



Article Nickel Coatings on Ceramic Materials Using Different Diffusion Techniques

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Abstract: Diffusion bonding is a process that has proven effective for the joining of metal to ceramic, but the differences in coefficient of thermal expansion still pose challenges during and after the bonding process. This work details the exploration of traditional diffusion-bonding processes using two traditional approaches, which include bonding of a 99.9+% pure Ni foil to SiC, Si₃N₄, and YSZ disks using (1) a hot isostatic press (HIP), with and without added weight to promote interfacial contact, and (2) field-assisted sintering (FAST). Samples were consolidated by heating to 1200 °C and held for 6 h under vacuum before cooling to room temperature during the HIP method. For the FAST technique, bonding experiments were performed at both 800 °C and 1200 °C in a vacuum environment under 10 MPa uniaxial pressure. After the Ni was bonded to the ceramics, diffusion heat treatments were carried out in the HIP. For electroless-plated samples, the heat-treatment temperature was chosen as 825 °C to avoid melting. For electroplated samples, heat treatment occurred at 925 °C or higher. Electroplated YSZ samples were heat-treated at 1150 °C as the Ni-Si eutectic is not a concern in this system. The time at temperature varied from 6 h to 48 h depending on the material combination tested. Post-heat-treatment diffusion characteristics were analyzed using scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS). A main cause of poor bonding performance in the HIP samples was reduced interfacial contact, while cohesive failures in the FAST samples are likely due to the formation of brittle intermetallic Ni-Si phases. Preliminary results indicate success in bonding Ni to SiC, Si₃N₄, and YSZ using a diffusion-enhanced approach on electroplated specimens.

Keywords: hot isostatic pressing; field-assisted sintering; diffusion bonding; ceramics

1. Introduction

Diffusion bonding is a specific process that has been proven effective in joining dissimilar materials. The process is based on the reduction of free energy and the chemical potential difference that results when two surfaces form an interface. This process occurs when extremely clean surfaces are brought into contact in ultrahigh vacuum (UHV). The free energy is reduced when close contact is established between the two surfaces. Generally, heat serves as a driving force for interfacial bonding, as the process is not spontaneous at atmospheric conditions. Factors such as temperature, diffusion coefficients, and reactivity of the species involved can help to increase the driving force. Reactive species present at the joining surface can enhance the joining process through the formation of stable compounds. An advantage of diffusion bonding is its ability to join large surfaces with little macroscopic deformation of the base materials during the process. Some disadvantages include long joining times and the requirement for a high-temperature environment during joining [1–5].

The broad term "diffusion bonding" is used to describe bond formation resulting from a solid-state diffusion process. There are many advantages to the diffusion-bonding



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). process, including bonds of similar strength to the strength of the bulk substrate materials, flexibility in the size of materials to be joined, ability to effectively join dissimilar materials, and corrosion resistance because fluxes are not required. In general, a well-sealed interface is created through diffusion bonding. However, substantial amounts of time are often necessary to achieve the required extent of diffusion. Hot presses or similar equipment are often used to provide adequate temperature and pressure in an inert or vacuum environment, limiting the size and geometry of components that can be bonded based on chamber size. Substrate surfaces must be carefully prepared to eliminate surface oxide films and contamination, which may reduce the strength of the bond or prevent bond formation altogether [1,3,6].

The three major parameters governing the diffusion-bonding process are temperature, time, and pressure. Temperature is the parameter with the largest impact on the diffusion process. Generally, temperatures between 50 and 80% of the melting point of the joined materials are sufficient to produce strong bonds via diffusion, though up to 90% is sometimes required for metal-ceramic bonds due to the dissimilarity of the materials. Higher bonding temperatures lead to more extensive atomic diffusion [3,7]. Generally, the temperature dependence of the diffusion coefficient follows an Arrhenius relationship. Though Arrhenius behavior is common, it cannot be assumed in all situations, for example, in cases where multiple diffusion mechanisms are active or impurities are present [7]. Reaction zones increase in depth with increasing bonding time. One way to visualize the effect of increased process time is through concentration profiles. These indicate the concentration of diffusing species as a function of position in the sample, choosing an arbitrary location (often the interface) as the zero point. Concentration profiles taken after different diffusion times illustrate changes in elemental concentration at each time step, providing evidence for diffusion's dependence on time [3]. A third relevant parameter in the diffusion-bonding process is pressure. Pressure applied during bonding is usually less than 100 MPa, though it is material-dependent and is much less than the yield stress of the material at room temperature. Applied pressure imparts microscopic deformation on the surface asperities, breaking down surface oxides at the bonding interface, increasing contact area, and, as a result, increasing bond strength [3]. Applied pressure has also been shown to decrease the concentration of vacancies in the material by limiting the increase in volume of the solid that is caused by vacancy formation. As a result, the rate of diffusion occurring by vacancy mechanisms is expected to decrease with increasing pressure [8].

