analysis scheme was to start the analysis at the solidus temperature of the braze, then to cool the structure down slowly to 20°C. Output from ABAQUS analyses consisted of element stresses and strains at integration points within the elements and the displacements at the nodes. Nodal stresses were also obtained, but were not as accurate as those at element integration points. Therefore, comparisons were done using integration point stresses. The results are presented for the critical tensile regions in the ceramic since the primary concern was the magnitude and location of tensile stresses in the ceramic.

A description of the models used for each of the joint geometries, followed by pertinent results from these analyses, will now be discussed. Schematics of each of the joint geometries are illustrated in Figures 2.3 a-e. In Figure 2.3 a-c, solid metals were joined to the ceramic by a butt joint, while hollow metals were joined to the edges of the ceramic in Figure 2.3 d-e. All parts are round and the points, $x = 0$, denote the center of the bars. Figure 2.4 shows the finite element meshes used for flat and parabolic geometries in this analysis. Relatively fine meshes were used for the joint area and the outer surface of the joint components, where maximum residual stresses were expected. For conical and cylindrical geometries, finer meshes were used, as shown in Figure 2.5. These fine meshes were also utilized for the flat butt joint geometry to study the effect of temperature on the the residual stress.

Figure 2.4 Meshes used in FEA of ceramic-metal joints. (a) Flat joint, (b) Parabolic joint - small convex ceramic, (c) Parabolic joint - large convex ceramic, (d) Parabolic joint - small concave ceramic, (e) Parabolic joint - large concave ceramic.

Figure 2.5. Fine meshes used in FEA of ceramic-metal joints. (a) Flat butt joint, (b) Thick conical joint, (c) Thin conical joint, (d) Square ended cylindrical joint, and (e) Tapered cylindrical joint.

Flat Joint. This is the simplest butt joint geometry. The braze had an area of 154 mm^2 and a thickness of 0.05 mm . Figure 2.6 is a plot of σ_y versus y position at $x \approx 7$, i.e., the outer edge of the ceramic at 20°C for material system A. σ_y denotes the residual stress "along the y -axis" and the edge of the ceramic part was at the left side of the x -axis, $x < 0$. Large tensile stresses occur in the ceramic near the joint area, $y = 0$. The maximum principal stress is nearly equal to σ_y , and hence σ_y was used to represent the level of the residual stress. The results from various parabolic joints are shown in the same plot. Figure 2.6b shows an enlarged view of Figure 2.6a. The peak stresses of all these geometries occurred in the ceramic some distance away from the joint. The flat butt joint had the lowest maximum residual stress compared to levels in the parabolic butt joints.

Figure 2.7 shows a plot of σ_y versus y position at $x \approx 7$ at different cooling stages using the fine mesh in Figure 2.5a. These results show that σ_y continues to increase until the temperature reached 400°C , after which there was little reduction in σ_y . Dramatic changes in the residual stress occurred between 600 and 700°C . Below 400°C , large plastic strains in the braze relaxed some of the differential contraction and, therefore, did not increase the level of residual stress.

Figure 2.6.

σ_y versus y at the ceramic surface for different butt joints. (a-top) $\diamond$ and $+$ are convex ceramics, $\times$ and Δ are concave ceramics, and $\square$ is a flat joint. (b-bottom) Enlarged figure of part a. σ_y is the residual stress along the y-axis.

Figure 2.7 σ_y versus y for the flat butt joint at various temperatures during cooling of the braze joint.

Parabolic Joint. Two different geometries were considered for the parabolic joint, one with a downward contour, and the other with an upward contour. The y location of the braze is given by

$$y = h \left(\frac{2x}{d} \right)^2 \quad \text{and } d = 14 \text{ mm}, \quad \text{Eq. 3.34}$$

where h is the dip at the outer surface. The distance between the lower and upper surface of the braze was kept constant at 0.05 mm. The meshes for the parabolic joints are shown in Figures 2.4 b-e. In order to have a regular mesh near the joint area, all the element edge lines between $y = \pm 4.0$ were downward parabolic curves.

A plot of σ_y versus y position at $x \approx 7$ for the parabolic joint are shown in Figure 2.6 along with the results from the flat joint. As discussed earlier, the flat joint resulted in the lowest value for the maximum tensile stress in the ceramic. The shift of the maximum stress points for the parabolic joints was attributed to the changes in the location of the joints with parabolic geometry.

Conical Joint. For the conical joint, the metal shaft had a hollow cross-section with an inner radius, a , and an outer radius, $b = 7$ mm. Since the braze area was held constant at πb^2 , the parameters shown in Figure 2.3d were related geometrically by

$$a^2 = b^2(1 - \sin \alpha) \quad \text{Eq. 2.35}$$

and

$$h = \frac{b - a}{\tan \alpha} \quad \text{Eq. 2.36}$$

If τ_o^M and τ_o^B are the shear yield stresses for the metal and the braze, respectively, the fully plastic torque, neglecting residual stresses, is

$$T_o^M = \frac{2\pi}{3} (b^3 - a^3) \tau_o^M \quad \text{Eq. 2.37}$$

for the metal, and

$$T_o^B = \frac{2\pi}{3 \sin \alpha} (b^3 - a^3) \tau_o^B \quad \text{Eq. 2.38}$$

for the braze. Hence,

$$\frac{T_o^M}{T_o^B} = \left(\frac{\tau_o^M}{\tau_o^B} \right) \sin \alpha \geq 1 \quad \text{Eq. 2.39}$$

gives limiting values for α and (a/b) . For the joint geometry and material system A considered in this study,

$$\sin \alpha \geq \frac{\tau_o^B}{\tau_o^M} = \frac{271}{1033} = 0.26 \quad \text{Eq. 2.40}$$

$$\alpha \geq 15.2^\circ \quad \text{and} \quad \frac{a}{b} \leq 0.86 \quad \text{Eq. 2.41}$$

Two relevant values of (a/b) were chosen to study the effect of thickness of the conical geometry, Figure 2.3d, on the residual stress within boundary conditions imposed by the material system:

- i) $(a/b) = 0.5$, $a = 3.5$ mm, $b = 7.0$ mm, $\alpha = 49^\circ$ and $h = 3.09$ mm: thick conical joint, and
- ii) $(a/b) = 0.8$, $a = 5.6$ mm, $b = 7.0$ mm, $\alpha = 21^\circ$ and $h = 3.63$ mm: thin conical joint.

The mesh for the thick and thin conical joints are shown in Figure 2.5b and 2.5c, respectively. The bottom edge of the braze lies between the levels $y = 0$ and $y = -3.63$. The mesh refinement in the critical region of the interface, close to the point $x = 7.0$, $y = -3.63$, was done similarly to that of the previous case.

Plots of σ_y versus y position at $x = 6.951$ for the conical joints are shown in Figure 2.8. When $(a/b) = 0.5$, as in Figure 2.8a, convergence problems with ABAQUS were encountered for temperatures lower than 200°C , and hence the final result at 20°C was not obtained for the thick conical joint mesh. These results showed that σ_y continued to increase as the temperature was reduced, and that the peak stresses occurred adjacent to the braze. Lower tensile stresses were observed for $(a/b) = 0.8$ than for $(a/b) = 0.5$, Figure 2.8b. Hence, the geometry with $(a/b) = 0.5$ was not considered for further analysis.

Figure 2.8. σ_y versus y for the conical joints at various temperatures during cooling of the braze joint. (a-top) Thick wall, $(a/b) = 0.5$. (b-bottom) Thin wall, $(a/b) = 0.8$.

Cylindrical Joint. The metal shaft (outer radius b and inner radius 7.05 mm) fits outside the ceramic shaft. For a constant braze angle, the length of the joint, h , must be half of the radius of the inner shaft, i.e., $h = 3.5$ mm. Two detailed geometries were considered for the lower edge of the metal shaft, a square edge geometry (Figure 2.3e), and a tapered edge geometry (Figure 2.3f). The meshes for the cylindrical joints with the square-edge and the tapered-edge are shown in Figure 2.5 d and e.

Figure 2.9 shows Plots of σ_y versus y as a function of temperature at $x = 6.951$ for the cylindrical joints. The results showed that the maximum tensile stress occurred near the ends of the braze ($y = -3.5$ and $y = 0.0$) with compressive stress in the middle. This is equivalent to the stress observed along the x -axis in butt joints. It was noted that the tapered edge resulted in slightly lower σ_y at $y = -3.5$ than did the square end whereas the opposite is true at $y = 0$.

The stress values in the ceramic at $x = 6.951$ were compared in Figure 2.10 for different joint geometries. The results showed that other joint geometries provided little improvement in minimum σ_y over the flat butt joint.

Selection of Joint Geometry. Figure 2.10b shows that the cylindrical joint with the tapered end had a higher residual stress near the joint than did the flat butt joint (320 MPa versus 200 MPa at $y = -0.2$ mm). The maximum residual stress would be the determining factor in the selection of a joint design if the ceramic in use could not survive that level of stress during cooled down to room temperature. If, however, the fracture strength of the ceramic exceeds the level of the residual stress, comparison of different geometries should be made using a probabilistic approach to fracture.

The probability of ceramic survival can be expressed as:

$$P_s = \exp \left(- \int_v \left(\frac{\sigma}{\sigma_0} \right)^m dv \right) \quad \text{Eq. 2.42}$$

where σ_0 is a normalization parameter with no physical significance, m is the Weibull modulus ($m > 1$), and " v " is the volume of material exposed to stress σ . In the case of a ceramic-metal joint, where stress σ is strongly dependent on the location, qualitative comparison of P_s is only possible with FEA based on finalized dimensions of the joint geometry and on materials properties.

While the cylindrical joint has the highest residual stress level, its P_s is much smaller than that of the flat butt joint. The cylindrical joint has a lower P_s because the volume exposed to the stress is significantly smaller than in the flat butt joint. Therefore, failure associated with the residual stress will be less for the cylindrical joint than for the flat joint. Based on this information, cylindrical joint was selected over flat joint.

Figure 2.9. σ_y versus y for the cylindrical joints at various temperatures during cooling of the brazed joint. (a-top) Square-ended joint, (b-bottom) Tapered joint.

Figure 2.10.

(a-top) σ_y versus y for several joints at $x = 6.951$ mm.
 (b-bottom) Close-up of (a). $\diamond$ and $+$ are for cylindrical joints with tapered and squared ends, respectively, while Δ and $\square$ are for conical and flat joints.

2.4 EFFECT OF INTERLAYER MATERIAL

On the basis of the failure criteria, Equation 2.20, it was suggested that low yield strength and low coefficient of thermal expansion (CTE) properties should reduce the tendency of ceramic failure. Since both properties are not found in one material, a FEA study was done to investigate the relative effectiveness of these properties in controlling residual stress. For this study, Ni was selected for its low shear strength, while Mo was selected for its low CTE. Results showed that low yield stress Ni was more effective than low expansion coefficient Mo in reducing the residual stress in the ceramic at room-temperature after brazing.

Additional FEA of the joint was conducted with modified constitutive equations derived as a function of temperature; the mechanical properties of the braze were assumed to be temperature-independent. Also, the number of elements was increased to highlight the stress distribution around critical crack initiation sites. The number of elements used was 166, 56, 140, and 192 for the ceramic, braze, interlayer, and structural alloy, respectively. While the predictions of the model were unchanged from those reported earlier, the accuracy of those predictions was improved.

Temperature-dependent power law equations were used for the plastic deformation of the metal joint components with the following assumptions:

- The strain hardening exponent, n , is independent of temperature.
- The strength coefficient, $f(T)$, is a linear function of temperature.
- The young's modulus, $E(T)$, is a linear function of temperature

$$\sigma = E(T)\epsilon \quad \text{in elastic range}$$

$$\sigma = f(T)\epsilon^n \quad \text{in plastic range}$$

$$E(T) = E_0(1 - a \frac{T}{T_m}),$$

where σ , ϵ , $E(T)$, n , and $f(T)$, are true stress, true strain, Young's modulus, strain hardening exponent, and "a" is a strength coefficient, respectively. The ceramic was treated as a perfect elastic material, while the braze alloy was treated as an elastic-perfect plastic material.

The materials' properties as a function of temperature were used to calculate $E(T)$, n , and $f(T)$ for the materials in the ceramic-metal joint system, Table 2.5. An improved FEA of the joint was performed using these modified constitutive equations, Section 2.2.

Table 2.5. Temperature dependence of the elastic modulus, $E(T)$, strain hardening exponent, n , and strength coefficient, $f(T)$.

Material	$E(T)$ (GPa)	n	$f(T)$ (ksi)
Ni	$-0.052T + 215.04$	0.235	$0.23T + 390.96$
Mo	$-0.060T + 329.37$	0.099	$-4.33T + 1136.51$ $(20^\circ\text{C} \leq T < 200^\circ\text{C})$ $1.57T + 238.53$ $(200^\circ\text{C} \leq T < 300^\circ\text{C})$ $-0.54T + 588.71$ $(300^\circ\text{C} \leq T < 800^\circ\text{C})$ $-0.15T + 277.53$ $(800^\circ\text{C} \leq T < 1000^\circ\text{C})$
Incoloy 909	$-0.0054T + 158.69$	0.0575	$-0.35T + 1387.98$
PY6 Si_3N_4	$-0.049T + 279.52$	1.00	N/A
Au-18 Ni Braze	$-0.035T + 58.88$	0.00	99.5

Mises equivalent stress determines the deformation of the metal components, while the maximum principal stress will determine cracking of the ceramic components. Therefore, contours of Mises equivalent stress in the metal and of the maximum principal stress in the ceramic were used to judge the joint's materials and design. Figure 2.11 shows the finite element mesh for the analysis. For all of the analyses, 8-node biquadratic elements were used for the metal components. A fine mesh spacing was used for the interlayer to show the nonlinear plastic behavior of that layer.

Figures 2.12 - 2.15 show the results of FEA where 20 contours were drawn to a 2.00×10^8 Pa maximum stress. As shown in Figures 2.12 and 2.13, the Ni interlayer resulted in a lower principal stress in the ceramic compared to the Mo interlayer. The tensile stress in the ceramic with a Ni interlayer was about one-fifth of the stress in the ceramic with a Mo interlayer. Comparing contour #14 in Figure 2.12 and 2.13 gives 1.05×10^7 versus 5.26×10^7 Pa for the maximum tensile stress in the ceramic with a Ni and Mo interlayer, respectively. Therefore, a Ni interlayer will reduce the chance of cracking in the ceramic. Figures 2.14 and 2.15 show the similar advantage of a Ni interlayer over a Mo interlayer. Mises equivalent stress in the Mo interlayer exceeds 2.00×10^8 Pa, whereas the Ni interlayer sees this level of stress only in the vicinity of the interface between the Ni and Incoloy 909.

In conclusion, at room-temperature, even for the temperature-dependent constitutive models used in this study, the low yield strength Ni interlayer resulted in lower residual stress levels in the joint than did the Mo interlayer. Shear testing of coupon lap joints, discussed in Section 3.3, supported this conclusion.

Figure 2.11. Finite element mesh used for interlayer study.

1	-4.00E+08
2	-3.68E+08
3	-3.36E+08
4	-3.05E+08
5	-2.73E+08
6	-2.42E+08
7	-2.10E+08
8	-1.78E+08
9	-1.47E+08
10	-1.15E+08
11	-8.42E+07
12	-5.26E+07
13	-2.10E+07
14	+1.05E+07
15	+4.21E+07
16	+7.36E+07
17	+1.05E+08
18	+1.36E+08
19	+1.68E+08
20	+2.00E+08

Figure 2.12. Contours of maximum principal stress in ceramic-metal brazing joint with Ni as the interlayer.

1	-2.00E+09
2	-1.84E+09
3	-1.68E+09
4	-1.52E+09
5	-1.36E+09
6	-1.21E+09
7	-1.05E+09
8	-8.94E+08
9	-7.36E+08
10	-5.78E+08
11	-4.21E+08
12	-2.63E+08
13	-1.05E+08
14	+5.26E+07
15	+2.10E+08
16	+3.88E+08
17	+5.26E+08
18	+6.84E+08
19	+8.42E+08
20	+1.00E+09

Figure 2.13. Contours of maximum principal stress in ceramic-metal brazing joint with Mo as the interlayer.

- 1 +4.73E+01
- 2 +4.73E+07
- 3 +9.47E+07
- 4 +1.42E+08
- 5 +1.89E+08
- 6 +2.36E+08
- 7 +2.84E+08
- 8 +3.31E+08
- 9 +3.78E+08
- 10 +4.26E+08
- 11 +4.73E+08
- 12 +5.21E+08
- 13 +5.88E+08
- 14 +6.15E+08
- 15 +6.63E+08
- 16 +7.10E+08
- 17 +7.57E+08
- 18 +8.05E+08
- 19 +8.52E+08
- 20 +9.00E+08

Figure 2.14. Contours of Mises equivalent stress in ceramic-metal braze joint with Ni as the interlayer.

