Joining Silicon Carbide to Metals Using Advanced Vacuum Brazing Technology

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Introduction

This paper is based on research conducted during a ten-week summer internship in the Ceramics Branch at the NASA Glenn Research Center in Cleveland, OH. The project involved experimental research to investigate the joining response of bulk silicon carbide ceramics to a controlled expansion alloy, Kovar[1], and a light-weight high-temperature metal, titanium. The research project originated within the joining subtask of a technology development program at NASA Glenn to develop a Micro-Electro-Mechanical System Lean Direct (Fuel) Injector (MEMS LDI) for advanced aircraft gas turbine engines. The main goal of the research program is to reduce NOx emissions by 70% over the 1996 International Civil Aviation Organization standard and to reduce CO_2 emissions by 15% from modern high-tech gas turbine engines. NASA researchers are evaluating chemical vapor deposited (CVD) bulk silicon carbide (SiC) ceramics for the fuel injector substrates while Kovar and titanium are being evaluated as fuel supply tubes. The joining subtask aims to develop enabling technology to produce thermally stable, hermetic joints between SiC and metallic substrates.

Silicon carbide was selected because of its excellent thermal and mechanical properties; this allows for higher injector operating temperatures which increase the efficiency of gas turbine engines as well as reduce NOx and

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1. *Kovar is a nickel-cobalt ferrous alloy with thermal expansion characteristics similar to borosilicate glass. Kovar is a trademark of Carpenter Technology Corporation. The nominal composition (in wt %) of Kovar is53Fe-29Ni-17Co(<1.0% C, Si, Mn).*

CO_2 emissions. Kovar (density: 8,360 $kg.m^{-3}$) and titanium (density: 4,510 $kg.m^{-3}$) were chosen for testing because of relatively small mismatch between their coefficients of thermal expansion (CTE) and that of SiC which can reduce residual stresses introduced from joining. The CTE of SiC, Kovar and Ti are $4.1x10^{-6}$ K^{-1}, $5.1x10^{-6}$ K^{-1} and $8.6x10^{-6}$ K^{-1}, respectively.

Although ceramic joining technology for low use temperatures and low structural stresses has been highly developed since the 1940s, the technology of joining ceramics and ceramic-based composites for use at elevated temperatures, at high stress levels, and in corrosive (e.g., oxidizing) environments is less developed. Despite its enabling role, joining is often considered as secondary in importance in the design process. A designer may incorporate ceramics into a component as though they were metals, giving little attention to the unique joining and service requirements of ceramics. This may lead to two outcomes: i) either the part fails and the design engineers conclude that the ceramic was unsuitable and they must revert back to using metals as before, or ii) a costly redesign may be required if a ceramic must be used.

The ceramic joining technologies used today range from simple mechanical attachment such as the compression fit used in spark plugs to liquid phase processes such as brazing that is used in ceramic turbocharger rotors. Brazing is a process to join closely spaced solids by introducing a liquid metal that melts above 450C (840 F) in the gap followed by solidification of the metal supported and constrained by the solid surfaces.

Two fundamental requirements must be satisfied for a brazed joint to form: i) braze metal must wet and adhere to the joined surfaces, and ii) the joined materials must have similar expansion properties to avoid residual stresses being introduced in joined materials. Unlike brazing of metal parts for which these requirements are rather easily met, brazing of ceramics to metals at elevated temperatures poses considerable challenge.

Most ceramics are inherently difficult to wet using common filler metals which simply ball up when melted in contact with ceramics. A new family of alloys, collectively called Active Braze Alloys (ABA), has been developed to braze ceramics. In addition, the significantly different contraction properties of metals and ceramics induce considerable residual stress and increase the propensity for the brittle ceramic to fracture. These problems are compounded by the extreme reactivity of molten fillers with atmosphere or contaminants from flux residues (when protective fluxes are used). Ideally, the braze filler should react with the ceramic in a controlled manner in order to form a thin interfacial layer of wettable reaction products that would promote wetting and facilitate braze spreading and bonding upon solidification while avoiding excessive chemical attack and degradation of the ceramic.