Diffusion bonding is typically achieved through a hot press setup, where mechanical rams are used to apply a uniform force to the materials while a furnace heats the materials to the desired bonding temperature. In a hot press, heating is achieved through resistance or induction heating of the die where uniaxial pressure is applied, causing increased compression on the top and bottom resulting in anisotropic properties in the component. To address this issue, hot isostatic pressing (HIP), which applies isostatic pressure through a liquid or gas fluid, thereby facilitating the collapse of internal voids, is used to create a uniform structure and resulting properties. The HIP process accommodates temperatures up to 2500 °C and pressures up to 320 MPa, producing near-net shaped, full-density compacts with negligible microstructural variations.

An emerging technique, field-assisted sintering technology (FAST), also known as spark plasma sintering (SPS), is quite similar to traditional hot pressing. Much like hot pressing, uniaxial pressure is applied to the die or green body to aid in compaction and sintering. However, during the FAST process, rapid heating is achieved by a low-voltage, pulsed current induced in the green body. For conductive materials, current can pass directly to the materials to be sintered, causing them to heat up via Joule heating. For nonconductive materials, a conductive die, such as graphite, is heated via Joule heating to increase the temperature of the green body. When composite materials whose components have different electrical conductivities are sintered, current flows through the die and into the sample, passing easily through the conductive component [9]. Three main factors impact the FAST process: (1) mechanical impacts due to applied pressure, (2) thermal impacts due to high heating rates, and (3) electrical effects due to current flows through the die and material [9]. During the FAST process, a compressive load is applied to the material in the die. For powder compaction and sintering via FAST, this helps to increase contact between the particles, sometimes by deforming them. This also helps to accelerate densification by promoting grain boundary diffusion, lattice diffusion, and viscous flow while also initiating other mechanisms such as plastic deformation or grain boundary sliding.

One distinguishing characteristic of the FAST process is a rapid heating rate [10-13]. This can be exceptionally advantageous in powder sintering and compaction if the main mechanism resulting in densification has a higher activation energy than the mechanism responsible for coarsening (grain boundary diffusion vs. surface diffusion, respectively). By rapidly heating the material, the densification rate can be increased while slowing the rate of microstructural coarsening. The rapid heating rate can also increase the rate of power-law creep in metals. Another advantage of the rapid heating achieved in FAST is the reduction in negative interactions between the material and the die because they are in contact for shorter amounts of time. Finally, locally increased temperatures and temperature gradients can result from the rapid heating. These thermal gradients provide a driving force for diffusion. However, they can also induce thermal stress due to the creation of macroscopic temperature fields [9]. The rapid heating of FAST can also be advantageous in diffusion bonding of bulk materials due to the creation of an additional driving force for diffusion (Ludwig-Soret diffusion). Grain growth is avoided, promoting the diffusion and bonding processes and leaving more grain boundaries for rapid diffusion. Finally, the use of an electric field during the bonding process impacts the resulting densified and sintered material. The electrical conductivity of the powder determines the current's impact. For conductive powders, high levels of electrical current can pass through the green body directly, instead of being isolated to the graphite die. The current can result in percolation effects, the Peltier effect between the die and the green body, electrochemical reactions, and electromigration. A green body has not reached full density and thus has inhomogeneous regions. This leads to inhomogeneous current flow, creating local hot spots that can lead to the development of microstructures that differ from those expected from traditional sintering experiments. Electrochemical reactions and electromigration can also occur, leading to unexpected microstructures [3]. Electrical current may impact the diffusion-bonding process, as well. Additionally, electromigration may promote diffusion from one substrate to the other. Though the technique is commonly used for sintering green bodies, some research has explored the possible application of FAST technology in bonding dissimilar materials. Lin et al. [10] studied the joining of dissimilar Ni-based alloys for turbine applications. Traditional bonding techniques, such as friction welding, electron beam welding, and laser beam welding were successful in bonding the two materials but led to microstructural differences in the heat-affected zone at the interface. In contrast, FAST technology successfully joined the dissimilar alloys without a heat-affected zone or detrimental microstructural changes. Additionally, Zhou et al. [11] successfully bonded carbon-fiber-reinforced carbon composites using a Ti₃SiC₂ film interlayer with FAST. As the composite is electrically conductive, bonding was successful without the use of a graphite die. Strongly bonded couples were created whose strength was dependent on the bonding temperature based on the phases formed due to interfacial reactions.