- 1 +5.78E+01
- 2 +5.78E+07
- 3 +1.15E+08
- 4 +1.73E+08
- 5 +2.31E+08
- 6 +2.89E+08
- 7 +3.47E+08
- 8 +4.05E+08
- 9 +4.63E+08
- 10 +5.21E+08
- 11 +5.78E+07
- 12 +6.36E+07
- 13 +6.94E+07
- 14 +7.52E+07
- 15 +8.10E+07
- 16 +8.88E+07
- 17 +9.26E+08
- 18 +9.84E+08
- 19 +1.04E+09
- 20 +1.10E+09

Figure 2.15. Contours of Mises equivalent stress in ceramic-metal braze joint with Mo as the interlayer.

2.5 ANALYSIS OF FINAL BRAZE JOINT MODEL

The objective of this analysis was to find the residual stress and strain state in a detailed model of the ceramic-metal braze joint. These analyses should accurately model the geometry and material properties of the joint used for subsequent torsion tests. The results of this analysis were used to superimpose residual deformations with the deformations imposed by the service torque loads on the structure for strength and reliability predictions.

The temperature- and strain-dependent material properties of the components given in Section 2.3 were used. In particular, the following material system was selected in this analysis:

Ceramic	-	PY6
Structural Alloy	-	Incoloy 909
Interlayer	-	Ni
Braze	-	Au-5Pd-2Ni

The brazing process was considered to be "slow" and not to affect the rate-dependent properties of the material system above; therefore, rate effects were not considered in this study.

No cracking or relative motion at the interfaces of component materials was permitted in the FEA model. This was thought to be a valid assumption since most of the interface regions are in compression, thus ensuring contact. Also, the interfaces associated with the braze or nickel layers will remain in contact with other materials throughout the deformation process.

During thermal loading, it was assumed that small strain behavior applies and that the material was initially isotropic. Isotropic hardening of materials was permitted after the von Mises yield condition was satisfied, based on J_2 flow theory. Materials were assumed to be isotropic during and after the deformation phase.

A cylindrical coordinate system was used where the "z" direction was the axial or "long" direction of the structure, "r" was the radial direction, and "θ" was the circumferential direction. The model was axisymmetric; therefore, the center line, i.e., "z" direction, of the model was constrained in all other degrees of freedom except "z". A single node at the base of the structural alloy, at the center line, was fixed in all degrees of freedom. No additional constraints were placed on the structure and no forces or pressures were applied to the nodes.

The residual deformation state of the joint was calculated at 20°C and at 650°C. Since the deformation was history-dependent, the following scheme was used to study the results at these temperatures. A thermally expanded finite element mesh of the braze joint was created. Thermally expanded means that the dimension of the structure at 20°C was increased by $\alpha_i \Delta T_i L_i$, where α_i was the thermal expansion coefficient of the i^{th} material, ΔT_i was the change in temperature from 20°C to the solidus temperature of the braze (1180°C), and L_i was a characteristic dimension. In other words, a stress-free state was assumed at the solidus temperature, and all portions of the structure reached this temperature. The model was then uniformly, slowly cooled to 20°C and the results output. Then the deformed state at 20°C was uniformly, slowly heated to

650°C, and the results were then output. This process considers the history dependence of the plastic deformation. At each stage, the temperature was uniform, since it was assumed that the brazing process and subsequent cooling were slow compared to the thermal conditions of the materials used.

The mesh of the structure is shown in Figure 2.16. The refinement of the mesh in the z and r direction near the braze layers was arrived at through the previous studies on braze-joint shape. The region between the ceramic and the structural alloy consisted of three materials. From the ceramic, a layer of braze was input, then an interlayer of Ni, followed by another braze layer between the nickel and the structural alloy. 1218 quadratic axisymmetric elements were used in this study.

Once the analysis was complete, results were reported for the deformation states at 20 and 650°C. Stress and strain results were output by ABAQUS at the integration points for each element and extrapolated to the nodes for contour plots. Deformed shapes were constructed using nodal displacements without extrapolation.

The deformed shape of the structure at 20°C, magnified to show detail, is shown in Figure 2.17. Maximum principal stress and von Mises stress at 20°C are shown in Figures 2.18 and 2.19, respectively. Similar results for the braze joint at 650°C are shown in Figures 2.20 - 2.22. Plots of the results are indicative of trends and stress gradients throughout the structure. When detailed investigation of a region was warranted or when actual values of a stress component were required, then the actual data from the output sets were used. Care was taken to use element data extrapolated from gauss point information and not to average all relevant stress and strain components at material boundaries.

Deformation of the braze joint for 20 and 650°C was shown for the entire structure. This indicates which regions have undergone the greatest strain and permits us to select regions of greatest deformation for further study. At both temperatures, the greatest deformation occurs in the braze region. This was expected since the braze had the lowest yield stress of the materials in the joint. The structural alloy exerts a "downward pull" on the braze. This downward pull was attributed to larger changes in length for the metal structural alloy than for the ceramic component. This downward motion puts the braze material at the ends of the joint region in simple shear, thus permitting large plastic deformations of the braze layers. This shear mechanism occurred in both braze areas.

The deformed shapes of the model at 20 and 650°C clearly show that larger deformations existed at 20°C. This was due to the larger temperature difference from the braze temperature. Therefore, the structure is subject to larger residual strains at room-temperature than at the operating temperature of the joint. Some amount of stress relaxation occurred when the joint was heated from room-temperature to its operating temperature. Complete relaxation did not occur because the operating temperature is lower than the brazing temperature, and because permanent deformations have occurred in some regions of the structure.

This relaxation phenomenon is shown in the maximum principal stress distributions at 20 and 650°C, Figures 2.18 and 2.21. Not only does the value of the maximum principal stress become reduced from 20°C to 650°C, but the location of this maximum also changes. At 20°C, the Ni interlayer contains the maximum principal stress, thus performing its function of reducing the likelihood of ceramic fracture. The central region of the braze regions puts

the ceramic in residual compression, away from the edges. At 650°C, however, this compression changes to positive values of σ_1 for most of the ceramic material.

The von Mises stress was concentrated in the two braze layers. The von Mises stress is an indication of the amount of distortional energy contained in a volume of material. The large values shown in the braze layer at 20°C emphasize the amount of deformation that these regions undergo. The von Mises stress are also an indication of incipient yielding, depending on the current yield stress of the material. Similar behavior was displayed at 650°C. At 650°C the maximum values of von Mises stress were reduced, and the distribution of these maximum values was more diffuse compared to the results at 20°C, because of the relaxation which occurs at this temperature.

In summary, the braze material undergoes large deformations at both room and operating temperatures, and the interlayer provides a mechanism for ensuring that the largest maximum principal stress occurs outside of the ceramic component at room-temperature. Also, some stress relaxation occurs in the structure when heated from room to operating temperature, permanent deformations notwithstanding.

Figure 2.16. The FEA mesh, used for detailed thermal X-Y-Z coordinate system shown, maps to r-z- θ of the cylindrical coordinate system used in the analysis.

Figure 2.17. (a-right) Mesh at 1180°C shows the initial condition without residual stress. (b-left) Mesh at 20°C demonstrates the deformation associated with residual stress.

Figure 2.18. Contour plot of maximum principal stress (σ_1 in Pa) at 20°C in the vicinity of the joint.

Figure 2.19. Contour plot of von Mises stress (Pa) at 20°C in the vicinity of the joint.

Figure 2.20. (a-right) Mesh at 1180°C. (b-left) At 650°C after reheating from 20°C.

Figure 2.21. Contour plot of maximum principal stress (σ_1 in Pa) at 650°C in the vicinity of the joint.

Figure 2.22. Contour plot of von Mises stress (Pa) at 650°C in the vicinity of the joint.

3 JOINT MATERIAL DEVELOPMENT

Brazing is a complex process in which chemical factors, metallurgical factors, and residual stress distributions affect the joint simultaneously. All of these issues must be considered when designing a high-performance joint between ceramics and metals.

The chemical dissimilarity between the ceramic and the braze gives rise to wetting and adhesion problems. Differential expansion between joint components places the joint, particularly the ceramic, under stress. It is necessary to optimize the materials system under the guidance of analytical mechanics in order to develop ceramic-metal braze joints for high performance applications such as heat engines.

The materials system refers to the ceramic and structural alloy parent materials, the braze, interlayer or compliant layers, and coatings. The generalized materials system chosen for this program is shown in Figure 3.1. A complete optimization of the materials system would require a systematic evaluation of each of the bulk materials and interfaces in the joint.

Figure 3.1. Generalized materials system.

The program required development of joints between Si_3N_4 and a structural alloy and SiC and a structural alloy for 650 and 950°C applications. The PY6 Si_3N_4 and Hexaloy SA SiC materials chosen for evaluation in this

program were representative of structural ceramics suitable for use in the high-temperature, oxidizing environment associated with heat engines. Both PY6 Si_3N_4 and Hexaloy SA SiC are commercially available materials.

SNW1000 and AY6 Si_3N_4 were used as model materials, while PY6 Si_3N_4 was the final choice because of its excellent high-temperature strength and its compatibility with the coating material selected. Hexaloy SA SiC was chosen as the SiC material. The low-expansion superalloy was an Fe-Ni-Co alloy, Incoloy 909. The Ni-based superalloy was Inconel 718. GTE's Nicro (Au-18Ni) braze was used as a model braze throughout the program because of its ductility and oxidation resistance. An experimental braze alloy, Au-5Pd-2Ni, and a commercial braze alloy, 30Au-34Pd-36Ni (Palmiro 4), were selected due to their oxidation resistance, ductility, and relatively high melting points. The following section discusses the properties of each component of the joint in more detail.

A general methodology was applied to make the materials screening effort systematic and comprehensive. For example, in selecting coating materials, the necessity of chemical reactions at the interface led to examination of published Gibbs free energy data. After evaluation of thermodynamic data, the reaction kinetics were studied. This involved heating powder mixtures of the ceramic and coating material followed by x-ray diffraction. The wetting behavior of a joint system was studied by sessile drop tests. Additional constraints included the necessity of minimizing the damage from chemical reactions at the ceramic-coating interface. A new set of procedures were developed to quantify the potentially damaging effect of interfacial reactions. Using a combination of thermodynamics, reaction kinetics, and finite element analysis (FEA), it was possible to efficiently screen materials and to optimize the joint system.

3.1 INTRINSIC PROPERTIES OF JOINING MATERIALS

Structural Alloys

For the 650°C application Incoloy 909 was selected because of its low coefficient of thermal expansion (CTE) as well as its high-temperature properties. Room-temperature tensile properties of Incoloy 909, after a 1000 hour exposure at 650°C, were essentially unaffected compared to unexposed material. The low-cycle fatigue strength, fracture toughness, and creep crack growth rate at 540°C were better than those of other Incoloy series alloys. Furthermore, rupture strength of age-hardened Incoloy 909 after 3500 hours at 650°C, a typical engine life, is over 20 ksi. For the 950°C application, Inconel 718 was chosen solely for its high-temperature capabilities. Rupture strength of Inconel 718 after 3500 hours at 650°C exceeds 40 ksi. Tables 3.1 and 3.2 show the compositions and mechanical properties of these two structural alloys. Figure 3.2 shows the CTE of Incoloy 909 and Inconel 718 as a function of temperature.

Table 3.1. Compositions of the structural alloys used in this study.

Alloy	Composition (Wt %)							
	Fe	Ni	Cr	Co	Nb	Ti	Mo	Al
Incoloy 909	42.17	38.2	---	13.0	4.7	1.5	---	0.03
Inconel 718	16	50-55*	17-21	---	4.75-5.5*	0.65-1.15	2.8-3.3	0.2-0.8

* Inconel 718 has 50-55 Ni+Co and 4.75-5.5 Nb+Ta.

Note: Incoloy 909 is available from Huntington Alloys, Huntington, WV, and Inconel 718 is available from Carpenter Technology, Reading, PA.

Table 3.2. Properties of the structural alloys used in this study.

Property		Incoloy 909	Inconel 718
Youngs Modulus	25°C	23.0 x 10 ⁶ psi	29.0
	650°C	22.6	23.7
	950°C	18.4	18.1
	1100°C	15.2	14.3
Tensile strength (0.2% Yield strength)	25°C	185 (150) ksi	195 (164)
	540°C	168 (125)	171 (142)
	650°C	150 (125)	145 (125)
Poisson's Ratio	25°C	0.337	0.294
	650°C	0.352	0.283
	950°C	0.354	0.337
	1100°C	0.401	0.402
Smooth bar rupture strength in air at 650°C			
	100 hr	75 ksi	107
	1000 hr	50	87
	3500 hr	35	-----
Weight gain after 500 hr in air at 650°C		6 mg/cm ²	0.4
Stress to produce 0.2% plastic creep after 100 hrs			
	650°C	--- ksi	90
	760°C	---	14

Figure 3.2. Coefficient of thermal expansion (CTE) of Incoloy 909 and Inconel 718 as a function of temperature.

Structural Ceramics

GTE's PY6 Si₃N₄ and Sohio's Hexaloy SA SiC were selected as the structural ceramic materials. PY6 Si₃N₄ was selected over both SNW1000 and AY6 Si₃N₄ due to its superior high-temperature strength and its compatibility with the coating material. The CTE of PY6 is $3.4 - 4.0 \times 10^{-6}/^{\circ}\text{C}$ in the temperature range of 25 - 1000°C, while that of SiC is $4.0 \times 10^{-6}/^{\circ}\text{C}$ in the temperature range of 25 - 750°C. PY6 retains excellent high-temperature strength up to 1300°C; the strength in 4-point bending was over 60 ksi at 1300°C. Table 3.3 shows the compositions of Hexaloy SA SiC and the various Si₃N₄ materials, and Table 3.4 lists properties of PY6 Si₃N₄ and Hexaloy SA SiC. The SNW1000 Si₃N₄, AY6 Si₃N₄, and PY6 Si₃N₄ will be referred to as SNW1000, AY6, and PY6 throughout the remainder of the report. In general, PY6 Si₃N₄ has a lower CTE, a better fracture toughness, and a higher strength than Hexaloy SA SiC.

Table 3.3. Compositions of the different ceramics used in this study.

Material	Composition (Wt %)			
	Y ₂ O ₃	Al ₂ O ₃	Other	Balance
Hexaloy SA SiC	---	---	0.5 B	SiC
SNW1000 Si ₃ N ₄	13	2	---	Si ₃ N ₄
AY6 Si ₃ N ₄	6	2	---	Si ₃ N ₄
PY6 Si ₃ N ₄	6	---	---	Si ₃ N ₄

Table 3.4. Properties of Hexaloy SA SiC and PY6 Si₃N₄.

Property	PY6 Si ₃ N ₄	Hexaloy SA SiC
Young's Modulus		
25°C	43 x 10 ⁶ psi	59
Strength in 4-point bending		
25°C	102 ksi	118
1000°C	---	87
1200°C	97	59
Poisson's Ratio		
25°C	---	0.14
Coefficient of thermal expansion		
25 - 700°C	3.5 x 10 ⁻⁶ /°C	4.0
Indentation Fracture toughness		
25°C	4.5 MPa√m	2.2

Braze Alloys

The properties of the final braze alloys, Au-5Pd-2Ni and 30Au-34Pd-36Ni (Palniro 4), are summarized in Table 3.5. The major difference between these two braze alloys is that the Au-5Pd-2Ni braze alloy has a much lower yield strength than does the 30Au-34Pd-36Ni braze alloy. Both alloys have melting points higher than 1100°C and adequate ductility, both of which are needed for the 650°C application.

Table 3.5. Room-temperature properties of the braze alloys.

Property	Au-5Pd-2Ni	30Au-34Pd-36Ni (Palniro 4)
Liquidus Temperature	1131°C	1169
Solidus Temperature	1100°C	1135
Young's Modulus	4.1 x 10 ⁶ psi	4.7
Tensile strength of fully annealed material (0.2% Yield strength)	27.3 (16.8) ksi	120 (90.8)
% elongation (in 2" gauge length)	28 %	> 17%
Coefficient of thermal expansion	15.5	14.2
Strain hardening coefficient	---	0.249

3.2 COATING MATERIALS DEVELOPMENT

For most brazing systems, a reactive coating on the ceramic or a reactive component to the braze is needed to provide a driving force for wetting. The thermodynamics of reactions between active metals and ceramics are important in predicting the behavior of ceramic-metal interactions.

The wetting of a ceramic by a metal depends on the chemical compatibility between the two. The concept of chemical compatibility includes the nature of the wetting atmosphere, chemical bonds, chemical reactions, surface energy of the ceramic, and surface tension of the metal⁸⁻¹⁰.