Thus, formation of brazed joints is controlled by a number of key variables such as contact angle, surface tension, viscosity, density, filler/ceramic reactivity, surface preparation, joint design and clearance, temperature and time, rate of heating and cooling, atmosphere and thermal expansion properties of substrates and filler metal, and the strength, stiffness, and ductility of the filler and joined materials.

The self-joining behavior of silicon carbide ceramics has been reported in earlier studies [1-3]; however, research studies on joining of SiC to high-temperature alloys are scant. The present work aims to contribute to the technical literature in this area while attempting to demonstrate the feasibility of joining SiC to metals for NASA's fuel injector program. The research reported in this paper was conducted as part of Lewis' Educational and Research Collaborative Internship Program

(LERCIP) over a ten-week period during June-August 2009. The objective was to demonstrate the joining of silicon carbide to titanium and Kovar, and investigate the integrity, microstructure, chemical interaction, and microhardness of the joint with the aid of optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and Knoop microhardness testing.

Experimental Procedure

The first step in the research was to identify a braze filler suitable for joining the silicon carbide ceramics to Kovar and Ti. For this purpose, an Active Braze Alloy (ABA), was identified. The ABAs have been designed to contain a reactive element (e.g., Ti, Cr, Zr etc) that induces a reaction of braze with the ceramic and decreases the contact angle thus facilitating braze spreading and bonding. Three ABA's, Incusil-ABA, Cusil-ABA, and Ticusil, each containing different percentages of Ti as an active metal, were selected for brazing runs. The chemical composition, liquidus temperature, and selected physical and mechanical properties of these baze alloys are listed in Table 1. These brazes were obtained from Morgan Advanced Ceramics, Hayward, CA in either foil or powder form. Two types of silicon carbide substrates were used for brazing: chemical vapor deposited (CVD) silicon carbide, and sintered silicon carbide (called, Hexoloy SiC). Unlike the chemical vapor deposited (CVD) SiC, Hexoloy SiC (a product of St. Gobain) is a sintered silicon carbide (α~phase) material. The material is designed to have a homogeneous composition and is produced via pressure-less sintering of fine (submicron) silicon carbide powder.

Silicon carbide and metal substrates were sliced into 2.54 cm x 1.25 cm x 0.25 cm pieces using either a diamond saw (for SiC) or a ceramic blade (for Ti and Kovar). The braze foils (~50 μm thick) were cut into 2.54 cm x 1.25 cm pieces. All materials were ultrasonically cleaned in acetone for 15 min. prior to joining. The braze foils were sandwiched between the metal and the composite, and a normal load of 0.30-0.40 N was applied to the assembly. Braze foils are easier to use than braze powders especially for small gaps in which powder paste application could be difficult. Additionally, the residual organic solvents in powder pastes could cause soot formation and furnace fouling. However, as braze powders are used in industrial work, a few braze runs were made using braze powders in place of foil in order to examine the differences, if any, when using foils and powders. For this purpose, braze powders were mixed with glycerin to make a thick paste with dough-like consistency, and the paste was applied using spatula to the surfaces to be joined. The assembly was heated in an atmosphere-controlled furnace to the brazing temperature (typically 15-20 °C above the braze liquidus) under vacuum (10^{-6} - 10^{-5} torr), isothermally held for 5 min. at the brazing temperature, and slowly cooled to room temperature. A total of 35 separate joints were created.