FAST is gaining popularity due to its relatively low processing time compared to traditional methods like HIP [12]. In addition to producing complex materials that traditional methods are unable to produce, FAST has other advantages such as producing complex shapes and microstructures [11–14]. Ghasalia et al. [13] successfully created FGM composites made from laminated Ni powder and WC-based cermet using the SPS technique. They attributed the significant hardness to the formation of intermetallic compounds and carbides as well as the location of the Ti-based layer in the consolidated material. Other researchers [14] found success using the SPS technique to synthesize fully dense titanium laminated composites from Ti and carbon materials. The benefits of the FAST process enticed Luo et al. [15] to produce AlB₁₂-AlB₁₂C₂-TiB₂ composites with resulting high hardness and K_{IC} values that they attributed to the TiB₂ elongated microstructure. More recent work, where the researchers focused on studying the sintering mechanism [16,17], demonstrated similar results. The FAST process parameters can be tailored to achieve desired microstructure and material properties. To accomplish this, parameters need to be optimized, and using trial and error is often costly and time-consuming. With this in mind, some researchers [17–19] believe numerical simulation of FAST in parallel with experimental tests is necessary for optimization. The summary of the literature reveals that for predicting the density evolution in the sintering process, there is no existing systematic material parameter identification framework that can demonstrate valid results using various processing conditions. As such, Kumar et al. [20] set out to fill this research gap and developed a numerical-experimental framework for modeling the FAST process at different heating rates. Their approach involved dividing the sintering process into two stages, where material parameters are identified in each stage based on porosity values. They validated their modeling using two different materials under different heating-rate conditions and successfully demonstrated the predictive capability of the sintering model for copper and nickel [20].

The current work involves the use of HIP and FAST to bond nickel foil to silicon carbide (SiC), silicon nitride (Si_3N_4), and yttria-stabilized zirconia (YSZ) substrates. The difference in electrical conductivity between the Ni foil and SiC, Si₃N₄, and YSZ disks will lead to high current flow through the metal and lower current flow through the ceramic. The greater resistance of the ceramic causes it to heat more quickly or to a higher temperature than the surrounding die. The applied load aids in creating contact between the two layers, as observed in powder compaction and sintering. The load may also facilitate breaking up any interfacial oxide layers. SiC, Si_3N_4 , and YSZ have high tolerance for compressive stress, high values of fracture toughness, and high corrosion resistance. These properties make them ideal materials for applications where high compressive strength and low tendency for degradation are necessary. Unmanned underwater vehicles (UUVs) are used for ocean-floor exploration, oceanic research, ocean-bottom seismometers, and military applications [21,22]. Currently, most UUV shells are constructed entirely of metallic materials, such as aluminum, titanium, or high-strength steels. However, as UUVs are required to operate in deeper underwater regions at higher speeds, shells that are stronger and lighter-weight are required. It is known that ocean pressure increases by approximately 1 atm for every 10 m of ocean depth [21,22]. Thus, a vessel diving to great depths in the ocean will be subjected to high levels of compressive stress. In order to operate a unit composed of a metallic shell at great depths, extremely thick shell walls would be required in order to withstand these high levels of compressive stress. Though strength would be added to the structure, the UUV would also be very heavy and possibly exceed its buoyancy limits. Corrosion resistance is also an important consideration in the design of underwater vehicles, as exposure to salt water has been shown to cause corrosion and degradation in many metallic materials, further limiting the possible materials of construction. Finally, it is desirable to produce the shell from a lightweight material to enable faster underwater travel [23]. In choosing a new material for UUV shells, ceramics attract attention. Many ceramic materials are resistant to corrosion, exhibit high compressive strength, and have low specific gravity, improving their buoyancy [21,22]. Thus, their use is proposed for the construction of UUV shells. Some desired properties for the construction of a structural shell are high hardness, high corrosion resistance, and wear resistance. Though ceramics possess some of these desirable properties, they also tend to be brittle. Care must be taken to select ceramic materials with high toughness to prevent crack propagation and eventual failure [22]. These materials also can be susceptible to wear, particularly fretting wear if a component is rubbed back and forth across the surface, leading to catastrophic failure [24]. This fretting wear could occur during operation of a UUV as well as during movement and handling. Undersea vessels face continual challenges to dive deeper and move more quickly through the water. With increasing ocean depth comes substantial increase in pressure, requiring that vessels be constructed of materials with a high tolerance for compressive stress. In addition, the material must be tough in order to prevent fracture and failure if damage is caused, either on land or in operation. With this application in mind, it is proposed that a metallic pad be added to the surface of the ceramic shell as a wear surface that prevents contact between the hardware and shell, thus reducing the likelihood of damage. This work explores the application of a metallic layer, in this case nickel, to these tough ceramic materials to act as a wear surface to prevent ceramic damage. However, the joining of metals to ceramics can be challenging due to differences in their mechanical and chemical properties, and this issue was expected when executing the present study.