For weakly reacting systems, such as Pt on Al₂O₃, the wetting angle, θ , can be described by the familiar Young equation¹⁰:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta, \quad \text{Eq. 3.1}$$

where γ_{SV} , γ_{SL} , and γ_{LV} are the solid-vapor, solid-liquid, and liquid-vapor interfacial energies, respectively, and θ is the wetting angle. Wetting is said to occur for θ less than 90°. The work of adhesion, W , is the free energy change associated with the separation of a unit area of interface and is described by the Dupre equation:

$$W = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad \text{Eq. 3.2}$$

Combining equations 3.1 and 3.2,

$$W = \gamma_{LV} (1 + \cos \theta). \quad \text{Eq. 3.3}$$

In reactive systems, where chemical reactions occur at the ceramic-metal interface, the free energy associated with the reaction can be much larger than the energies of the surfaces involved¹¹. In systems of this type, such as Ti on Al_2O_3 , the surface energies are insignificant, and the wetting reaction is driven by the free energy change associated with the reaction at the ceramic-metal interface. For a system of pure liquid B wetting pure solid A, forming phase C (A_xB_y), the equilibrium wetting angle, θ_c , is always smaller than it would have been if a reaction had not taken place at the interface.

The driving force for wetting, dE/dr , is given by the sum of the contribution due to reactions between the substrate and liquid, σ , and the contribution due to surface energies, $\Gamma(\theta)$:

$$\frac{1}{2\pi r} \frac{dE}{dr} = \sigma + \Gamma(\theta). \quad \text{Eq. 3.4}$$

$$\Gamma(\theta) = \gamma_B (\cos \theta - \cos \theta_c) \quad \text{and} \quad \cos \theta_c = \frac{\gamma_A - \gamma_{AC} - \gamma_{BC}}{\gamma_B}. \quad \text{Eq. 3.5}$$

$$\sigma = \frac{\rho_A t_A}{x M_A} \Delta G_f, \quad \text{Eq. 3.6}$$

where E is the internal energy of the system, ΔG_f is the Gibbs free energy of formation of the compound A_xB_y , ρ_A is the density of A, t_A is the thickness of compound A that reacts to form compound A_xB_y , x is the number of A atoms in compound A_xB_y , and M_A is the atomic mass of A. By comparing the values of σ and $\Gamma(\theta)$, the relative importance of the interfacial reaction and the surface energies to the wetting process can be evaluated.

As an example, σ and $\Gamma(\theta)$ can be calculated for a Au-Ni braze wetting a Ti coated Si_3N_4 substrate. Assume that the reaction proceeds by the Au-Ni braze dissolving the Ti coating, and that the Ti and Si_3N_4 react to form TiN. To calculate σ , we use $\rho_{\text{Ti}} = 4.5 \text{ gm/cm}^3$, $t_{\text{Ti}} = 0.05 \text{ }\mu\text{m}$, $M_{\text{Ti}} = 49 \text{ gm/mole}$, $x = 4$, and $\Delta G_f = -80 \text{ kcal/mole TiN}$. From Equation 3.6, $\sigma = -90,000 \text{ erg/cm}^2$, and because the cosine term in Equation 3.5 cannot be larger than 1, we approximate $\Gamma(\theta) = \gamma_B \approx 660 \text{ erg/cm}^2$ ¹². These numbers indicate that the free energy of the reaction at the interface provides a very large driving force for wetting.

Some of the most promising coating materials were selected and their wetting behavior was studied. These will be described in the following section.

These materials were also investigated to verify the effects of the coatings on the mechanical properties of the ceramic substrate and on the joint strength of brazed coupons using a model system such as Mo-(Au-18Ni)-SNW1000.

Screening of Candidate Coating Materials

A series of tests were conducted to determine the optimal coating for use in ceramic-metal brazing. Candidate coating materials were selected on the basis of published thermodynamic data¹³. Nitrides and silicides were the expected reaction products. Given favorable thermodynamics, the reaction kinetics were evaluated with powder mixtures and x-ray diffraction.

An accelerated test was used to examine reaction kinetics to determine the most effective coatings to promote wetting and adhesion between the braze and the Si₃N₄. In this procedure, candidate coating materials were mixed with pure, commercially available Si₃N₄ powder in a ratio of 1:1 by volume. The mixtures were compacted in a die with a diameter of 9.5 mm to produce 3.2 mm thick discs and heat-treated at 1200°C and 1500°C for 24 hours in vacuum (10⁻⁴-10⁻⁵ torr). This extended exposure of the samples to high-temperature accelerated the reaction between Si₃N₄ powder and candidate coating materials. Heat-treated samples were ground into powder and analyzed by x-ray diffraction to identify the reaction products.

Table 3.6 shows the standard free energy changes for the probable reactions between Si₃N₄ and the candidate coating materials. Coating compounds such as B₄C, Al₄C₃, and B₂O₃ did not react to an appreciable extent with Si₃N₄ in spite of favorable driving forces. Reactive elements such as Ti, Zr, Hf, and Ta resulted in substantial quantities of TiN, ZrN, HfN, and TaN, respectively, at 1500°C. Al reacted with Si₃N₄ to form AlN^{14,15}. Oxide and silicide formation were observed with V and Nb. In the case of Ti, which is the most common choice as a coating material, the driving force favors the formation of various silicides as shown below:

$\Delta G_{\text{xn}}^{\circ}$ is the free energy of reaction in the standard state at 1200°C. However, since TiN formation is preferred when Ti and Si₃N₄ come to contact, there is a relatively insignificant amount of silicide formation after reactions at 1200 - 1500°C for 24 hours. Similar reactions seemed to occur with Zr, Hf, and Ta in the formation of nitrides and silicides. It was apparent that V and Nb favor silicide formation at 1500°C. From this preliminary screening procedure, Ti, Zr, Hf, Al, and Ta were chosen as coating materials for Si₃N₄-based ceramic substrates.

Table 3.6. Free-energy change for various reactions and X-ray diffraction results obtained from heat-treated powder mixtures.

Reaction expected	at 1200°C		at 1500°C	
	$\Delta G^\circ_{1200^\circ\text{C}}$ (kcal/mole)	Phases	$\Delta G^\circ_{1500^\circ\text{C}}$ (kcal/mole)	Phases
$\text{Si}_3\text{N}_4 + 4\text{B} \rightarrow 3\text{Si} + 4\text{BN}$	-56.0		-56.8	
$\text{Si}_3\text{N}_4 + 2\text{B}_2\text{O}_3 \rightarrow 3\text{SiO}_2 + 4\text{BN}$	-94.3	$\alpha\text{-Si}_3\text{N}_4$	-89.6	
$\text{Si}_3\text{N}_4 + \text{B}_4\text{C} \rightarrow \text{SiC} + 2\text{Si} + 4\text{BN}$	-62.8	$\alpha\text{-Si}_3\text{N}_4, \text{B}_4\text{C}$	-63.0	$\text{Si}, \alpha\text{-Si}_3\text{N}_4(\text{minor})$
$\text{Si}_3\text{N}_4 + 4\text{Al} \rightarrow 3\text{Si} + 4\text{AlN}$	-91.5	$\text{Si}, \text{AlN}(\text{minor})$	-84.3	$\text{Al}_2\text{SiO}_5, \text{AlN}(\text{minor})$
$\text{Si}_3\text{N}_4 + \text{Al}_4\text{C}_3 \rightarrow 3\text{SiC} + 4\text{AlN}$	-118.6	$\alpha\text{-Si}_3\text{N}_4, \text{Al}_4\text{C}_3$	-114.2	$\text{SiC}, ?$
$\text{Si}_3\text{N}_4 + 4\text{Ti} \rightarrow 3\text{Si} + 4\text{TiN}$	-131.3	$\alpha\text{-Si}_3\text{N}_4, \text{TiN}, \text{TiO}_2, \text{Si}_2\text{ON}_2$	-130.6	$\text{TiN}(\text{single phase})$
$\text{Si}_3\text{N}_4 + 4\text{Zr} \rightarrow 3\text{Si} + 4\text{ZrN}$	-158.9	Si, ZrO_2	-158.3	$\text{ZrN}(\text{major})$
$\text{Si}_3\text{N}_4 + 4\text{Hf} \rightarrow 3\text{Si} + 4\text{HfN}$	-151.1	$\alpha\text{-Si}_3\text{N}_4, \text{HfN}, \text{HfO}_2, \text{Hf}$	-150.9	$\text{HfN}(\text{major}), \text{HfO}_2$
$\text{Si}_3\text{N}_4 + 4\text{V} \rightarrow 3\text{Si} + 4\text{VN}$	-31.7	?	-35.1	Si_3V_5
$\text{Si}_3\text{N}_4 + 8\text{Nb} \rightarrow 3\text{Si} + 4\text{Nb}_2\text{N}$	-36.6	$\text{Nb}_2\text{O}_5, \text{Nb}_2\text{N}(\text{minor})$	-34.6	$\text{NbSi}_2, \text{Nb}_5\text{Si}_3, \text{Nb}$
$\text{Si}_3\text{N}_4 + 4\text{Ta} \rightarrow 3\text{Si} + 4\text{Ta}_5\text{N}$	-67.0	$\alpha\text{-Si}_3\text{N}_4, \text{Ta}_5\text{Si}_3$	-73.8	$\text{Ta}_5\text{Si}_3, \text{TaSi}_2, \text{Ta}_5\text{N}$

The same approach was used in selecting possible coatings for brazing SiC as was used for Si₃N₄. Possible chemical reactions were examined from a thermodynamic standpoint using the JANAF data. Reactions of the type listed below, in Table 3.7, were considered.

Table 3.7. Reactions considered in selection of coating materials for SiC.

Si + C → SiC	ΔG_f° at 1500K = - 17.943 kcal/mol
SiC + Ta → Si + TaC	ΔG_{Txn}° at 1500K = - 33.561 kcal/mol
SiC + Ti → Si + TiC	ΔG_{Txn}° at 1500K = - 40.185 kcal/mol
SiC + Zr → Si + ZrC	ΔG_{Txn}° at 1500K = - 43.453 kcal/mol
SiC + Hf → Si + HfC	ΔG_{Txn}° at 1500K = - 49.155 kcal/mol

Since TaC, TiC, ZrC, and HfC have a lower free energy of formation than SiC, these reactions are favored. In general, SiC is unstable at high temperatures compared with Si₃N₄.

Cross-section samples were prepared for transmission electron microscopy from a SNW1000-Ti-(Au-18Ni) brazed joint and from a SiC-Ti-(Au-18Ni) brazed joint. Figure 3.3 shows the cross-section of the SNW1000-Ti-(Au-18Ni) brazed joint. The reaction layer was identified as TiN. The interface between the braze and the ceramic is shown in Figure 3.4 for the SiC-Ti-(Au-18Ni) brazed joint. The reaction layer was identified by electron diffraction and electron energy loss spectroscopy as TiC. In both of these samples, no titanium silicides were seen in the interface region. The silicon liberated from the formation of TiN and TiC probably dissolved into the molten braze.

Figure 3.3. TEM image of the interface in a brazed joint between Au-18Ni braze and Ti coated Si₃N₄.

Figure 3.4. TEM image of the interface in a brazed joint between Au-18Ni braze and Ti coated SiC.

Wetting Behavior

Coatings applied to ceramic surfaces must promote wetting of the ceramic by the braze in order to be useful. Wetting behavior was studied using the sessile drop method with a video camera recording the drop shape for contact angle measurements. The substrate surface was polished to a finish of $0.1\text{ }\mu\text{m}$ ($3\text{ }\mu\text{in}$) and coatings were applied using an electron beam evaporator at 300°C in a 10^{-5} - 10^{-6} torr vacuum. Two grams of braze alloy were melted on the coated substrates. Contact angles between substrates and liquid braze were measured as a function of temperature and time. Coatings investigated included Ti, Zr, Hf, Ta, and Al. Substrate materials were SNW1000 and Hexaloy SA SiC.

The results of the wetting tests on SNW1000 are given in Figure 3.5. Ti, Zr, and Hf performed comparably, reaching a contact angle of about 0° in approximately 250 seconds. Ta exhibited a wetting angle of 20° at the end of the test. Liquid Au-18Ni did not wet the Al coated surface of SNW1000, $\theta > 150^\circ$ at 1000°C , indicating that the Al coatings did not interact chemically with the Si_3N_4 at the testing temperature. Therefore, Al was ruled out as a coating material.

Figure 3.5. Wetting of Au-18Ni braze on Ti, Zr, Hf, and Ta coated SNW1000.

Ti coatings on Hexaloy SA SiC reached a 0° contact angle in 60 seconds, Figure 3.6. The other coatings showed contact angles of about 15° with Au-18Ni. In terms of wetting behavior, the coatings were roughly comparable. Therefore, choices between these must be based on other considerations, such as mechanical properties and chemical interactions at the interface.

Figure 3.6. Wetting of Au-18Ni braze on Ti, Zr, Hf, and Ta coated SiC.

Effect of Coatings on the Mechanical Properties of the Ceramic

Reactive coatings were applied to ceramics to provide adequate adhesion and wetting between the braze and the ceramic. It is desirable to have coating materials which can perform without degrading the properties of the ceramic substrates. It is common to find that massive reaction products cause deterioration of the mechanical properties of parent materials due to the change in properties and volume, and the strain and thermal mismatch. In the current study, a methodology was developed to evaluate the effect of coatings on the mechanical strength of the substrate.

The effect of Ti, Zr, Hf, and Ta coatings on the mechanical properties of ceramic materials was investigated using modulus of rupture (MOR) tests. As shown in Figure 3.7, MOR bars were machined from various Si_3N_4 ceramics and then coated and vacuum heat-treated to examine the effect of reactive coatings on the mechanical properties of the ceramic substrate. Effort was made to minimize the effect of lot-to-lot variations in mechanical properties on the interpretation of test results. The same number of MOR bars were prepared from each ceramic blank for each coating. One side of the MOR bars' (25.4 mm x 2.54 mm x 1.3 mm) surface was polished to 0.1 μm and coated with one of the reactive coating materials. Coatings were electron beam deposited at 300°C in a 10^{-5} - 10^{-6} torr vacuum. A thickness of 3 μm was used, except for Hf, which had a 6 μm coating. Coated MOR bars were exposed to 940°C for 10 minutes and loaded at room-temperature in 4-point bending. An Instron Model 1320 and strain rate of 0.0085 mm/s (0.02 in/min) were used for the tests. Scanning electron microscopy (SEM) was used to understand the role of the coating layer and interface reactions.

Figure 3.7. Procedure to evaluate the effect of coating on the mechanical properties of ceramic materials.

Si₃N₄ System. Figure 3.8 shows a Weibull plot of SNW1000 MOR bars with various coatings. The interactions between the reactive coatings and the ceramic substrate caused a reduction in strength of 5% - 20% compared with as-polished bars. In contrast, the MOR strengths of the coated bars without heat-treatment were essentially unchanged. Furthermore, the Weibull slope of as-polished bars was steeper than that of heat-treated, coated bars. The difference in Weibull slope was attributed to the relatively short reaction time between the coatings and the ceramic substrate. The short reaction time resulted in nonuniformity in the reaction at the ceramic-metal interface. The MOR strength of as-polished bars was equivalent to that of uncoated, vacuum heat-treated bars.

Figure 3.8. Effects of Ti, Zr, Hf, and Ta coatings on the MOR strength of SNW1000.

The formation of various oxides, such as TiO_2 , ZrO_2 , HfO_2 , and TaO_2 , was expected due to the vacuum level used for the heat-treatments in the experiments discussed above. From Auger analysis, oxygen contamination during the coating process was found to be insignificant. In order to separate the effect of oxide formation from the effect of substrate-coating reactions, similar experiments were carried out in which reactive coatings were immediately followed by Ni coating in vacuum. Figure 3.9 showed that the combined (Ti,Ni) coating reduced the MOR strength as much as the Ti coating did. This indicates that the reduction in MOR strength was directly related to ceramic-reactive coating reactions. It was also found that the MOR strength decreases with an increase of coating thickness.

Figure 3.9. Effects of Ti-Ni coating on the MOR strength of SNW1000.

A study was done with a nonreactive coating, Ni, to determine whether the coating process itself was responsible for the reduction of the mechanical properties of Si_3N_4 . The MOR bars, coated with $3.0\text{ }\mu\text{m}$ Ni, were exposed to a brazing thermal cycle, 940°C or higher for 10 minutes, and tested by 4-point bending. In contrast to the reactive coatings, the Ni coating had no effect on the MOR strength after the heat treatment, Figure 3.10. In the as-coated, no heat-treatment condition it was found that the MOR strength values were at least equivalent to those obtained from as-polished bars for all coatings. An additional nonreactive Ni layer on the ceramic bar always increased the strength of the bar, probably by reducing the number of potential areas of crack initiation sites.

Figure 3.10. Effects of Ni coating on the MOR strength of SNW1000.