The joined samples were visually examined, then mounted in epoxy, ground and polished on a Buehler automatic polishing machine using the standard procedure, and examined using optical microscopy (Olympus DP 71 system) and scanning electron microscopy (SEM) (JEOL, JSM-840A) coupled with energy dispersive x-ray spectroscopy (EDS). The elemental

Table 1.
Selected Properties of ABAs and Substrate Materials used for Brazing

Braze	Braze Composition (wt%)	TL, C	E, GPa	YS, MPa	UTS, MPa	CTE×106, K-1	% El	K, W/mK
Incusil-ABA®	59Ag-27.3Cu-2.5In-1.25Ti	715	76	338	455	18.2	21	70
Cusil-ABA®	63Ag-35.3Cu-1.75Ti	815	83	271	346	18.5	42	180
Ticusil®	68.8Ag-6.7Cu-4.5Ti	900	85	292	339	18.5	28	219
SiC	100% α-phase	-	466	-	-	~4*	-	-
Kovar	53Fe-29Ni-17Co (<1.0% C, Si, Mn)		137	344	516	11.5**	30	17.3
Ti	Commercial purity		105	480	550	9.7**	15	17.2

E: Young's modulus, YS: yield strength, TS: tensile strength, CTE: coefficient of thermal expansion, %El: percent elongation, K: thermal conductivity. * 0 -1000°C, **30 – 900°C, *** 0 – 540°C, ® Morgan Advanced Ceramics, Hayward, CA.

composition across joints was accessed with the EDS and presented as relative atomic percentage among the alloying elements at point markers on SEM images. The polished joints were subjected to microhardness test with a Knoop micro-indenter on Struers Duramin-A300 machine under a load of 200 g and loading time of 10 s to develop hardness profiles across joints. Multiple hardness scans were accessed across joints to check the reproducibility of the measurements.

Results and Discussion

All self-joined SiC substrates with the three brazes revealed excellent, crack-free joints. Similar baseline data on self joined Ti and Kovar substrates confirmed the bonding capabilities of all braze alloys. Figure 1 shows the joint microstructure in self-joined SiC (Fig. 1a & b) and self-joined Kovar (Fig. 1c) made using Ticusil braze. The braze interlayers in self-joined SiC were well-defined and very consistent. The self-joined Kovar revealed some voids, possibly due to solidification shrinkage. In self-joined Ti, the braze layer appeared to reconstitute itself with the Ti substrates and obliterated the braze layer boundary which was no longer visible thus yielding a homogenous material (some shrinkage voids formed during braze solidification and decorated the boundary). Overall, these self-joining trials confirmed that the active metal Ti induces a surface modifying reaction and promotes wettability (contact angle < 90°). These baseline tests were used to confirm the wettability enhancing role of titanium in ABAs in the absence of residual stresses resulting from a mismatch between the coefficients of thermal expansion (CTE) of joined substrates.

In CVD SiC/Cusil ABA (1 foil)/Ti joints, SiC did not bond with Ti because of incomplete wetting of SiC by braze. However, there was good wetting of Ti by braze. Using two braze foils in place of one did not yield improved surface coverage; additionally, three braze layers were also used. With 2- and 3- braze foils, the braze region was consistent but with some voids present, and a reaction layer (possibly nickel- or titanium silicide) had formed. However, the SiC substrate in both samples exhibited significant cracking, both parallel and perpendicular to the braze region. Significant areas near the joint showed evidence of melting of the Kovar substrate. Some of the braze constituents may have diffused and dissolved into Kovar thus lowering its liquidus temperature. Large voids visible throughout the braze layer also suggested possible melting and solidification.

With Cusil-ABA paste in place of foils (Fig. 2), however, no cracking was visible. The braze region was very consistent (Fig. 2a), and there was no separation between braze and SiC. Optical microscopy and SEM showed a distinct dark layer (~3-5 μm thick) at the braze/SiC interface (Figs. 2b & c); presumably a titanium silicide reaction layer based on the elemental concentrations accessed via EDS (Figs. 2d & e). The Knoop hardness profiles (Fig. 2f) displayed the expected behavior with a sharp discontinuity at the SiC/braze interface. Although the joint exhibited good wetting, preliminary mechanical testing showed that the joint was not very strongly bonded. Research on diffusion bonding of SiC laminates using titanium interlayers has shown that titanium silicides exhibit strong thermal expansion anisotropy [4]; this behavior could lead to uneven shrinkage during cooling of the joint leading to residual stresses that would weaken the joint in spite of good chemical wetting and bonding. Reaction layers in self-joined SiC using Ag-Cu-Ti filler have been shown to be composed of Ti_5Si_3 and TiC[1].