The goal of the current study was to successfully bond a nickel layer to tough ceramic substrates such as SiC, Si_3N_4 , and YSZ. A well-sealed, strong metal–ceramic bond is necessary in applications to prevent seawater intrusion that may cause corrosion or separation of the two layers. Bonding of the layers was accomplished through traditional diffusion-bonding approaches, in which bond formation is due to elemental interdiffusion and diffusion-enhanced bonding techniques, where elemental diffusion is used to enhance the bond formed. Diffusion-enhanced bonding approaches focused on bonding the Ni to the ceramic prior to diffusion treatment, so that diffusion enhances the sealing of the interface and the bond strength rather than forms the bond. To the knowledge of the authors, the studying of the utilization of these manufacturing techniques and comparing their effects on the bonding processes of these specific materials have not yet been performed.

2. Materials and Methods

Substrate surface preparation ceramic disk substrates were polished using Cameo Disk prepolishing disks (Leco Corp., St. Joseph, Michigan, USA) on a Leco GPX300 automatic polishing system. Cameo disks are grinding disks composed of diamonds embedded in a polymer matrix and are available in diamond grain sizes comparable to standard SiC grinding paper grits. These were used to efficiently grind the hard ceramic substrates while avoiding embedded SiC grit that may result from the use of traditional SiC abrasive papers. A special fixture was designed and fabricated in-house from Al6061 to securely hold the ceramic disk that could be used with the polisher's individual sample head. Substrates were prepared to four different roughnesses using the procedure outlined in Table 1. The average roughness achieved from each grinding condition is shown in Table 2.

Table 1. Grinding parameters used to prepare ceramic substrates.

Step Number	1	2	3
Time (min)	3	2	2
Wheel Direction	CW CW		CW
Wheel Speed (rpm)	150	150	150
Head Type	Central	Central	Central
Head Force (lbf)	3	3	3
Head Direction	CCW	CCW	CCW
Head Speed (rpm)	150	150	150
Pad Type	Cameo PI	Cameo P2	Cameo P3

Table 2. Average surface roughness obtained for each disk type.

	As-Received	Step 1	Step 2	Step 3
SiC	$1.457\pm0.514~\mu\text{m}$	$0.182\pm0.047~\mu m$	$0.130\pm0.033~\mu m$	$0.077\pm0.014~\mu m$
Si ₃ N ₄	$0.578\pm0.140~\mu\textrm{m}$	$0.208\pm0.076~\mu m$	$0.100\pm0.076~\mu\text{m}$	$0.049\pm0.010~\mu m$
YSZ	$0.661\pm0.205~\mu m$	$0.316\pm0.087~\mu m$	$0.316\pm0.087~\mu m$	$0.047\pm0.016~\mu m$

The purpose of the grinding/polishing procedure was to produce disks of four distinct, uniform surface roughness. The surface roughness goals were 0.05 μ m, 0.1 μ m, 0.3 μ m, and 0.5 μ m (2, 4, 12, and 20 μ in, respectively). The average obtained for the disks varied from the goals, though individual disks were selected for use from each group that were closest to the roughness goal for that group.