SEM micrographs of Ni and Ti coating are shown in Figure 3.11. Both MOR bars were exposed to a brazing cycle after coating and were tested by 4-point bending. The fractured pieces were placed together with the coated sides adjacent for metallography. The Ni coating remained intact on the Si_3N_4 during the test without secondary cracks in the layer near the fracture area, Figure 3.11a. This may indicate that the Ni layer did not facilitate crack initiation. A similar result was found for Ti, Figure 3.11b. The apparent lack of cracks in the coatings reinforced the conclusion that TiO_2 or other environmental products did not cause degradation of the mechanical properties.

Figure 3.11. SEM micrographs of (a) Ni coated and (b) Ti coated MOR bars, after heat-treatment.

Zr and Hf coatings caused the least damage to the ceramic MOR strength, while Ti coating caused the most. The slopes of Weibull plots also indicate that the Ti coating caused the most variability in properties. This implies that the reaction between Ti and the ceramic is more aggressive and time dependent than other coating materials.

MOR tests were used to evaluate the effect of coatings on the mechanical properties of AY6 and PY6. Bars were coated with various materials in vacuum and exposed to 980°C for 10 minutes. Figure 3.12 shows the Weibull plots for AY6. Ti coatings caused a dramatic 50% reduction in MOR, similar to that seen for Ti coatings on SNW1000. The influence of Zr or Hf coatings on the MOR strength was minimal. Ta coatings decreased the MOR strength by 20 - 50 ksi. The impact of various coatings including Ti on the MOR strength of PY6 was almost insignificant, Figure 3.13.

Figure 3.12. Effects of Ti, Zr, Hf, and Ta coatings on the MOR strength of AY6.

Figure 3.13. Effects of Ti coatings on the MOR strength of PY6.

Separate experiments indicate that Ti coatings reduced the MOR strength of Si_3N_4 by reacting with the grain boundary glass phase in the Si_3N_4 materials. SNW1000 and AY6 were affected strongly by Ti coatings. These both contain 2 wt% Al_2O_3 , Table 3.3, which causes the grain boundary phase to be more glassy. The theory that the glassiness of the grain boundary affects the degree of degradation of the MOR strength of Si_3N_4 is also supported by similar experiments with $\text{Si}_3\text{N}_4\text{-TiC}$. $\text{Si}_3\text{N}_4\text{-TiC}$ also showed a small decrease in strength after Ti coating. $\text{Si}_3\text{N}_4\text{-TiC}$ has about 1.2 wt% Al_2O_3 along with 39 wt% TiC, which can minimize the impact on strength from Ti coating.

SiC System. A series of coated SiC MOR bars were prepared to evaluate the effect of various coatings on the mechanical properties of SiC. Groups of 15 samples were either coated with 3 μm of Ti, Zr, Hf, or Ta or were uncoated. They were then subjected to a thermal cycle at 980°C for 10 minutes. MOR testing was done in the same manner as with Si_3N_4 , i.e., the coated side was placed in tension to measure any change in strength caused by the interfacial reactions. The results are shown in Figure 3.14. The uncoated specimens serve as baseline values. Ta coatings resulted in a small but noticeable improvement in MOR strength. Ti and Zr each had small negative effects on the MOR strength. Hf had an extremely damaging impact on the MOR strength of the SiC samples.

Figure 3.14. Effects of Ti, Zr, Hf, and Ta coatings on the MOR strength of Hexaloy SA SiC.

Zr and Hf coatings were suitable for SNW1000, and Ta was the preferred coating material for Hexaloy SA SiC, with Ti and Zr as second and third choices, respectively. Ti was considered to be unacceptable for SNW1000 and AY6, whereas the impact of Ti coating was minimal for PY6. Hf was detrimental for Hexaloy SA SiC.

Mechanical Strength and Microstructure

The behavior of material systems was characterized by shear testing of rectangular brazed coupon specimens as shown in Figure 3.15. The effects of coatings, and other joint components such as the ceramic, braze, and structural alloy, on the joint strength of two dissimilar materials produced by brazing was studied as a system.

Figure 3.15. Schematic of the shear test samples.

Various ceramic-metal joints were prepared and tested to evaluate the joint strengths. All substrate materials were polished to a 0.1 μm finish, and the polished surfaces of the ceramic substrate were coated with one of the coating materials to promote the wetting of the braze alloy. Joints were brazed with Au-18Ni at 980°C for 10 minutes and shear tested with an Instron 1320 in compression mode. The same joint area, i.e., 1.0 cm^2 (0.15 in^2), was used in all tests for comparison. Failure loads were recorded at the point of the first load drop to avoid inflated strength values due to scraping during shear tests. Most of the strength values are an average of two or three tests.

Si₃N₄ System. Three different joint systems were prepared: Incoloy 909-SNW1000, Mo-SNW1000, and SNW1000-SNW1000 using Au-18Ni braze alloy with various coating materials. Table 3.8 shows the shear test results for the joint systems. Zr and Hf were the preferred coating materials over Ti. The joints of Mo to Si₃N₄ were significantly stronger than those of Incoloy 909 to Si₃N₄. The low CTE of Mo ($\sim 6 \times 10^{-6}/^\circ\text{C}$ in the range of 20 - 925°C) resulted in higher joint strengths compared to Incoloy 909, with a CTE of $\sim 9 \times 10^{-6}/^\circ\text{C}$ in the range of 20 - 627°C. The residual stress due to the difference in the CTE between SNW1000 and Incoloy 909 was sometimes large enough to crack the ceramic surface after a brazing cycle.

Table 3.8. Si₃N₄ shear coupon test data.

Materials system	Average shear strength (ksi)
Incoloy 909-(Au-18Ni)-Ti-SNW1000	0.7
Incoloy 909-(Au-18Ni)-Zr-SNW1000	3.0
Incoloy 909-(Au-18Ni)-Hf-SNW1000	3.8
Mo-(Au-18Ni)-Ti-SNW1000	7.1
Mo-(Au-18Ni)-Zr-SNW1000	11.5
Mo-(Au-18Ni)-Hf-SNW1000	7.7
SNW1000-Ti-(Au-18Ni)-SNW1000	42.3
SNW1000-Zr-(Au-18Ni)-SNW1000	45.1
SNW1000-Ta-(Au-18Ni)-SNW1000	27.5

The effect of coatings on the shear strength appeared to be minimized when a joint had a low residual stress at the braze interface. The results from the SNW1000-SNW1000 joints which had almost zero residual stress at the interface support this observation. The difference in the shear strength between SNW1000-SNW1000 and other systems was attributed to differential

expansion, implying that Incoloy 909-SNW1000 and Mo-SNW1000 joints had large residual stresses, approximately 30 - 40 ksi.

The fracture modes of these three systems were distinct from each other. All samples of the Incoloy 909-SNW1000 joints were found to be either cracked in the ceramic portion after brazing or had significant unbonded areas, and no strength. In the Mo-SNW1000 joints, a mixed fracture mode was seen where the crack path was associated with both the ceramic and the Mo. In this system, cracks which initiated in the ceramic propagated into the Mo substrate. In both systems, Incoloy 909-SNW1000 or Mo-SNW1000, cracking was initiated at a point in the ceramic substrate where the maximum tensile stress was predicted by finite element analysis¹⁶. The SNW1000-SNW1000 joints did not show any pattern in the crack path, implying that there were no highly stressed regions in the system for preferred crack propagation.

SiC System. Table 3.9 shows the shear test results of three joint systems: Incoloy 909-SiC, Mo-SiC, and SiC-SiC. These tests provide a considerable amount of information concerning the effect of differential contraction on residual stress, SiC cracking, interlayer effectiveness, and shear properties.

Table 3.9. SiC shear coupon test results.

Materials system	Average shear strength (ksi)
Incoloy 909-(Au-18Ni)-Ti-SiC	0
Incoloy 909-(Au-18Ni)-Zr-SiC	0
Incoloy 909-(Au-18Ni)-Hf-SiC	0
Incoloy 909-(Au-18Ni)-Ta-SiC	0
Mo-(Au-18Ni)-Ti-SiC	2.9
Mo-(Au-18Ni)-Zr-SiC	3.5
Mo-(Au-18Ni)-Hf-SiC	1.6
Mo-(Au-18Ni)-Ta-SiC	2.4
SiC-Hf-(Au-18Ni)-Hf-SiC	13.9

The Incoloy 909-SiC samples all failed on cooling to room-temperature. They were unable to withstand the relatively large differential contraction between Incoloy 909 and SiC. The lower expansion of Mo made it possible to make braze couples for shear tests with reasonable strengths.

The work on SiC joining included two pairs of SiC-SiC joints. Each piece of SiC was coated with 3 μ m of Hf, brazed with Au-18Ni, and shear tested. The mean shear stress of these samples was 13.9 ksi. This was significantly higher than was obtained with SiC-metal joints in the variety of configurations discussed above. The low values reported for SiC-metal joints raised the

concern that perhaps chemical degradation, rather than residual stress from differential expansion, was responsible. The coating used for the SiC-SiC joints, Hf, had resulted in the largest reduction in properties in the coated MOR tests. However, the fact that even the most chemically damaging coating yielded high shear strength values in the absence of differential expansion demonstrated that chemical attack was not the primary factor responsible for the low strength of SiC-metal pairs. All of the tested SiC samples had a common feature: i. e., they all failed entirely in the ceramic. This is significant in terms of interpretation of results, since it makes it possible to rule out the effect of unbonded areas in the brazed joint.

The coating material effected the mechanical strength of the Mo-SiC joints, as seen with the MOR strength tests of the coated SiC MOR bars. Ti and Zr were the best coatings for Mo-SiC joints.

Effects of Brazing Processes

A series of tests were performed to determine whether Mo diffusion into the liquid braze, with the resultant effect on liquidus temperature, would limit the acceptable window of processing variables. Figure 3.16 shows the extent of Mo diffusion in the SNW1000-Zr-(Au-18Ni)-Mo system. Significant diffusion of Mo is noted in the braze layer after 980°C for 10 min. Based on this observation, two extreme processing conditions were selected: 1) brazing at 960°C for 3 minutes and 2) brazing at 1100°C for 30 minutes in order to determine the effect of the diffusion on bonding performance.

Figure 3.16. Microprobe result showing the extent of Mo diffusion in the SNW1000-Zr-(Au-18Ni)-Mo-Incoloy 909 system.

Fast diffusion of Mo is evident for both sets of brazing conditions. Brazing at 960°C for 3 minutes resulted in a braze layer of 40 - 45 μm in thickness which had moderate alloying with Mo, 20 μm thick. Brazing at 1100°C for 30 minutes extended the Mo diffusion further and caused severe alloying with braze alloy, 30 μm in thickness. The diffusion and the reaction between braze alloy and Mo in the presence of a liquid phase were extensive in both cases, even at 960°C for 3 minutes. However, acceptable brazes were obtained over the wide range of processing variables. A faceted phase in the braze layer after brazing at 1100°C for 30 minutes, was probably due to the interaction between Zr and Mo-(Au-18Ni) phase.

Table 3.10 shows the results of shear strength testing. As shown in this table, there is no noticeable difference in strength among three different processing conditions. Also, excellent bonding was obtained in all three cases. It was concluded from this investigation that brazing conditions such as temperature and holding time have little effect on bonding performance.

Table 3.10. The effect of processing parameters on bond strength of Mo-SNW1000 joints.

Brazing Conditions	Shear Strength (ksi)	Bonding Results
960°C for 3 min.	5.4	excellent
960°C for 3 min.	21.5	excellent
960°C for 3 min.	9.4	excellent
960°C for 3 min.	11.9	excellent
Average	12.1	
1100°C for 30 min.	18.9	excellent
1100°C for 30 min.	5.7	excellent
1100°C for 30 min.	12.7	excellent
1100°C for 30 min.	10.8	excellent
Average	12.0	
980°C for 10 min.	11.3	excellent
980°C for 10 min.	18.9	excellent
980°C for 10 min.	4.2	excellent
Average	11.5	

Two additional brazed joints were used to study the reactions between the braze and Si_3N_4 and the braze and Mo. Backscattered electron images along with Si, Au, Ni, Mo, Ti, and Zr elemental x-ray maps were taken from the Ti coated Si_3N_4 -Mo and Zr coated Si_3N_4 -Mo joints which were brazed with Au-Ni alloy at 980°C for 10 minutes, Figure 3.17 and Figure 3.18, respectively. The Si x-ray maps showed that Si was only present in the Si_3N_4 , and are not shown.

In both joints, the molten braze aggressively attacked the Mo. This reaction was essentially between the Mo and the Ni in the braze alloy. The braze alloy was enriched in Au as columnar grains of a Mo-rich Mo-Ni phase formed at the braze-Mo interface and grew into the molten braze. This phase was surrounded by a Au-rich phase. After the Mo-rich Mo-Ni layer grew to 10-20 μm thick, an additional Mo-Ni phase formed.

In the Zr coated Si_3N_4 -Mo joint, a Ni-Zr phase was present in the Au-rich region of the braze. In the Ti coated Si_3N_4 -Mo joint, the phase that formed in the braze was a Ni-rich Ni-Mo phase.

The Zr and Ti were concentrated at the Si_3N_4 /braze interface and did not dissolve into the braze to any appreciable extent. The Au was uniformly distributed throughout what was the molten phase at the brazing temperature. In both joints, the Au was also concentrated at the Mo/braze interface. The Au formed a semicontinuous layer between the Mo and the Mo-rich, Mo-Ni crystals.

Figure 3.17. Backscattered electron image (BSE) and x-ray maps of a brazed joint between Ti coated SNW1000 and Mo. Sample was vacuum brazed with the Au-18Ni alloy for 10 minutes at 980°C.

Figure 3.18. Backscattered electron image (BSE) and x-ray maps of a brazed joint between Zr coated SNW1000 and Mo. Sample was vacuum brazed with the Au-18Ni alloy for 10 minutes at 980°C.

3.3 INTERLAYER MATERIALS DEVELOPMENT

There are two approaches to minimize the effects of thermal stresses. The first is by selecting the metal, ceramic, and braze system to minimize the CTE differences¹⁷⁻²². However, in most cases, this is not practical; the particular ceramic and metal components of the joint are selected based on other properties and requirements such as strength, chemical inertness, or application temperature. The second, and most common, way to handle the thermal stresses is to use an interlayer to minimize them.

Suganuma et al.¹⁷ studied the effects of Mo and Nb interlayers on the residual stress and bond strength of Al_2O_3 -steel joints and found that low CTE metals reduced the residual stresses in the joint by a factor of 2. Analytical mechanics studies in this program also showed the effectiveness of interlayers in accommodating residual stress resulting from differential expansion, Section 2.2. Therefore, in ceramic-metal joint systems, an interlayer was used to manage the CTE mismatch.

Analytical mechanics indicated that low CTE and low yield strength were the properties sought from the interlayer materials. In practice, it is not possible to have both of these properties simultaneously in one material. Two different classes of interlayer materials, i.e., low expansion materials and low yield strength materials, were used to determine the effectiveness of these materials as interlayers^{18,23,24}. The optimum thickness of each interlayer material was also studied. Mo, Nb, and W were selected for their low CTE, high stiffness, and high yield strength, while Cu and Ni were chosen for their low yield strength and low stiffness²⁵.

Interlayer materials were screened using rectangular coupon samples and shear tests as mentioned in the previous sections. Figure 3.19 shows a brazed coupon sample containing an interlayer. The results of shear strength measurements are the average of 3-6 tests.

Figure 3.19. Schematic of the shear test samples containing an interlayer.

Interlayer for Si₃N₄ System

For the Si₃N₄ system, test coupons were prepared by one-step brazing using Au-18Ni braze at 980°C for 10 minutes in vacuum. As shown in Table 3.11, a significant difference in bond strength was found between two classes of interlayer materials, except W, even though all these materials were processed with the same brazing conditions. In particular, the joint strength values obtained from the Mo interlayer system were low compared with those from the Cu and Ni interlayer systems. This experimental data was consistent with the modeling predictions that Ni would outperform Mo, Section 2.3.

Table 3.11. Effect of interlayer material and thickness on shear strength.

Materials System	Interlayer Thickness (inch)	Shear Strength (ksi)
SNW1000-Zr-(Au-18Ni)-Nb-Incoloy 909	0.04	6.9
SNW1000-Zr-(Au-18Ni)-Mo-Incoloy 909	0.01, 0.04	10.2
SNW1000-Zr-(Au-18Ni)-W-Incoloy 909	0.04	17.4
SNW1000-Zr-(Au-18Ni)-Cu-Incoloy 909	0.02, 0.04	19.2
SNW1000-Zr-(Au-18Ni)-Ni-Incoloy 909	0.005-0.02	15.0

The geometry of test samples resulted in inconsistent, improper bonding between the ceramic and metal. This was due to the bimetal warp associated with thermal mismatch between the interlayer and the Incoloy 909. This warping was particularly noticeable in refractory interlayer materials which exhibited 40 - 90% unbonded area, rather than in soft interlayer materials like Cu and Ni. The Cu interlayer system provided excellent bonding performance, > 95% bonded area, with high shear strength. Samples with a 0.020" thick Cu interlayer showed the highest shear value, 23.1 ksi. Since the thickness of the interlayer materials changed the sensitivity to the warping problem, it was difficult to understand the effect of thickness on the joint strength. Thicker interlayers seemed to work better with stiff materials like W, Nb, and Mo, while Cu and Ni had a greater range in thickness for brazing with this test geometry.