In Hexaloy SiC/Cusil ABA (1 Foil)/Kovar joints, significant cracking in SiC substrate perpendicular and parallel to the braze region occurred. Additionally, micro-cracking occurred within SiC/braze reaction layer and Kovar/SiC reaction layer. The reaction layer plus the braze region was ~180 μm thick. The Hexoloy SiC/Cusil-ABA/Kovar joints with double braze foils also displayed cracks within SiC both transverse and parallel to the joint (Fig. 3a). The braze region appeared to be microstructurally consistent (Fig. 3b) and displayed a reaction layer at SiC/braze interface. Nickel and silicon enrichments were detected in this reaction layer using EDS; this could suggest possible formation of nickel silicide. The SiC/Cusil-ABA/Kovar joint made using braze paste displayed significant cracking in SiC both perpendicular and parallel to the braze region. The braze region exhibited considerable variation in its microstructure together with significant interaction between braze and both SiC and Kovar. These joints were fabricated using SiC and Kovar substrates of the same thickness (3mm) to reduce warping; however, residual stresses in the joint were evidently high as was evidenced by the significant amount of cracking in the SiC substrates. In spite of large residual stresses, Cusil-ABA formed an adherent joint with SiC and Kovar and revealed a reaction layer (possibly nickel silicide) further supporting the conjecture that nickel silicide possibly forms a stronger bond with SiC than does titanium silicide.

In SiC/Incusil-ABA/Kovar joints with either single- or double braze foils, cracking parallel and perpendicular to the braze region occurred in the SiC substrate (Fig. 4a). The braze region was consistent and revealed chemical interaction with the substrate together with the formation a dark layer at the joint interface (Fig. 4b). The microhardness distribution for this joint is shown in Fig. 4c. In SiC/Incusil-ABA (1 foil)/ Titanium joints, major cracking parallel and perpendicular to the braze region occurred throughout SiC and a large gap appeared between SiC and braze. A diffused reaction layer formed at Ti/Incusil-ABA interface. Use of 2 foils eliminated cracks parallel to the joint; however, cracks transverse to the joint persisted in the SiC substrate. There was a ~20 μm gap between SiC and braze region but the bonding between the braze layer and Ti was excellent. There shall be less effective stress accommodation in Incusil-ABA than Cusil-ABA owing to the former's higher yield strength (338MPa) than the yield strength (271 MPa) of Cusil-ABA; the lower yield strength of Cusil-ABA will facilitate stress accommodation via plastic flow. Initial results suggest that, although the SiC/Incusil ABA/Kovar bonds are strong, residual stresses are higher and produce more significant cracking than when using Cusil ABA as a braze material.

These preliminary research outcomes suggest that as far as wettability enhancement and surface coverage are concerned, the selected ABAs (Cusil-ABA, Ticusil and Incusil-ABA) are adequate to join SiC to Ti and Kovar. However, extensive substrate cracking without joint failure observed in some joints suggests that residual stresses during joint fabrication possibly override and inhibit the beneficial effects of chemical reaction-induced wettability and bonding.

Thus, engineering considerations related to residual stresses and strains could take precedence over chemical factors that facilitate joining.

Large residual stresses from brazing could cause the ceramic to fracture without failure of the brazed joint. Residual stresses are a major concern in ceramic-to-metal joints because of the inherent brittleness of ceramics and fracture may occur if these stresses cannot be managed. One strategy to manage residual stresses is judiciously arranged compliant interlayers within the joint prior to brazing [5]. Residual stresses in joints are more effectively accommodated by multiple interlayers than single layers. However, multiple interlayers also increase the number of interfaces and the probability of defects besides increasing the joint thickness.