Field-assisted sintering technology (FAST) was used to bond pure Ni foil to as-received SiC disks. An FCT Systeme GmbH FAST with maximum capacity of 25 tons was used in these experiments. Bonding experiments were performed at both 800 °C and 1200 °C in a vacuum environment under 10 MPa uniaxial pressure. Pressure was applied at ambient temperature and maintained throughout the experiment. Prior to bonding, samples were ground to the desired surface roughness, wiped with isopropyl alcohol, and dried in a stream of compressed air. The substrates were then layered into a graphite die, with the Ni disk in contact with the ceramic substrate. The system was held at temperature for 10 min before naturally cooling to room temperature. Figure 1 shows an illustration of the specimen configuration in a graphite mold before the sintering process.



Figure 1. Schematic illustration of the FAST (left) and HIP (right) processes before sintering and consolidation.

Diffusion bonding was carried out using an American Isostatic Presses hot isostatic press (HIP). Nickel was applied to ceramic substrates in several ways before treatment in the HIP. The first method was the use of pure nickel foil (99.9+% pure, Edgetech Industries, LLC, Weston, FL, USA) placed in contact with the ceramic substrate prior to heat treatment. Prior to bonding, samples were cleaned in ethanol. The first trial involved placing an asreceived Ni foil disk on top of a ground Si₃N₄ substrate or a ground YSZ substrate within an Al₂O₃ o-ring that was used to maintain alignment of the two materials (Figure 1). The HIP was heated to 1200 °C and held for 6 h under vacuum before cooling to room temperature naturally. In the second experiment, a 7.9 lb weight (approximately 2.6 lbs/sample) was placed on top of three nickel–ceramic couples with a piece of Al₂O₃ rod used as a spacer to prevent reaction between the couple and the weight. The HIP was heated to 1200 °C and held for 6 h under vacuum before cooling naturally to room temperature. A higher temperature (1150 $^{\circ}$ C) was used to treat one YSZ electroplated sample, as the Ni-Si eutectic is not a concern in this system. The time at temperature was varied from 6 h to 48 h depending on the material combination being tested. The heat-treatment procedure was as follows:

- 1. Load sample(s) into Al_2O_3 HIP crucible.
- 2. Pressurize chamber with Ar to 30 MPa.
- 3. Heat to $20 \degree C$, hold for 1 h.
- 4. Ramp to hold temperature at $5 \,^{\circ}C/min$.
- 5. Hold at 825 °C or 925 °C or 1150 °C for x h.
- 6. Turn off heater, allow system to cool to room temperature naturally.
- 7. Depressurize the chamber and remove sample(s).

3. Results and Discussion

Two main approaches were tested that involved bond formation and diffusion occurring simultaneously, with bonding resulting from diffusion. The first approach tested was joining Ni foils to Si_3N_4 and YSZ in a hot isostatic press, either with or without the use of a weight to increase interfacial contact. The second approach was the use of field-assisted sintering technology (FAST). This approach is similar to the use of a hot press but varies in the mechanism of heating.

3.1. Nickel Foil in Hot Isostatic Pressing

The first approach explored for joining of 1" diameter $\times 0.02$ " thick nickel disks of 99.9% purity to ceramic substrates. The ceramic disk was simply stacked on top of the nickel disk within an alumina o-ring with an inner diameter slightly larger than the outer diameter of the substrates. The materials were heated in a vacuum environment, held at 1200 °C for 6 h, and allowed to cool in the furnace before removal and analysis. The time and temperature combination was chosen based on literature [19], where sintered Si_3N_4 disks were bonded to Ni foil in a vacuum hot press at 1100 °C or 1200 °C at 10 MPa for 0.5-6 h. Si₃N₄ decomposition and diffusion occurred at 1200 °C, leading to the choice of temperature. In this work, the Si₃N₄ substrate was ground to Sa = $0.118 \pm 0.020 \ \mu$ m, while the Ni foil was used in the as-received condition (Sa = $0.293 \pm 0.048 \mu m$). After 6 h, the samples were removed and examined. There was no bonding between the ceramic and metal disk, though a slight color and surface texture change was observed on the edge of each disk, indicating some limited reaction between the two materials. Figure 2 shows digital images of the bonding faces of the Si₃N₄ and Ni after removal from the HIP. EDS analysis showed the presence of a trace amount of silicon along the edge of the nickel disk where apparent reaction occurred. The Si₃N₄ disk also showed evidence of nickel along the corresponding reacted region.