It was found that the system with the Cu interlayer fractured predominantly at the interface between the braze and the ceramic. For the systems with Mo, fracture occurred in the ceramic. The system with a copper or nickel interlayer, low strength and high CTE materials, was effective in reducing residual stresses generated by the CTE mismatch.

Shear strengths of the ceramic-ceramic joint were in the range of 40-45 ksi. This ceramic-ceramic joint strength gives the base strength for a joint with minimal residual stress. This allows the level of residual strength in metal-ceramic joints, with interlayers, to be approximated.

Overall results indicated that materials such as Mo and W seemed to be moderate choices for their intermediate CTE and high-temperature capability. It is believed that the low oxidation resistance of these materials can be addressed by utilizing designs which do not expose them to oxygen. Mo was chosen over W since Mo has slightly more ductility than W. Cu and Ni were also shown to be promising metals for use at relatively low temperature.

Interlayer for SiC System

A two-step brazing practice was used to avoid the warping problem of the interlayers encountered during brazing process in the Si_3N_4 system. During the first step, a 73.8Au-26.2Ni braze alloy was used to braze the Cu or Mo interlayer to Incoloy 909. The liquidus and solidus of the 73.8Au-26.2Ni braze are 1010°C and 980°C, respectively. After this first brazing step, the sample surface was repolished and then brazed to SiC with Au-18Ni. The 950°C liquidus of Au-18Ni made it possible to perform the second braze without remelting the first.

The samples survived cooling to room-temperature when the interlayer was 0.040" thick using either Cu or Mo. Samples using thin, 0.010" Cu or Mo were unable to survive the cooling cycle. The results of these tests are shown in Table 3.12.

With a Ni interlayer, a very strong reaction was seen between the Ni and the SiC, forming a two-phase mixture of nickel-silicide and graphite²⁶. Based on the severity of this reaction, nickel interlayers should not be used with SiC when the braze alloy dissolves a large amount of nickel from the interlayer. Since a Cu interlayer can not perform at high temperatures, Mo was selected as an interlayer for the SiC system.

Table 3.12. Effect of interlayer material and thickness on shear strength.

Materials System	Interlayer Thickness (inch)	Shear Strength (ksi)
SiC-Ta-(Au-18Ni)-Cu-Incoloy 909	0.01, 0.04	0.4
SiC-Zr-(Au-18Ni)-Cu-Incoloy 909	0.04	2.6
SiC-Ta-(Au-18Ni)-Mo-Incoloy 909	0.04	0.3

All observed failures from SiC systems were in the ceramic, indicating that unbonded areas did not play a role. Reactive metal coatings on the ceramic appeared to affect the ceramic strength in brazed coupons. However, residual stress was the principal factor affecting strength level in brazed pairs.

3.4 BRAZING ALLOY DEVELOPMENT

Most ceramic-metal braze systems are based on chemical interactions occurring at the interface²⁷. The free energy change for the reaction between the braze, coating material, and ceramic is frequently used to predict the success or failure of a candidate braze system.

Many brazes are binary alloys with additions of reactive metals, such as Ti or Zr²⁸⁻³². For mechanical joints, the current maximum use-temperatures are near 400°C. Combining a use-temperature of 400°C and the desire to minimize creep and thermal stresses results in typical brazing temperatures in the range of 800 - 1000°C. Binary alloys of Ag-Cu and Au-Ni are commonly used, with Sn or In sometimes added to further lower the melting temperature of the braze. These precious metal braze alloys have the advantages of high ductility and good flow characteristics. However, some of these brazing alloys have poor oxidation resistance³³.

The work on braze alloy development was focused on bulk brazing alloys. In order to be of interest, the braze material must meet the following requirements:

- Wet the ceramic, but not necessarily have to flow.
- Have a melting temperature above 1100°C for the 650°C application.
- Contain elements with a low vapor pressure at the brazing temperature.
- Resist oxidation up to 1000 hours at 650°C in air.
- Be capable of forming a slight fillet between the ceramic and metal.
- Be sufficiently ductile.
- Meet the mechanical stress requirements at 650°C.

Experimental Alloys

A total of seven different alloy systems were studied as possible 650°C braze alloys. The braze alloy systems were all Au-based for good ductility and oxidation resistance. All of the systems contained Ti. The Ti acted as an active alloy addition to promote wetting and adhesion between the braze alloy and the ceramic. To adjust the melting point, a third and possibly fourth element was selected from Pd, Ni, In, Sn, and Si. The various alloy systems evaluated are listed below:

Au-Ti	Au-Cu-Ti	Au-Ni-Si-Ti
	Au-In-Ti	Au-Ni-Sn-Ti
	Au-Ni-Ti	
	Au-Si-Ti	

The experimental alloys were prepared by weighing 5-gram samples to 0.01 gram accuracy, and melting them in a skull melter under an argon atmosphere. The buttons were remelted about 4 times to homogenize.

43 of the alloys studied were based on the most favorable Au-Ni-Si-Ti alloy compositions. The liquidus and solidus for these alloys were about 1025

and 950°C respectively. In total, 59 alloys were investigated. They were tested for ductility by cold rolling. Of these alloys, 56 were melted on alumina for wettability tests. Of the most ductile alloys, 48 were studied by differential thermal analysis (DTA).

Tests showed that the above alloys wet alumina (99.5% Al_2O_3) well; however, some dewetting was noted when high brazing temperatures were used. The hardening effect of 1 wt% Ti was very pronounced. The effect of Ti on the melting temperature of the alloy was slight. Ni had a hardening effect on the alloy, but much less than Ti, by wt. percent. The addition, Ni decreased the melting temperature of the braze. The addition of Si decreased the contact angle and increased wetting of the ceramic. The melting temperature was very slightly affected by the addition of 1 wt% Si. All of the above alloys were ruled out for the 650°C application due to their low melting points.

A series of Au-Pd-Ni-Ti alloys were developed to meet the 650 and 950°C requirement. These alloys wetted both Si_3N_4 and Mo at 1100°C in a 10^{-5} torr vacuum. A high-temperature braze between Si_3N_4 and Si_3N_4 was made at 1450°C using a Au-Pd-Ti alloy. To meet the mechanical properties at 650°C, a solidus temperature of about 1050°C was targeted. Table 3.13 shows the compositions and properties of the Au-Pd-Ni-Ti alloys.

Table 3.13. Alloys studied for the 650°C application.

Alloy Number	Composition (Wt %)				T_L/T_S (°C)	Knoop Hardness
53-0	92 Au	5 Pd	2 Ni	1.0 Ti	1114/1084	117
53-21	91.75 Au	5 Pd	2 Ni	1.25 Ti	1113/1078	138
53-15	91.50 Au	5 Pd	2 Ni	1.50 Ti	1133/1078	170
53-22	91.25 Au	5 Pd	2 Ni	1.75 Ti	1124/1078	190
53-16	91.0 Au	5 Pd	2 Ni	2.00 Ti	1119/1082	209

Alloys with 1.5% Ti and above were found to be too hard and would not allow the braze layer to plastically deform during the post-braze cooling cycle.

Si_3N_4 and Mo were brazed using alloy composition 53-21 as a 0.004" thick braze foil, and brazing conditions of 1110°C $\pm$ 10°C for 2 - 3 minutes under a 10^{-5} torr vacuum. Excess time and temperature will alter the brazing alloy composition, making the alloy less ductile. Substituting Zr for Ti degraded the properties of these braze alloy systems.

The optimum amount of Ti addition was determined to be 1.25 wt%. The Au-5Pd-2Ni-1.25Ti braze had enough Ti to promote wetting of the ceramic but not too much to reduce ductility of the braze to an unacceptable level. However, wetting experiments between the Au-5Pd-2Ni-1.25Ti braze and Si_3N_4 resulted in uneven wetting. This uneven wetting led to the development of a braze without Ti. Wetting between the braze and Si_3N_4 ceramic was achieved

with the use of a 3 μm thick Ti coating on the Si_3N_4 ceramic. The Au-5Pd-2Ni braze consistently wet the Ti coated Si_3N_4 . Therefore, the Au-5Pd-2Ni braze alloy was selected for the 650°C application.

Alloys of Au-Pd-Ti were developed for the 950°C application, as shown in Table 3.14. The 950°C braze alloy was based on precious metals since the braze joint must survive the 950°C temperature for an extended time in an oxidizing air atmosphere. The braze temperature or the solidus temperature of the brazing alloy should be about 1450°C. For purposes of this study, Si_3N_4 - Si_3N_4 joints were made and brazing was carried out at 1400°C, 1450°C, and 1500°C.

Table 3.14. Alloys studied for the 950°C application.

Alloy Number	Composition (Wt %)		
53-6	39.2 Au	60 Pd	0.8 Ti
53-9	48.5 Au	50 Pd	1.5 Ti

These Au-Pd alloys had melting temperatures in the range of the melting temperatures of structural alloys such as Incoloy 909 and Inconel 718. Therefore, the development of these Au-Pd alloys in Table 3.14 was not pursued further. Consequently, Au-Pd-Ti and other commercial alloys were selected for the 950°C application.

Commercial Alloys

Table 3.15 shows the compositions and melting points of several commercially available, high-temperature braze alloys. Au and Pd were the base metals selected to provide the necessary ductility and oxidation resistance. Palni and Palniro 1, 4, and 7 were selected and examined in terms of joint strength, application temperature, and compatibility with other joint components.

Table 3.15. Composition and melting points of commercial braze alloys.

Braze Alloy	Composition (Wt %)			Liquidus Temperature (°C)	Solidus Temperature (°C)
Palni	-----	60 Pd	40 Ni	1238	1238
Palniro 1	50 Au	25 Pd	25 Ni	1121	1102
Palniro 4	30 Au	34 Pd	36 Ni	1169	1135
Palniro 7	70 Au	8 Pd	22 Ni	1037	1005

Wetting tests of the 950°C braze alloys were conducted on Ti coated SNW1000. The procedure was previously described. The test temperatures were 110% of the alloy's liquidus in °K. All of the braze alloys wet the substrate. Figure 3.20 shows the wetting angle as a function of time for all four braze alloys.

Figure 3.20. Wetting angle of 950°C brazes (Palni and Palniro 1, 4, and 7) on Ti coated PY6.

When a Zr coating was used for the wetting tests with Palni braze, a large amount of outgassing occurred. Wetting tests were carried out in a mass spectrometer/vacuum system to determine the nature and source of this gas. Mass spectroscopy showed that a large amount of N₂ gas was given off as the Palni braze wet the Zr coated SNW1000, Table 3.16. Experiments with the

Au-5Pd-2Ni-1.25Ti and Au-18Ni brazes showed much smaller amounts of outgassing. The data suggest that the Pd in the Palni braze reacts with Si_3N_4 to form Pd_2Si or PdSi and N_2 . This type of strong outgassing reaction could result in a significant amount of unbonded area in the brazed joint. Therefore, the Zr coating was not used with Pd containing alloys.

In screening the commercial alloys for the 950°C application, Palniro 1 and 7 were ruled out due to their relatively low melting points. Palni and Palniro 4 were investigated further with high-temperature testing, described in Section 4.1.

Table 3.16. Mass spectroscopy results for braze, coating, ceramic interactions at 1300°C.

Sample	Total Gas Pressure	Major Gas Species
SNW1000	193 μm	N_2 , H_2
Palni w/o Zr	75	N_2
Palni-Zr	800	N_2

4 FINAL JOINT SELECTION

In the previous sections, the potential materials for each layer in the joint system were screened using a model system such as SNW1000-(Au-18Ni)-Mo. Mechanical strength of the joints was mostly evaluated at room-temperature, knowing that the joint properties at room-temperature were significantly affected by residual stress due to thermal mismatch in ceramic-metal joints. At high temperatures, however, the role of the residual stress becomes less important, while the strength of the brazed area becomes critical. Also, a lap joint geometry was used for testing for screening. From an analytical mechanics point of view, a cylindrical joint has a definite advantage in performance with a given bonded area compared to a butt joint. While lap-joint samples provide a general indication of the ability to bear a load in the presence of residual stress, the stress conditions in these joints are less severe than the actual cylindrical samples. Therefore, cylindrical samples were required to finalize the material system. In selecting final systems for the 650 and 950°C applications, attention was paid to (1) the high-temperature strength of the systems, and (2) the material system's compatibility during brazing, using a cylindrical joint geometry.

4.1 HIGH-TEMPERATURE STRENGTHS OF THE SYSTEMS

Si₃N₄ System. The high-temperature strength of joints with the Palni and Palniro series brazes was measured with coupon lap joint samples. The substrate materials chosen for 950°C were Zr or Ti coated SNW1000, Mo, and Nb as model systems.

Hot shear testing was performed in an argon atmosphere. The test temperature, 500°C, was selected due to the temperature limit of the testing fixture. The samples were equilibrated at 500°C for 30 minutes before being tested at a crosshead speed of 0.01 inch/min. Ti was substituted for Zr as a coating for the Nb-SNW1000 coupons. This substitution was made because a strong interaction between the Zr coating and braze alloys at 1200°C prevented the Nb-SNW1000 system from bonding.

Table 4.1 shows the results of hot shear tests. The braze alloys studied did not show significant weakening at 500°C. For the SNW1000-Zr-Mo system, Palniro 4 resulted in a high shear strength. However, Palni provided strength equivalent to the room-temperature strength of the SNW1000-Zr-(Au-18Ni)-Mo system. Fracture always occurred in the braze. This type of fracture implies that the thermal stresses developed at the ceramic-metal interface were not high enough to cause cracking of the ceramic. Overall results from this limited number of tests indicate that the performance of the brazed joints at 500°C is better than or equivalent to strength levels seen at room-temperature. This was supported by the FEA study, Section 2.5. The increase in joint strength at 500°C is primarily due to the reduction of the thermal mismatch between the ceramic and metal substrates.

Table 4.1. Results of hot shear tests.

Material System	Bond Area (cm ²)	Testing Temperature (°C)	Shear Strength (ksi)	Comments
SNW1000-Zr-Palni-Nb	0.96	---	---	No bonding after brazing
SNW1000-Zr-Palnio 4-Nb	0.96	---	---	" " "
SNW1000-Ti-Palni-Nb	0.96	525	12.3	
SNW1000-Ti-Palnio 4-Nb	0.96	525	7.4	
SNW1000-Zr-Palni-Mo	0.96	525	6.2	
SNW1000-Zr-Palni-Mo	0.96	525	4.8	
SNW1000-Zr-Palnio 4-Mo	1.10	525	>15.2	No failure at 15.2 ksi
SNW1000-Zr-Palnio 4-Mo	1.10	525	---	Failed during preloading

With this information, a group of coupon specimens were brazed and sheared to evaluate the remaining issues in materials systems development. These results are summarized in Table 4.2. The shear strengths of Ti coated PY6 brazed to Mo with either Au-5Pd-2Ni or 30Au-34Pd-36Ni (Palnio 4) were excellent. Shear strengths at 500°C reached up to 24 ksi and 36 ksi, for Au-5Pd-2Ni and 30Au-34Pd-36Ni, respectively. The PY6-Ti-(30Au-34Pd-36Ni)-Mo joint was strong enough to deform the Mo without breaking.

SiC System. Mechanical property results are reported in Table 4.3 for SiC-Mo joints. However, comparable samples of SiC-Ni joints were not obtained because of the large differential expansion between the SiC and Ni and compatibility problems between these two, as described in the previous section. These difficulties resulted in all of the SiC-Ni coupon samples failing during cool down from the brazing temperature. Based on the above results, Mo was chosen as the interlayer for high-temperature use, and the SiC-(30Au-34Pd-36Ni)-Mo and SiC-(Au-5Pd-2Ni)-Mo systems were selected for further study.

Table 4.2. Shear tests with Au-34Pd-36Ni, Au-5Pd-2Ni, and Pd-40Ni brazes in the Si₃N₄ system.