Table 2
Calculated Strain Energy in SiC in SiC/Ti and SiC/Kovar Joints made using Ni and Cu Interlayers

Joint with Interlayer	Strain Energy in Silicon Carbide (mJ)		
	Incusil-ABA	Cusil-ABA	Ticusil
SiC/Cu/Kovar	1.59	1.66	1.73
SiC/Cu/Ti	1.44	1.49	1.54
SiC/Ni/Kovar	6.74	6.97	7.16
SiC/Ni/Ti	6.17	6.34	6.49

In order to investigate how residual stresses influence and are influenced by multilayer joints, the combined effects of metal (M), ceramic (C), and interlayer material (I) must be considered. Analytical and numerical models of residual stress distribution have been developed [6,7]. A numerical model for strain energy in ceramics in brazed joints developed at MIT [6,7] allows analytical approximations to the numerical model. For well-bonded ceramic-metal joints, the elastic strain energy, U_{eC}, in the ceramic substrate for a flat-back (e.g., disc-shaped) joint configuration can be estimated from [6,7]

Ue,c = (σYI2r3/EC){0.03ΠI + 0.11φ + 0.49}

where $\Phi = 1 - (\frac{\alpha_M - \alpha_I}{\alpha_C - \alpha_I})^m$, and $\Pi_I = \frac{(\alpha_M - \alpha_C)\Delta T E_I}{\sigma_{YI}}$

Here σ_{YI} is the yield strength of the interlayer, r is the distance from the center of the joint, E_C and E_I are the elastic moduli of the ceramic and the interlayer, respectively, and α is the CTE of the subscripted phases (i.e., C, M and I). The exponent m=1 for $\alpha_I > (\alpha_M + \alpha_C)/2$, and m=–1 for $\alpha_I < (\alpha_M + \alpha_C)/2$. Using the preceding model equations and the property data in table I (and handbook data for Ni and Cu interlayers), strain energies for joints made using the three ABAs were calculated using MS-EXCEL. The results summarized in Table 2 show that the strain energy varies between 1.4-6.7 mJ. Similar calculations for joints made without ductile interlayers yield higher strain energy values; for example, for SiC/Kovar joints made using Cusil-ABA, the calculated strain energy, U_{eC}, is 17.9 mJ, which is appreciably greater than the strain energy obtained with the use of ductile Cu and Ni interlayers (Table 2). Thus, judicious arrangement of stress-absorbing compliant layers of ductile metals such as Cu and Ni within the joint could reduce the strain energy and propensity for joint failure. Research on the use of single and multiple Ni and Cu layers to join SiC was also undertaken during the ten-week period at NASA Glenn. Several joints with multiple interlayers of Ni, Cu and other metals were created and characterized to test the effectiveness of this strategy to manage residual stresses. The results of these tests will be presented elsewhere [8].

Future Research and Applications

Future research will include further investigation of single and multiple Ni and Cu layers utilizing mechanical testing in order to evaluate the effectiveness of this approach and its ability to absorb residual stresses. Joints consisting of Kovar and titanium tube material bonded with SiC substrates will be fabricated and characterized to determine the effect of increased geometric complexity on residual stress levels within the joints. These joints will be sectioned and characterized in a similar fashion to the rectangular substrates previously discussed. Optical microscopy, scanning electron microscopy coupled with energy dispersive x-ray spectroscopy, microhardness testing and mechanical testing will be conducted to assess the ability for the brazes to produce thermally stable, hermetic joints between SiC substrates and metallic tube materials. Applications for this research as a key enabling technology are broad. Direct applications include the completion of a Micro-Electro-Mechanical Lean Direct Injector for subsonic gas turbine engines. The injector can be utilized in many applications ranging from military ground and aero turbine engines as well as commercial jet engines. This would have a direct impact on emissions as well as the efficiency of the engines allowing for cleaner and lower cost operation. With the increased interest in utilizing ceramics within turbine engines to allow for higher operating temperatures, metal to ceramic joining optimization will become an increasingly important enabling technology for ceramic integration.

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