Figure 2. HIP bonding of Ni to Si_3N_4 at 1200 °C for 6 h without the use of added weight. Images showing the bonding faces of (**a**) Si_3N_4 and (**e**) Ni after HIP. Regions around the disk edges darkened, indicating reaction. (**b**) SEM micrograph with accompanying EDS maps of (**c**) Si and (**d**) Ni concentrations at the edge of bonding face of Si_3N_4 disk. A ridge of Ni remains adhered to the Si_3N_4 even though the two materials separated. (**f**) SEM micrograph with accompanying EDS map of (**g**) Si and (**h**) Ni concentrations at the edge of bonding face of nickel disk. This region of nickel appears to have melted and solidified, with some Si scattered throughout.

It is evident that some reaction occurred under the selected bonding conditions; however, the separation of nickel from silicon nitride and the limited size of the reaction zone indicate that the two materials were not in good enough contact to promote uniform diffusion across the entire interface and create a strong bond. Bonding was also tested using YSZ substrates. A polished YSZ disk (Sa = $0.150 \pm 0.009 \mu$ m) was placed on top of a piece of nickel foil in as-received condition (Sa = $0.270 \pm 0.064 \mu$ m) within an alumina o-ring and heated. Figure 3a,e show digital images of the bonding faces of the YSZ and Ni after removal from the HIP. Discoloration of the YSZ disk and roughening at the edge of the Ni disk indicated that some reaction had occurred. SEM/EDS analysis of the disks detected a small band of Ni (d) left on the YSZ disk where the reaction had occurred and a small band of Zr (g) on the edge of the Ni disk where reaction had occurred. Though it is evident that some reaction occurred, it was not extensive enough to produce a strong bond. The likely reason is the lack of intimate contact between the two materials. Diffusion bonding relies on intimate contact between the materials at the joining interface in order for atomic diffusion to occur. Without any weight or pressure keeping the two disks in good contact, diffusion along the entire disk face is unlikely.



Figure 3. HIP bonding of nickel to yttria-stabilized zirconia at 1200 °C for 6 h without the use of added weight. Image showing the bonding faces of (**a**) YSZ and (**e**) Ni after removal from the HIP. The YSZ disk darkened, with some roughening of the nickel disk around the edge. (**b**) SEM micrograph with accompanying EDS maps of (**c**) Zr and (**d**) Ni concentrations at the edge of bonding face of YSZ disk. A ridge of Ni remains adhered to the YSZ even though the two materials separated. (**f**) SEM micrograph with accompanying EDS map of (**g**) Zr and (**h**) Ni concentrations at the edge of bonding face of nickel disk. This region of nickel appears to have melted and solidified, with a ridge of Zr adhered to the Ni.

In order to increase contact between the ceramic and metal, a weight was added on top of the nickel–ceramic couple. Si₃N₄ substrates of two different roughnesses (Sa = $0.044 \pm 0.003 \ \mu m$ and Sa = $0.087 \pm 0.011 \,\mu$ m) were used. Before bonding, the nickel disk was manually sanded on a piece of SiC grit paper to remove any oxides that may have formed on the surface. The roughness of the nickel was not measured after removing the oxide film. These samples were treated similarly to the first trial, with the only variations being the addition of the weight and the oxide removal from the nickel foil. A 7.9 lb weight was added across three samples, so that the average weight on each couple was 2.63 lb. The alumina o-ring was still used to help maintain the alignment during heating, and a cut section of alumina rod was used as a spacer between the steel weight and the nickel disk. After the 6 h HIP treatment, the samples were removed from the HIP and analyzed. In this case, the Ni was weakly bonded to the Si_3N_4 substrates and separated from the ceramic during sectioning. Though the Ni separated from the Si_3N_4 , the two pieces were clipped together using Metclips, mounted, and analyzed by SEM and EDS. Both samples showed trace amounts of silicon in the nickel foil based on peaks in the spectrum of the EDS line scan. The large, sharp peaks are due to imperfections in the sample surface, such as scratches. The bonding between the Ni and Si_3N_4 was extremely weak. Figure 4a,b show digital images of the weakly bonded Ni-Si₃N₄ couple after removal from the HIP; Figure 4c shows a cross-sectional micrograph of the couple after sectioning. Note the epoxy layer between the Ni and Si_3N_4 layers that

resulted from separation during sectioning. Figure 4d–f show an EDS line scan through the Ni-Si₃N₄ interface. Very low levels of Si (e) along with some large Si peaks are indicated in the Ni layer but are likely due to contamination introduced in the sample preparation process or surface topography. No diffusion was detected of Ni into the Si₃N₄ or Si into Ni.