System	Load (lbs)	Area (in ²)	Shear Stress (ksi)	Comments
PY6(Ti)-(30Au-34Pd-36Ni)-Mo	4325	0.138	31.3	525°C
	2750	0.150	18.3	525°C
	4925	0.135	36.4	525°C
	>4800	0.132	>36	500°C, Mo substrate bent
	>4800	0.149	>30	500°C, Mo substrate bent
PY6(Ti)-(30Au-34Pd-36Ni)-Ni	650	0.145	4.4	Room temperature
	1360	0.145	9.3	Room temperature
	1825	0.157	11.6	525°C
	1225	0.157	7.8	525°C
	450	0.157	2.8	525°C
PY6(Zr)-(30Au-34Pd-36Ni)-Mo	2225	0.157	14.1	525°C
	2250	0.153	14.7	525°C
	3000	0.153	19.6	525°C
	2925	0.153	19.1	525°C
	2900	0.139	20.8	525°C
PY6(Ti)-(Au-5Pd-2Ni)-Mo	2710	0.132	20.5	500°C
	3055	0.123	24.8	500°C
	765	0.125	6.1	Room temperature
	885	0.149	5.9	Room temperature
	2350	0.149	15.7	Room temperature
PY6(Zr)-(Au-5Pd-2Ni)-Mo	—	—	—	525°C, broke under preload
	2560	0.128	20.0	525°C
	2800	0.131	21.3	525°C
	2050	0.149	13.7	525°C
	4040	0.136	29.7	525°C
PY6(Ti)-(Pd-40Ni)-Ni	2150	0.144	14.9	525°C
	—	—	—	Severe reaction between braze and Ni, all samples broke with little force

Note: the 500 and 525°C tests were conducted under an argon atmosphere.

Table 4.3. Shear tests with Au-34Pd-36Ni and Au-5Pd-2Ni brazes in the SiC system.

System	Load (lbs)	Area (in ²)	Shear Stress (ksi)	Comments
SiC(Ti)-(30Au-34Pd-36Ni)-Mo	625	0.145	4.3	500°C, 3 other samples broke during preload
	700	0.149	4.7	Room temperature
	117	0.149	0.8	Room temperature
	500	0.145	3.4	Room temperature
SiC(Ti)-(Au-5Pd-2Ni)-Mo	—	—	—	500°C, all 3 samples broke during preload
	845	0.132	6.4	Room temperature
	320	0.149	2.1	Room temperature
	745	0.138	5.4	Room temperature
SiC(Ti)-(30Au-34Pd-36Ni)-Ni	—	—	—	Broke during cooling after brazing (all 3 samples)
SiC(Ti)-(Au-5Pd-2Ni)-Ni	—	—	—	Broke during cooling after brazing (all 3 samples)
SiC(Zr)-(Au-5Pd-2Ni)-Ni	—	—	—	Broke during cooling after brazing (all 3 samples)
SiC(Zr)-(Au-5Pd-2Ni)-Mo	—	—	—	500°C, all 3 samples broke under preload

Note: the 500 and 525°C tests were conducted under an argon atmosphere.

4.2 SYSTEMS COMPATIBILITY

A cylindrical geometry was selected for the ceramic-metal joint since it is easier to control residual stresses in a cylindrical joint. However, the vertical cylindrical geometry of the samples resulted in more extensive interactions between the braze, structural alloy, and interlayer materials than was seen with the horizontally oriented coupon samples. Furthermore, the vertical cylindrical geometry makes the system more sensitive to processing conditions and chemical interactions among the components in the system.

In the brazing process, suppression of the braze melting point due to alloying with the surrounding joint components has a significant effect on overall brazing performance. This melting point suppression is especially problematic with the cylindrical geometry. Suppression of the melting point will prolong the solidification time of the braze, further accelerating alloying. This effect was demonstrated with the Inconel 718-(Au-5Pd-2Ni)-Ni-Ti-PY6 system. Brazing was performed at 1180°C for 3 - 4 minutes in vacuum. This joint system resulted in excessive liquid phase formation, resulting in very poor bonding. DTA of the braze alloyed with Ni from the interlayer and from the Inconel 718 showed that the melting point of the braze had changed from 1140°C to 997°C. X-ray fluorescence confirmed that the composition of the braze changed from 2% Ni to 26% Ni.

The Incoloy 909-Ni-Ti-PY6 system gave reasonable joints with the Au-5Pd-2Ni braze, in contrast with the Inconel 718-Ni-Ti-PY6 system above. This is probably due to the difference in the Ni and Fe contents of Incoloy 909 (42Fe-38Ni-13Co-4.7Nb) and Inconel 718 (55Ni-16Fe-20Cr-5Nb). Fe, Cr, and Mo tend to increase the melting point of Au-based braze, while Ni decreases the melting point. Consequently, a Ni interlayer was not used for the Inconel 718-(Au-5Pd-2Ni)-Ti-PY6 system at 950°C.

4.3 FINAL JOINT SYSTEMS

Material System

Material systems for braze joints were finalized as summarized in Table 4.4. The selections were based on the high-temperature performance and system compatibility. As a coating material, Ti was chosen over Zr for all systems since Zr interacts with the current Pd-containing brazing alloys, evolving nitrogen gas. Also, Ti coating was found to have a minimal effect on the mechanical properties of PY6. Ni was selected as an interlayer material only for 650°C application with PY6 ceramic due to limited temperature capability and severe interaction with SiC ceramic. Even though 30Au-34Pd-36Ni (Palniro 4) provides high joint strength at 500°C, it was unable to consistently bond to Si₃N₄. Therefore, 30Au-34Pd-36Ni was replaced with Au-5Pd-2Ni for the 950°C Si₃N₄ application.

Table 4.4. Final material systems for the brazed joints.

Ceramic	Structural Alloy	Interlayer	Braze
650°C Application			
PY6/Ti coating	Incoloy 909	Ni	Au-5Pd-2Ni
SiC/Ti coating	Incoloy 909	Mo	Au-5Pd-2Ni
950°C Application			
PY6/Ti coating	Inconel 718	Mo	Au-5Pd-2Ni
SiC/Ti coating	Inconel 718	Mo	30Au-34Pd-36Ni

The interactions between the braze alloys and the structural and interlayer materials were studied with the three systems shown in Table 4.4: Incoloy 909-(Au-5Pd-2Ni)-Ni, Incoloy 909-(Au-5Pd-2Ni)-Mo, and Inconel 718-(30Au-34Pd-36Ni)-Mo.

The Incoloy 909-(Au-5Pd-2Ni)-Ni system did not form intermetallic compounds. However, the braze dissolved both the Incoloy 909 and the Ni to an appreciable extent. On the other hand, the Incoloy 909-(Au-5Pd-2Ni)-Mo system formed Mo-Ni intermetallic compounds at the braze/Mo interface. The Au-5Pd-2Ni braze dissolved the Incoloy 909 and the Mo, as in the Incoloy 909-Ni system. The Inconel 718-(30Au-34Pd-36Ni)-Mo system did not appear to react to any significant extent. No reaction zone was seen between the braze alloys and the Inconel 718 or the Mo. A limited amount of dissolution of the Inconel 718 and Mo was seen.

The Ni interlayer was uncracked in all of the joints made with a cylindrical joint, as shown in Figure 4.1. However, the Mo interlayer was cracked in all of the brazed joints with a Mo interlayer. Cracks from the Mo interlayer had propagated into the ceramic member in the Inconel 718-(Au-5Pd-2Ni)-Mo-Ti-PY6 brazed joint (Figure 4.2).

Inconel 718

Ni

PY6

Figure 4.1. SEM micrograph of a brazed joint between Inconel 718 and Ti coated PY6 Si₃N₄ with a Ni interlayer and the Au-5Pd-2Ni braze.

Inconel
718

Mo

PY6

Figure 4.2. SEM micrograph of a brazed joint between Inconel 718 and Ti coated PY6 with a Mo interlayer and 30Au-34Pd-36Ni braze. The top part of the PY6 was removed. Note: cracks in the Mo interlayer propagated into the PY6.

Joint Geometry

The final joint consists of a 0.5" diameter rod of ceramic brazed to a 0.766" outer diameter metal shaft. The end of the metal shaft is reduced to 0.5" diameter for gripping in the testing machine. The ceramic rod fits into a cup machined into the end of the metal shaft. The detailed geometry of the ceramic-metal joint is shown in Figure 4.3.

The upper ends of the metal piece have a 30° taper. This taper helps to reduce the squeeze of the ceramic by the metal. FEA showed that this type of taper was very effective in reducing the residual stress in the ceramic (Section 2.3). The interlayer is placed in the 0.641" diameter section. It is held in place by resting on the 0.5785" diameter section below it. This 0.5785" diameter section is empty space; however, occasionally it becomes partially filled with the braze alloy. The 0.500" section provides an alignment hole for the ceramic piece. A 0.125" diameter hole is used to place a thermocouple inside the joint for temperature measurement. The three 0.063" diameter through holes act as gas vents. These holes allow any gas to escape instead of being trapped and causing unbonded areas in the brazed layer. The wall thickness of the structural alloy and interlayer were 0.0525" and 0.0665", respectively, and have not yet been optimized.

Figure 4.3. Details of metal-ceramic joint geometry.

5 PERFORMANCE TESTS AND FEA MODEL PREDICTIONS

The ceramic-metal joints being developed are for use at 650 and 950°C in gas turbine heat engines. These joints will attach the ceramic turbine rotor to a metal shaft for power transmission. The major type of loading these joints will see is torsional. Therefore, the joint strength will be evaluated with torsion, torsion fatigue, and thermal fatigue tests.

The results from the torsion tests will be compared to the residual stress values predicted by FEA. The ability to compare the measured joint strength to the predicted residual stresses will allow the FEA model of the joints to be refined and will provide a tested method to aid in designing ceramic-metal joints in the future.

5.1 LINKAGE BETWEEN FEA PREDICTIONS AND EXPERIMENTS

Linkage between the FEA predictions and mechanical testing experiments was established based on the following assumptions:

- The brazing process provides ideal joints without defects, i.e., no unbonded area.
- Alloying effects are negligible on the material properties.
- Each of the structural ceramic members has an equal probability for surface cracks.

While these assumptions may not be applicable to the brazed joints presently being studied, they represent a necessary assumption to make the problem tractable.

FEA predicts the location and level of the residual stresses built up in the joint due to thermal mismatch between the ceramic and metal in terms of the maximum principal stress. The maximum principal stress controls the failure of the ceramic part in the joint at the temperatures presently being studied. FEA can also provide the same information in terms of Mises equivalent stress. Mises equivalent stress governs the failure of the braze and interlayer materials at the temperatures presently being studied, i.e., 650 and 950°C.

The situations with and without residual stresses are represented by the properties of the brazed joint and of the unbrazed ceramic sample, respectively. The following relationships can be established in a tension test.

$$\sigma_{\text{fracture}} = \sigma_{\text{residual}} + \sigma_{\text{applied}} \quad \text{Eq. 5.1}$$

Expressing Equation 5.1 in terms of shear stresses:

$$\tau_{\text{fracture}} = f(\tau_{\text{residual}}, \tau_{\text{applied}}), \quad \text{Eq. 5.2}$$

where τ_{fracture} is the measured fracture shear stress of the unbrazed ceramic calculated using Equation 5.3, and τ_{residual} is calculated from FEA. τ_{applied} is the measured fracture shear stress of the brazed joint calculated using Equation 5.3:

$$\tau = \frac{16 M_T}{\pi D^3}, \quad \text{Eq. 5.3}$$

where M_T , and D are the applied torque at failure and the diameter of the specimen gauge section, respectively. The maximum shear stress occurs at the surface of the specimen, which will eventually cause fracture of the material.

The residual stresses in the joint are determined by FEA. The stresses σ_{zz} and $\sigma_{\theta\theta}$ are the maximum principal stresses taken from the free surface in the vicinity of the ceramic-metal joint (i.e., σ_1 and σ_3 respectively). These stresses can be converted into a maximum shearing stress for comparison with the measured joint strength by a Mohr's circle analysis.

Substituting for the residual stress quantities in Equation 5.1, the relationship between the residual stress in the joint and the strength of the joint, $\tau_{\text{predicted}}$, becomes

$$\sigma_{\text{max}} = \frac{\sigma_{zz} + \sigma_{\theta\theta}}{2} + \sqrt{\left(\frac{\sigma_{zz} - \sigma_{\theta\theta}}{2}\right)^2 + [\tau_{\text{predicted}}]^2} \quad \text{Eq. 5.4}$$

where σ_{max} is equals τ_{max} . τ_{max} is the measured shear strength of the unbrazed ceramic from a torsion test based on the following relationship:

$$\tau_{\text{max}} = \frac{\sigma_{11} - \sigma_{33}}{2} = \frac{\sigma_{11} - (-\sigma_{11})}{2} = \sigma_{11} = \sigma_{\text{max}}. \quad \text{Eq. 5.5}$$

For real, nonideal samples, Equation 5.4 becomes

$$\sigma_{\text{max}} = \frac{\sigma_{zz} + \sigma_{\theta\theta}}{2} + \sqrt{\left(\frac{\sigma_{zz} - \sigma_{\theta\theta}}{2}\right)^2 + [\tau_{\text{applied}} + \Delta\tau]^2} \quad \text{Eq. 5.6}$$

where τ_{applied} is the shear strength for fracture measured from brazed samples. $\Delta\tau$ is the change in the principal stress due to processing, testing, and the probability factor for cracking in the ceramic material. τ_{applied} is calculated from Equation 5.3.

Therefore, a comparison can be made between the predicted values, $\tau_{\text{predicted}}$, in Equation 5.4 and the measured values, τ_{applied} , in Equation 5.6, assuming that $\Delta\tau = 0$. Setting $\Delta\tau = 0$ is equivalent to assuming that the brazed joint is perfect, the ceramic has not been damaged during the brazing process, and there is no unbonded area in the joint. Actual tests will be discussed in the following section.

5.2 TORSION TESTING

Testing Procedure

A brazed joint between Incoloy 909 and PY6 is shown in Figure 5.1. The PY6 is on the left side, and the Incoloy 909 is on the right side. This type of joint was used for the torsion and torsion fatigue tests.

All of the mechanical testing of the brazed joints was carried out on a MTS model 646.25S hydraulic Axial/Torsion machine. The maximum torque of the machine is 20,000 in-lbs, and the maximum axial load is 55,000 lbs. The machine is equipped with hydraulic grips that can accommodate 0.5" diameter samples. The gripping pressure was adjusted to 1,500 psi, to protect the ceramic from premature cracking in the gripped area during testing.

The torsion tests were run at a rate of $0.2^\circ \theta/\text{sec}$. During the test, the axial load was controlled to within ± 1.0 lbs of zero. An induction furnace was used to heat the joints to 650 and 950°C for the elevated temperature tests. A SiC susceptor was used for more even heating of the ceramic-metal joint. The joints were equilibrated at the test temperature before the tests. Five joints were tested at room-temperature for the 650 and 950°C systems. Large scatter in the torsion strengths of these joints made further torsion tests unnecessary until the source of the scatter can be addressed. The very low strengths at 650 and 950°C made further high-temperature tests futile until stronger joints can be designed.

The mechanical fatigue tests were run under torque control with the axial load controlled to within ± 1.0 lbs of zero throughout the testing. The tests were run between 35 and 185 in-lbs, with a mean torque level of 110 in-lbs. A 1.5 Hz loading frequency was used. Only five joints from the 650 and 950°C systems were fatigue tested. All of these joints easily met the test requirements and any further testing was felt to be unnecessary. The low high-temperature strengths of the joints made high-temperature fatigue testing impossible.

Figure 5.1. Brazed joint from the 650°C Si₃N₄ system, Incoloy 909-(Au-5Pd-2Ni)-Ni-Ti-PY6. (a) Sample used for torsion testing and mechanical fatigue testing. (b) Close-up of joint region. The ceramic is 0.5" in diameter.

Testing of Base Materials

Torsion tests were performed at room-temperature and 650°C with Incoloy 909, Inconel 718, and PY6. These tests measured the baseline properties of each material. The 650°C fracture strength of PY6 was the same as the room-temperature fracture strength; the twisting moment at failure was 2,110 in-lb (85,970 psi) and 0.4 degrees of rotation, as shown in Table 5.1.

Table 5.1. Torsional strength of the PY6 material.

Material	Test Conditions	Torque (in-lbs)	Shear Strength (psi)	Rotation	Diameter of gauge section
Si ₃ N ₄	RT torsion	530	172,753	1.83°	0.25"
"	"	2,110	85,970	0.40°	0.50"
"	650°C torsion	525	171,123	1.84°	0.25"

Samples with a gauge section diameter of 0.25" and 0.5" were used to measure the torsional strength of PY6. These samples had the same surface finish (6μ-inch) as the PY6 used to make the brazed joints. The sample with the 0.5" diameter had 50% of the strength of the 0.25" diameter sample. This is related to the difference in the circumference between the two samples. The fracture of PY6 samples occurred at the outer surface. The strength of the 0.5" diameter sample should be one-half of the 0.25" diameter sample since the 0.5" diameter sample had twice the circumference of the 0.25" diameter sample.

The torsional yield strength of Incoloy 909 and Inconel 718 at 650°C was lower than at room-temperature, while the rotational yield angle was unchanged at 2 - 3 degrees (Table 5.2). A 1-inch long gauge section was used in all of the tests.