Figure 4. HIP bonding of nickel to silicon nitride at 1200 °C for 6 h with the use of added weight. Image showing the bonded couple (**a**) Si_3N_4 and (**b**) Ni side by side after HIP. (**c**) Cross-sectional SEM micrograph. The couple separated during metallographic preparation, leaving a thin line of epoxy between the Ni and Si_3N_4 . (**d**) Micrograph region where EDS line scan was taken, showing Ni, epoxy, and Si_3N_4 from left to right; (**e**,**f**) show composition profiles of Si and Ni, respectively, across the bonding interface.

One YSZ disk was also tested (Sa = $0.121 \pm 0.021 \mu m$). When removed from the HIP, the Ni and YSZ were lightly bonded, as shown in Figure 5a,b. Line scans, shown in Figure 5d–g, through the interface indicate slightly elevated concentrations of both zirconia (f) and yttria (g) in the nickel foil after heating. However, the bonding between the two materials was very weak, indicating that modifications to the bonding process are required. Poor interfacial contact is believed to be a major cause of poor bonding performance in these samples.



Figure 5. HIP bonding of nickel to yttria-stabilized zirconia at 1200 °C for 6 h with the use of added weight. Image showing the bonded couple (**a**) YSZ and (**b**) Ni side by side after HIP. (**c**) Cross-sectional SEM micrograph. The couple separated during metallographic preparation, leaving a thin line of epoxy between the Ni and Si_3N_4 . (**d**) Micrograph region where EDS line scan was taken, showing Ni, epoxy, and YSZ from left to right; (**e**–**g**) show composition profiles of Ni, Zr, and Y, respectively, across the bonding interface.

Further study of this process is needed in order to better understand the effect of temperature and pressure and correlate the diffusion and bonding results. Intimate interfacial contact is essential to the diffusion process. For example, in the Ni-Si₃N₄ system, diffusion of Si from the Si_3N_4 to the Ni cannot occur if the two materials are not in contact as atoms cannot exchange sufficiently. Rough surfaces, in particular, require greater force to hold the two materials together so that any surface asperities can deform, creating greater contact. If asperities do not deform, unbonded regions will weaken the overall interface and leave gaps. If two bulk materials are to be diffusion-bonded in a hot isostatic press, a fixture could be developed to create better contact. The addition of the weight was the first step on this path but likely did not provide enough force to create the necessary contact throughout. In addition, the weight did not ensure uniform application of pressure to all samples. A better solution would be a fixture specifically designed for the size of the specimen that could be tightened to a desired specification and provide uniform pressure to the entire sample. Considerations in the design of a fixture include the use of materials that will not melt or deform at the bonding temperature and use of materials or liners that will not bond to or react with the nickel–ceramic couple. Finally, the fixture must be capable of repeatedly applying a uniform force across the entire sample. In addition to

an improved fixture, further studies on bonding times and temperature will yield more strongly bonded interfaces. Bonding should be carried out at as high a temperature as possible to promote diffusion without causing interfacial melting. Local compositions that reach eutectic compositions may cause melting at temperatures as low as 964 °C in the Ni-SiC and Ni-Si₃N₄ systems or 960 °C in the Ni-YSZ system.

3.2. FAST Processing

Field-assisted sintering technology (FAST) was viewed as another viable option for bonding nickel to ceramic substrates in a more traditional diffusion-bonding approach. Much like the foil-bonding experiments in the HIP, this method used 1" diameter $\times 0.02$ " thick nickel disks of 99.9% purity in contact with 1" diameter \times 0.125" thick ceramic disks. However, instead of placing the disks within an o-ring and heating in a vacuum atmosphere in the HIP, samples were loaded into graphite dies, where uniaxial pressure was applied during heating. FAST produces very rapid heating of the die and materials within through a high-density electric current. Though FAST is typically used for sintering materials, these experiments tested its viability for use in diffusion bonding [25]. Two bonding conditions were tested with SiC substrates that were bonded to Ni foil at both 800 °C and 1200 °C using field-assisted sintering technology. First, bonding was attempted at 1200 °C for 10 min; 10 MPa uniaxial pressure was applied at ambient temperature and maintained throughout the heating and cooling cycles. Upon removing the specimen from the graphite die, it was observed that the nickel foil had melted and resolidified as the die cooled, as shown in Figure 6a. This was not anticipated, as the bonding temperature was significantly below the melting point of pure Ni (1455 $^{\circ}$ C). The sample was carefully sectioned and metallographically prepared for further analysis. The Ni layer that had resolidified was very brittle, and much of it flaked away during the metallographic preparation. The cross section was analyzed by SEM and EDS, where a layered structure was observed in the resolidifed Ni layer as shown in Figure 6b. Layered, or lamellar, structures are commonly observed in systems that experienced a eutectic transformation.