Table 5.2. Torsional strength of Incoloy 909 and Inconel 718 materials.

Material	Test Conditions	Torque (in-lbs)	Shear Yield Strength (psi)	Rotation at yield	Diameter of gauge section
Incoloy 909	RT torsion	580	56,015	2.0°	0.375"
Inconel 718	"	550	53,118	2.5°	"
Incoloy 909	650°C torsion	400	38,631	2.3°	"
Inconel 718	"	480	46,437	2.3°	"

Inserting the corresponding values into the equation and solving for the bending moment at the joint, we get, M_{joint} , for the Incoloy 909-PY6 brazed joints:

$$M_{\text{joint}} = 2.5 P \quad (\text{in-lbs}) \quad \text{Eq. 5.9}$$

$$M_{\text{joint}} = 17,985 y \quad (\text{in-lbs}) \quad \text{Eq. 5.10}$$

The deflection was measured by clamping the metal end of the brazed joint and spinning the joint while the deviation of the ceramic end was measured, where the deflection is one-half the deviation. The magnitude of the bending moment is important because any misalignment between the metal and ceramic introduces a bending moment in the joint; when the sample is gripped in the testing machine, the testing machine was aligned within 0.001". A bending moment of approximately 150 in-lbs, a deviation of 0.016", did not seem to affect the joint strength. There was not a strong correlation between the bending moment and the shear stress of a joint for bending moments below 150 in-lbs. This suggests that other factors, such as residual stress, unbonded area, or pre-existing cracks, are the controlling factors of the joint strength.

In the samples shown in Figure 5.2 the fracture started in the ceramic near the top of the interlayer. Away from the interlayer, the fracture surface formed an approximately 45° angle, reflecting that the fracture was caused by the principal tensile stress in torsion loading. Near the top of the interlayer, the angle of the fracture surface varied from 45°. This deviation from a 45° angle near the interlayer reflects the fact that the stress pattern near the interlayer was significantly different than in the bulk Si_3N_4 away from the interlayer. The residual stress caused by the metal components of the joint was predicted by FEA to be concentrated to within approximately 5 mm from the top of the interlayer (Figure 2.10). The localization of the maximum residual stresses in the ceramic to the top of the interlayer was reflected by the fracture surfaces shown in Figure 5.2.

Figure 5.2. Fracture surface of the 650°C Si_3N_4 system fractured in a room-temperature torsion test.

Results from the 650°C torsion tests are shown in Table 5.4. In general, the strengths of these joints were very low. During the torsion test the ceramic would slip without fracturing. One sample was pulled apart in tension so that the fracture surface could be examined after such slippage occurred. Auger analysis of the fracture surface indicated that the fracture path was complex and occurred in the Si_3N_4 , in the TiN reaction layer, and in the braze alloy. A schematic of the fracture path is shown in Figure 5.3.

Table 5.4. Results of the 650°C torsion tests of the 650°C Si_3N_4 brazed joints.

Material System	Test Conditions	Torque (in-lbs)	Shear Strength (psi)	Rotation	Fracture mode
650°C Si_3N_4	650°C torsion	41	1,670	---	Slippage at braze/ceramic interface
"	"	14	570	0.10°	"
"	"	62	2,526	---	"
"	"	43	1,752	0.21°	"

Figure 5.3. Schematic of the fracture path for the 650°C Si_3N_4 brazed joints tested at 650°C. Crack passed through all 3 regions at the interface: the Si_3N_4 , the TiN reaction layer, and the braze layer.

Si₃N₄-Inconel 718 System. Results from the room-temperature torsion tests of the 950°C Si₃N₄ system are showed in Table 5.5. In general, the fracture behavior of these joints was similar to those in the 650°C system, Figure 5.4. However, the 950°C Si₃N₄ joints were significantly weaker than the 650°C Si₃N₄ joints. This difference in room-temperature joint strength is attributed to the higher residual stresses in the 950°C Si₃N₄ joints. The higher residual stresses are caused by the higher CTE of the Inconel 718 ($18 \times 10^{-6}/^{\circ}\text{C}$) compared to the Incoloy 909 ($12 \times 10^{-6}/^{\circ}\text{C}$)

Table 5.5. Results of the room-temperature torsion tests of the 950°C Si₃N₄ brazed joints.

Material System	Test Conditions	Torque (in-lbs)	Shear Strength (psi)	Bending Moment (in-lbs)	Rotation	Fracture mode
950°C Si ₃ N ₄	RT torsion	108	4,400	225	0.38°	Broke in ceramic
"	"	350	14,260	117	1.19°	"
"	"	200	8,148	153	0.70°	"
"	"	453	18,457	144	0.80°	"
"	"	360	14,667	144	0.64°	"

Figure 5.4. Fracture surface of the 950°C Si₃N₄ system fractured in a room-temperature torsion test.

Results from the 950°C torsion tests are shown in Table 5.6. In general, the strengths of these joints were very low. During the torsion test the ceramic would slip without fracturing. Several samples were tested at 950°C. However, all but one of the samples was cracked. The cracked samples did not

give meaningful results and are not reported. It was not known if the cracks formed on cooling from the brazing cycle or formed on heated to 950°C for the torsion test.

The joint tested at 950°C had a lower shear strength than did the joint tested at 650°C, 122 psi at 950°C versus over 1,000 psi at 650°C. This difference in strength is probably related to a reduction in strength of the braze alloy.

Table 5.6. Results of the 950°C torsion tests of the 950°C Si₃N₄ brazed joints.

Material System	Test Conditions	Torque (in-lbs)	Shear Strength (psi)	Rotation	Fracture mode
950°C Si ₃ N ₄	950°C torsion	3	122	---	Slippage at braze/ceramic interface

SiC-Incoloy 909 System. Results from the room-temperature torsion tests of the 650°C SiC system are showed in Table 5.7. The fracture behavior of these joints was similar to the Si₃N₄ joint systems. The SiC joints were appreciably weaker than the Si₃N₄ joints. This was probably related to the SiC being damaged more from the residual stresses generated during the brazing process. Since SiC has a lower fracture toughness than the Si₃N₄, the strength of SiC would show a greater drop in strength compared to the Si₃N₄.

Table 5.7. Results of the room-temperature torsion tests of the 650°C SiC brazed joints.

Material System	Test Conditions	Torque (in-lbs)	Shear Strength (psi)	Bending Moment (in-lbs)	Rotation	Fracture mode
650°C SiC*	RT torsion	106	4,324	162	0.25°	Broke in ceramic
650°C SiC	"	70	2,852	54	0.25°	"
650°C SiC	"	68	2,771	54	0.30°	"

* This sample was heated to 650 - 700°C, then gripped in MTS machine, and then cooled before testing to realign the sample for testing.

Figure 5.5. Fracture surface of the 650°C SiC system fractured in a room-temperature torsion test.

Results from the 650°C torsion tests are shown in Table 5.8. The strengths of these joints were approximately the same as the strength of the Incoloy 909 Si₃N₄ joints at 650°C, Table 5.6. Both the SiC and Si₃N₄ joints failed by slippage of the ceramic during the torsion test. The ceramic did not fracture in either the SiC or Si₃N₄ joints.

Table 5.8. Results of the 650°C torsion tests of the 650°C SiC brazed joints.

Material System	Test Conditions	Torque (in-lbs)	Shear Strength (psi)	Rotation	Fracture mode
650°C SiC	650°C torsion	10	408	---	Slippage at braze/ceramic interface
"	"	25	1,020	---	"
"	"	40	1,632	---	"

SiC-Inconel 718 System. No successful joints were made between SiC and Inconel 718. All of the samples brazed cracked in the SiC near the top of the interlayer during cool-down from the brazing temperature. This type of failure results from a residual stress level in the ceramic that is too high. New, low yield strength interlayer materials must be studied for successful joints to be made in this system.

5.3 VERIFICATION OF FEA PREDICTIONS

Various constitutive equations were derived for the joint materials and used with FEA to predict the residual stress in the all the joint components in terms of maximum principal stress or Mises equivalent stress. Maximum principal stress determines the failure of the ceramic component, while Mises equivalent stress determines the deformation of the metal components. The joints were assumed to have no unbonded area. Further, the influences of metallurgical reactions due to processing was not accounted for in the analysis. Bulk properties were used for each material in the joint.

Comparisons between the predicted value and the measured values from torsion tests were made. The equations developed in Section 5.1 and testing results from the base materials and brazed joints were used in the comparison. In this analysis the strength of the base materials were treated as theoretical values and failure of the joint was assumed to occur at the maximum stress point. The residual stress state was expressed in terms of σ_{zz} , $\sigma_{\theta\theta}$, and σ_{rr} .

The values of σ_{zz} and $\sigma_{\theta\theta}$ at 20 and 650°C from the FEA study are listed in Table 5.9. These values were taken from the centroid of the FEA mesh element on the free surface of the ceramic. This element was immediately above the joint and did not represent the exact stress conditions, i.e., plane stress, on the surface. However, these values were taken as the principal stresses since the stress values of the third component, σ_{rr} , were significantly smaller than those of σ_{zz} and $\sigma_{\theta\theta}$.

Table 5.9. Comparison between FEA predictions and experimental joint strengths.

Test Temperature	FEA Prediction		$\tau_{\text{predicted}}^*$	τ_{measured}	$\tau_{\text{corrected}}$	Testing Results of Brazed Joints
	σ_{zz}	$\sigma_{\theta\theta}$				
	(ksi)		(ksi)			
20°C	26.9	16.6	64	10.8 - 35.2	18.4 - 59.8	Failed in ceramic Failed at interface
650°C	-11.1	- 5.4	94.2	0.6 - 2.5	---	

* Calculation was based on $\tau_{\text{max}} = 86.0$ ksi.

Table 5.10. Comparison between FEA predictions and experimental joint failure strains. At 20°C the constant k in Equation 2.24 was 13,694 in-lbs/rad.

Test Temperature	FEA Prediction		$\gamma_{\text{predicted}}^*$	γ_{measured}	$\gamma_{\text{corrected}}$	Testing Results of Brazed Joints
	σ_{zz}	$\sigma_{\theta\theta}$				
	(ksi)		(radians)			
20°C	26.9	16.6	3.4	0.6-1.8	1.0 - 3.1	Failed in ceramic
650°C	-11.1	- 5.4	0.005	---	---	Failed at interface

* Calculation was based on $\tau_{\text{max}} = 86.0$ ksi.

Using Equation 5.4 and τ_{max} from Table 5.1, 86.0 ksi, the calculated value of $\tau_{\text{predicted}}$ at room temperature was 64.0 ksi while the measured values from the torsion tests were in the range of 10.8 - 35.2 ksi. The measured values change to 18.4 - 59.8 ksi when the stress concentration factor ($K_t = 1.7$) associated with the change in diameter at the joint (0.5" ceramic to 0.75" metal) is accounted for. The failure strain in Table 5.10, γ_f , was predicted with Equation 2.24, where $k = 13,694$ in-lbs/rad. The constant k was measured from the torsion tests. The measured values are 30 - 90 % of values predicted by FEA. The relatively large scatter in the strength values of the joints should be attributed to the handling of ceramic parts and to the difference in the ideal joints modelled and the real joints tested.

In FEA modelling, the statistical treatment of the surface flaw discussed in Section 2.3 was not performed, and we assumed that the probability of ceramic survival or failure was a function of stress only. This implies that the failure of the joint should always coincide with the point of maximum residual stress. This was an over simplification.

From the fracture mechanics point of view, the crack initiation site will be determined based on the flaw size, residual stress, and applied stress. Since the ceramic part in the joint was subjected to various residual stress states, a weakest link statistical treatment should be used. The joint failure stress depends on the volume of the ceramic subjected to the stress. Subsequently the cracking probability should be determined as a function of the stress and the volume within the isostress regions. Therefore, the FEA predicted value for the joint failure stress would probably be smaller than the value presently predicted.

The joints usually had some unbonded regions. Nonuniform bonding results in the loss of the axial symmetry of the joint. This results in the loss of the plane stress condition at the point of maximum residual stress. The triaxial stress state at the surface, caused by the unbonded area in the joint, may reduce the effective stress for the failure of the ceramic. This will increase

the difference between experimental values and FEA predicted values of the joint strength.

Also, during the brazing process, a change in the compositions and properties of the joint materials contributes to error in the FEA predictions. The presence of molten braze enhances the dissolution of other joint components. New phases form and the composition of the braze alloy changes. These will lead to changes in the mechanical properties of the joint. These property changes are thought to be one of the major factors causing disagreement between measured and predicted joint strengths.

Alignment of the ceramic part with respect to the metal component is another factor for the scatter. Misalignment in the range of 0.002 - 0.020" has been observed from the brazing practice with current test samples. This could induce large bending moments at the joint area, significantly lowering the measured strength values.

The FEA values of σ_{zz} and $\sigma_{\theta\theta}$ at 650°C were obtained from the joint model which was cooled down to room temperature and heated back up to 650°C. As shown in Table 5.9, $\tau_{\text{predicted}}$ increased to 94.2 ksi due to the compressive principal stresses. This value exceeded the strength values of any components in the joint at 650°C and failure did not occur in the ceramic. The values of τ_{measured} (0.6 - 2.5 ksi) represents the strength of the weakest component, i.e., the interface region, at 650°C. In this case, the stress concentration factor was not applicable.

Based on the discussions above, the following are recommendations for improving the analytical predictions of joint strengths and improving the consistency of the joint properties.

- Develop a statistical treatment of FEA results to determine the failure strength of the joints.
- FEA model should reflect changes occurring during the brazing process, such as; the formation of new layers, the change in mechanical properties of the layers, and the change in dimensions of the layers.
- Production of consist joints with no unbonded areas. Improvement in the alignment of the ceramic with respect to the metallic part is essential.
- Brazing alloys which have minimal interactions with other joint components at brazing temperature.

5.4 FATIGUE TESTING

Thermal and mechanical fatigue tests were used to evaluate the effects of temperature on the performance of the brazed joints. Thermal fatigue tests were used to access the the effects of repeated expansion and contract of the structural alloy and interlayer materials on the cracking behavior of the ceramic. Mechanical fatigue tests were used to determine if the brazed joints could withstand repeated loadings without loss of mechanical integrity.

Thermal Fatigue Testing

The geometry and mass of a gas turbine rotor play a large part in determining the internal temperatures of the rotor/shaft system; therefore, one system was chosen as a model. Thermal maps of the ceramic turbine rotor and structural alloy shaft cross-section of the chosen model were based on work done at General Motors on their gas turbine engine.

A temperature of 650°C is the lower of the two braze joint service temperatures for both Si_3N_4 and SiC . The location of the 650°C isotherm was marked on the thermal map for steady state, maximum power conditions for both materials. This area was then examined on the thermal maps for steady state, idle conditions. The idle temperatures were found to be 335°C and 465°C for the Si_3N_4 and SiC , respectively. The SiC required approximately 66 seconds to reach 650°C from 465°C and return again, while the Si_3N_4 cycle was approximately twice as long. Figure 5.6 is a graphical representation of the thermal cycle used for testing.

Figure 5.6. Thermal cycle used in thermal fatigue tests of brazed joints for a 650°C use temperature.

The same method was used to develop the thermal cycle for the 950°C joint. The idle temperature is raised as the entire operating temperature of the hot section is raised in the gas turbine engine. This is the most efficient way of operating the engine because of the increased response time when the temperature differences between maximum speed temperature and idle speed temperature are small. Therefore, the cycle time was left the same as in the previous cycle, Figure 5.7.

Figure 5.7. Thermal cycle used in thermal fatigue tests of brazed joints for a 950°C use temperature.

Thermal Fatigue of Brazed Joints

Braze joints were made for thermal fatigue tests at 650 and 950°C. These joints were identical to the joints shown in Figures 4.3 and 5.1 except that the metal and ceramic sections were only 1" long. The initial crack distribution was checked with microfocus x-ray. Microfocus x-ray detected cracks in the 650 and 950°C SiC systems immediately after brazing (Figure 5.8). However, no cracks were detected in the Si₃N₄ systems. The lack of cracks in the Si₃N₄ systems could be due to either no cracking in Si₃N₄ or to the cracks in the Si₃N₄ being smaller than the detection limit of the x-ray equipment, which is 40 μm.

The samples were examined by microfocus x-ray after 10, 100, and 1,000 cycles. The 650°C Si₃N₄ system survived all 1,000 cycles without evidence of cracking. Severe oxidation of the Mo interlayer in the 950°C Si₃N₄ system prevented testing of these joints.

The Si₃N₄ joints performed better than the SiC joints in the thermal fatigue tests. These results mirror the results observed in the torsion tests, where the Si₃N₄ joints were stronger than the SiC joints.

Figure 5.8. Microfocus x-ray image of 650°C SiC brazed joint immediately after brazing. Lateral cracks extend from the ceramic-metal interface into the SiC. Structural alloy (1). Lateral cracks (2). Uncracked SiC (3). Taken at 90kV, 0.35 mA.

Mechanical Fatigue Testing

The ceramic-metal joint was required to withstand 1,000 cycles of mechanical fatigue. As with the thermal fatigue evaluation, the mechanical cycle was developed with the idea of simulating the stresses developed in a gas turbine engine. The model used was the engine currently being tested by General Motors.

The braze joint area of a rotor/shaft assembly experiences many stresses. Torsional loading is the most severe. The torque experienced at minimum and maximum idle speeds is 35 in-lb and 185 in-lb, respectively. The cycle time, from minimum to maximum, was 1/3 seconds. A graph of the fatigue cycle is seen in Figure 5.9.

Mechanical Fatigue Testing of Brazed Joints

Five joints from the 650°C and 950°C Si₃N₄ system were successfully tested at room-temperature, Table 5.11. The tests were not run at 650 or 950°C since the joints were not strong enough to withstand the 185 in-lbs torque.

Figure 5.9. Mechanical cycle used for fatigue testing the brazed joints.

Table 5.11. Room-temperature fatigue tests of the Si₃N₄ brazed joints.

Material System	Test Conditions	Torque (in-lbs)	Bending Moment (in-lbs)	Rotation	Number of cycles for failure
650°C Si ₃ N ₄	RT fatigue	185 - 35	180	± 0.31°	> 1,000*
"	"	"	171	± 0.32°	> 1,000*
"	"	"	189	± 0.31°	> 1,000*
"	"	"	234	± 0.32°	> 1,000*
"	"	"	144	± 0.32°	> 1,000,000
950°C Si ₃ N ₄	RT fatigue	185 - 35	225	---	> 1,000*
"	"	"	162	± 0.26°	> 1,000

* These samples were heated to 650 - 700°C, then gripped in the MTS machine, and then cooled before testing to realign the sample.

A brazed joint from the 650°C Si₃N₄-Incoloy 909 system was first fatigued at room-temperature for 1,000 cycles. After this test was run, the joint was fatigued at room-temperature until failure. After 1,000,000 cycles, the joint was still intact. The joint showed no signs of degradation; the rotation required for 35 and 185 in-lbs of torque was unchanged at ± 0.32° from the start of the test.

6 SUMMARY AND CONCLUSIONS

In this program, analytical mechanics was used to identify important concepts for the design of the joint geometry and to understand the roles of materials parameters in reducing residual stress in ceramic parts. Material systems were defined for 650 and 950°C applications to verify the validity of mechanics predictions via FEA in the magnitude and distribution of the residual stress. Torsion tests were performed to characterize the properties of the brazed joints and were related to the FEA results.

Failure criteria (β and γ criteria) were developed with analytical mechanics for braze and ceramic failure. The β criterion was expressed as a function of thermal expansion coefficients, temperature, rupture strain, and size of the braze assuming that the braze deforms in simple uniform shear through the braze thickness. However, it was found that the shear rupture of the braze was governed by strain localization rather than by the β criterion.

Three concepts were examined in developing the γ criterion for ceramic failure. These are the maximum principal stress, a crack growth criterion, and a stress concentration criterion. The crack growth criterion was derived in terms of the ceramic toughness and flaw size. It was assumed that the critical region for crack growth was for the case of cracking at the edge of the braze/ceramic interface. The stress concentration criterion was developed in terms of the principal shear stress near the critical area with consideration of stress relief due to the flow of the braze. Both crack growth and stress concentration criteria recommended high fracture toughness ceramics and low shear strength braze alloys. These two criteria also showed the importance of the geometrical factor of the possible cracks on the surface of the ceramics. The stress concentration criterion, in addition, showed the advantage of metals with low thermal expansion coefficients. These two criteria directed the selection of interlayer materials for the final material systems.

Constitutive equations were derived for the joint materials. These equations were used to select an optimum joint geometry using the ABAQUS finite element code. The joint geometries examined in this program were a butt joint, parabolic joints with different angles, conical joints, and cylindrical joints. The cylindrical joint was investigated with two different edge geometries, i.e., square and tapered edges. It was shown in the analysis that the cylindrical geometry was more advantageous in controlling the residual stress and in preventing premature failure than other geometries due to lower failure probability, although an exact 1:1 comparison was difficult among those geometries. Also, the cylindrical joint with tapered edge resulted in a lower stress state in the ceramic than that with the square edge.

Extensive FEA was done to screen the interlayer materials. This study showed that low yield strength materials like Ni outperformed low thermal expansion materials like Mo. The analysis was continued with final material systems to verify the FEA predictions. FEA predicted the location and level of the residual stresses built up in the ceramic in terms of the maximum principal stress and Mises equivalent stress.

For material systems development, a new methodology was developed to quantify the selection of materials for the brazed joint. Using a combination of thermodynamics, reaction kinetics, and FEA, it was possible to efficiently screen materials and to optimize the joint system. This screening procedure included the following:

- FEA of the joint to optimize the geometry and interlayer thickness.
- Consideration of the oxidation properties, high-temperature strength, and CTE of the structural metal alloys.
- Consideration of the CTE, yield stress, and melting point of the interlayer materials.
- Evaluation of thermodynamic data to predict reactivity between the Si_3N_4 and SiC and various coating materials.
- A study of the reaction kinetics between Si_3N_4 and SiC and various coating materials.
- The wetting behavior of braze alloys on the various coating materials.

The high-temperature requirements and compatibility tests between material systems resulted in the following as final material systems used for the braze joints:

- Incoloy 909-(Au-5Pd-2Ni)-Ni-Ti-PY6 for 650°C
- Incoloy 909-(Au-5Pd-2Ni)-Mo-Ti-SiC for 650°C
- Inconel 718-(Au-5Pd-2Ni)-Mo-Ti-PY6 for 950°C
- Inconel 718-(30Au-34Pd-36Ni)-Mo-Ti-SiC for 950°C

PY6 was selected over SNW1000 and AY6 Si_3N_4 because of its excellent high-temperature strength and its compatibility with the coating material selected. Hexaloy SA SiC was chosen as the SiC material. Incoloy 909 was the low-expansion, Fe-based superalloy and Inconel 718 was the Ni-based superalloy. Both of these metal alloys provide adequate high-temperature strength and oxidation resistance while being representative of the wider range of Fe- and Ni-based superalloys.

The FEA study indicated that a material with a low CTE and a low yield strength was the ideal interlayer material. In practice, it is not possible to have both of these properties simultaneously in one material. Therefore, both types of interlayer materials were evaluated. Mo was selected for the 950°C application due to its low CTE, high stiffness, and high-temperature capability, while Ni was chosen for the 650°C application due to its low yield strength and low stiffness.

For most brazing systems, a reactive coating on the ceramic or a reactive component to the braze is needed to provide a driving force for wetting. The wetting experiments with the Au-5Pd-2Ni and the Au-5Pd-2Ni-1.25Ti braze alloys indicated that the Au-5Pd-2Ni braze wet the Ti coated PY6 and the Ti coated Hexaloy SA SiC with greater uniformity and consistency than

the Au-5Pd-2Ni-1.25Ti braze wet uncoated PY6 and uncoated Hexaloy SA SiC. Au-5Pd-2Ni and 30Au-34Pd-36Ni were selected due to their oxidation resistance, ductility, and relatively high melting points. The final braze alloys selected, Au-5Pd-2Ni and 30Au-34Pd-36Ni, did not contain Ti.

Ti coating was chosen over the Zr coating since Ti provided good reactivity with the PY6 and Hexaloy SA SiC. Ti also caused minimal degradation of the properties of PY6 as did the Zr coating.

For the verification of the FEA predictions with experiments, linkage between FEA and mechanical testing of brazed joints has been established under the assumptions that the effects of processing and the statistical factor for microcracking in the ceramic are not significant. However, large scatter in measured strengths and the difference between measured and predicted strengths indicate the importance of processing and statistical factors in the fracture. The measured strength values of the brazed joint were 30 - 90% of the joint strengths predicted by FEA.

The low high-temperature strength confirmed the need of new braze alloys and interlayer materials that can meet the high-temperature strength requirements. Nevertheless, the torsion strength of the joints at room-temperature were encouraging.

Overall results clearly showed that FEA is an effective tool to design the geometries for ceramic-metal joints and that joining by brazing is a suitable method for high-temperature heat engine applications.

PLANS FOR PHASE II AND III

Phase II. Material System and Design Optimization, and Joint Life Prediction

The goal of Phase II is to optimize materials systems and joint designs building on the results of Phase I. The work shall also include demonstration of the potential for scale-up of the joint size to interfacial areas of commercial significance, applicability of the analytical joint modeling tools and the ability to use these tools to design and predict the mechanical and thermal stability of the larger joints. These joints, referred to as "scale-up" joints, shall have the ceramic shaft at least 0.8 inches in diameter. The goal is to develop a system which can perform in an engine such as the ATTAP engine. The anticipated environment will be oxidizing and will have joint temperatures of up to 950°C. Improved joint materials systems shall be developed to optimize the combination of competing properties which include ductility, yield strength, and creep resistance. The effect of each of these properties on joint performance shall be examined using the FEM model. Finally, a program of mechanical testing shall be carried out to confirm the effectiveness of the modeling program. This shall include torsion tests, thermal and mechanical fatigue, and creep testing. In addition, an analytical and experimental program in service life prediction will be undertaken. The work in Phase II shall include five tasks (Tasks 5, 6, 7, 8 and 9):

Task 5. Materials System Optimization

Subtasks

In Phase I of this project, Inconel 718 and Incoloy 909 were selected as the structural alloys, nickel and molybdenum were selected as the interlayer materials, and PY6 (silicon nitride - 6 wt. % yttria) was shown to be the preferred ceramic. The continued program will be centered around these materials. Several braze alloys based on the Au-Pd-Ni and Au-Pd systems were studied. Because of the high-temperature strength of the structural materials and the joint geometry, the braze alloy is expected to be the weakest mechanical link in the joint system. Therefore, there is a need for the development of new braze alloys to provide the improved high-temperature properties required for the 650°C and 950°C ceramic-to-metal joints.

5.1. Braze Alloys

The starting point for braze alloy development will center on defining the limiting properties of a successful braze alloy. The FEM model developed during Phase I of this project will be used to define the amount of plastic deformation carried by the interlayer and braze materials. FEM will be used to determine the minimum amount of deformation in the braze alloy that is required to obtain a crack-free joint. The sensitivity of a successful, crack-free joint on the plasticity and yield strength of the braze alloy will also be determined. Once the limiting mechanical requirements of the braze alloy are

known, candidate material systems for the braze alloy will be identified and studied.

The first group of brazing alloys to be studied will be based on metal eutectic compositions with sufficient ductility and high-temperature oxidation resistance. Compositions of this type will promote fluidity and minimize porosity due to shrinkage during solidification. High melting point, oxidation-resistant metal systems will be evaluated with emphasis on metal eutectic systems (in contrast to non-eutectic Au-Ni or Pd-Ni) and on Ni-based alloys. The principle of diffusion solidification will be taken into consideration in the design of braze alloys.

A second group of candidate brazing alloys will be evaluated concurrently with the above group. These will be based on superalloy compositions and turbine blade repair braze alloys. Their relatively high yield stress and low ductility (compared with precious metals) should make them less forgiving and require reliance on the interlayer to accommodate differential expansion. The FEM model will be used to establish whether such a set of properties is a viable approach.

Initial screening of potential alloy systems will be based on published phase diagrams. Five samples will be required in each system to establish wetting. It will also be necessary to measure the mechanical properties of the braze with a minimum of three tensile specimens for each composition. The interactions between the braze alloy and metals will be examined using coupon samples. About twenty per composition are anticipated.

5.2. Interlayers

Previous work conducted in Phase I demonstrated the relative effectiveness of low yield strength materials and low CTE materials as interlayers in reducing the joint stress. Typical interlayer materials emphasized in Phase I were pure materials such as nickel, copper, molybdenum, tungsten and niobium. Improvements in performance are possible by using alloys which could provide combinations of properties unobtainable in pure materials. Service temperatures of the joints require combinations of high-temperature properties which are possible through alloying. For example, a nickel alloy could provide adequately low yield stress to avoid cracking the ceramic, while having improved creep resistance compared with pure nickel. Refractory metal alloys like Mo- and W-base could be acceptable with improved ductility, retaining their high-temperature properties and low CTE. Various alloys will be examined based on the working model developed in Phase I.

New interlayer ideas, such as multilayer materials, will also be examined in Phase II. An example of a multilayer material is an outer ring of Mo with an inner ring of Ni. Preliminary FEM conducted in Phase I show promise for these types of interlayers. The planned work would screen three or four candidate interlayers based on yield strength, CTE, creep strength, and oxidation resistance. Performance tests of room-temperature and creep strength will be carried out. Published data will be used to verify oxidation resistance and CTE.

5.3. Coatings

The study on new braze alloys and new interlayer materials will necessitate a review of the materials used to coat the ceramic component. Coatings on the ceramic are necessary in order to obtain wetting and adhesion between the chemically dissimilar braze and ceramic. The adhesion or wetting of a metal to a ceramic depends on the chemical compatibility between the metal and ceramic. Included in the concept of chemical compatibility is the nature of the wetting atmosphere, chemical bonds, chemical reactions, surface energy of the ceramic, and surface tension of the metal. The methodology for testing coatings developed in Phase I will be applied to the new study.

Task 6. Joint Design Optimization

Subtasks

6.1. Development of multiple interlayer joints (with Brown U.). Various multilayer systems shall be examined to minimize the stress generated from thermal expansion mismatch at the ceramic-metal interface. Analytical expressions shall be modified to account for the introduction of multiple interlayers in the structure. The modified expressions shall be used for the materials systems suggested by Task 5 with the use of finite element methodology.

6.2. Stress analysis of brazed joint and optimization (with Brown U.). Stress analysis shall be performed to take into account the dimensional change and composition change caused by the brazing process. FEM analysis of the joint system shall be done using the geometry of the joint and the properties of the braze alloy after brazing. Numerical stress analysis using the commercially available code, ABAQUS, shall be performed. The cylindrical joint shall be the basic joint design for consideration.

6.3. Stress analysis of structural alloy and optimization (with Brown U.). The effect of the overall macroscopic joint shape on the residual stress in the ceramic-metal brazed joint shall be studied by examining axisymmetric joints other than simple cylinders. The effects of tapers and reduced wall thickness are two of the geometrical factors that shall be addressed. The geometry of the structural alloy shaft shall be changed to reflect the findings.

Task 7. Joint Life Prediction Methodology and Testing

Subtasks

7.1. The gamma-criterion developed in Phase I shall be improved (with Brown University). Material data on the damage assessment and the crack growth, particularly for the ceramic components, shall be collected. Modeling of the crack growth failure mechanism shall be developed as a part of the ABAQUS-supported finite element braze joint model.

7.2. Mechanical fatigue. Mechanical fatigue tests shall be performed on the MTS machine purchased during Phase I. These tests shall cycle between 35

and 185 in-lbs with a frequency of 1.5 Hz. Ten samples (2 cm² joint area) shall be tested at each of two temperatures, 650°C and up to 950°C, for a total of twenty samples. Mechanical fatigue tests shall be run at constant temperature. The superimposed effects of mechanical and thermal cyclical loading may be investigated if time permits.

7.3. Creep characteristics of brazed joints. The creep characteristics of the final brazed joint shall be characterized. A brazed sample (2 cm² joint area) shall be loaded at a constant torque of 185 in-lbs and the rotational strain shall be measured as a function of time. These tests shall be carried out at 650°C and another temperature, up to 950°C. Ten samples shall be tested at each temperature, for a total of 20 samples.

Task 8. Fabrication and Evaluation of Scale-Up Size Ceramic-to-Metal Joints

8.1. Scale-Up Brazed Joint Production

Brazed samples shall be produced for performance testing. Joint design shall be based on analytical and experimental results from earlier portions of the program. These joints shall be prototypical of rotor-to-shaft joints in the ATTAP program. The ceramic shaft end in this engine has a diameter of about 0.8 inches. The length of the brazed ring around this shall be determined using FEM to evaluate the relationship between two competing effects. If the brazed length is excessively long, the likelihood of cracking the ceramic is high, resulting in weak joints. If the joint is too short, the stress in the braze would probably exceed its capacity. The FEM model shall be used to yield a workable solution and minimize the number of experimental samples needed. A minimum of 3 test joints shall be fabricated and tested, each at room-temperature, 650°C and 950°C.

Task 9. Reporting and Quality Assurance Requirements

Reporting and quality assurance requirements will be identical to those used for Phase I.

Phase III. Field Engine Testing and Development of Production Methodologies.

Phase III will involve engine testing to confirm the life cycle predictions of Phase II. Also, the issues associated with volume manufacturing and the development of realistic production yields of acceptable joints will be addressed.

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