Figure 6. (a) Digital image showing top surface of nickel after bonding to silicon carbide at 1200 °C for 10 min at 10 MPa. The nickel foil melted during the experiment, becoming brittle and flaking away from the substrate. A few pieces of recovered Ni are also pictured beside the disk, denoted by arrows. (b) Cross-sectional SEM micrograph of nickel foil bonded to SiC. The layered structure seen near the SiC substrate is characteristic of a eutectic microstructure.

Based on this result, a second bonding experiment was performed at 800 °C, and all other parameters were the same. This temperature was chosen to avoid any invariant transformations in the system while still maintaining high temperature to promote diffusion. No Ni melting was observed; however, the joint formed was weak. SEM analysis revealed regions of elemental contrast in mountainlike shapes along the Ni-SiC interface. EDS analysis indicated that these regions of darker coloration corresponded to elevated Si content in the Ni. Cohesive failures in this sample are likely due to the formation of brittle intermetallic Ni-Si phases. Figure 7b shows an SEM micrograph of the cross section, with the "mountain-like" regions outlined in orange. Figure 7c–e show EDS line scans

of the interface region, showing the Si content (d) and Ni content (e). An ideal diffusion interface would consist of a smooth concentration gradient, from 0% Si in the Ni layer to just under the composition of the first intermetallic compound in the Ni-Si binary system (approximately 26 at% Si). Further parameter development and postbonding analysis are required to develop an understanding of the relationship of interface structure, bond strength, and bonding parameters such as time, temperature, and pressure. Point analysis in the regions of darker coloration and bulk nickel would provide better insight into which phases were formed during this lower-temperature diffusion.



Figure 7. (a) Digital image showing top surface of nickel after bonding to silicon carbide at 800 $^{\circ}$ C for 10 min at 10 MPa. The nickel foil remained intact, without melting, during this experiment. (b) Cross-sectional SEM micrograph of Ni foil bonded to SiC. Several regions of darker coloration were observed, outlined here in orange. The yellow line indicates the location of the line scan data, shown in (c). (c) Region where EDS line scan was taken, passing from bulk Ni through region of darker coloration in nickel layer corresponding to higher Si content into the SiC substrate; (d,e) show the composition of Si and Ni, respectively.

Based on initial bonding trials, FAST is a promising route for further studies that will produce successful nickel–ceramic bonding. The first experiment showed that local silicon concentration could meet or exceed 21 at%, leading to eutectic melting. Consultation of the phase diagram indicated that a temperature lower than 964 °C was required to avoid all eutectic transformations in the Ni-Si system. Using this knowledge, the second experiment was performed at 800 °C, where weak bonding was achieved between the two materials. These two experiments provide a strong basis for future study, proving that FAST can be used to tailor diffusion and create a bond between Ni and SiC. The four major bonding parameters that could be varied in future experiments are temperature, ramp rate, time, and pressure. Temperature is capped at 964 °C to avoid eutectic melting but could be increased closer to this limit to promote diffusion. Based on the shallow diffusion observed after bonding at 800 °C for 10 min, experiments could also study the impact of time at bonding temperature. Increasing the time at 800 °C is expected to lead to more uniform, deeper diffusion of Si into the Ni layer. The mountainlike diffusion observed in the second experiment also suggests that these regions were in better interfacial contact, allowing Si

diffusion. Increasing the bonding pressure will aid in deforming any surface asperities and breaking any oxide films that may have formed on the Ni surface, ultimately leading to better surface contact between the two layers and promoting diffusion.

The mechanism of diffusion bonding in this study is similar to that of pressure sintering (Figure 8), where the material at the surface yields plastically and the surface asperities are deformed [26,27]. Material transfer is believed to occur through two stages: surface diffusion that begins from a single source at the surface to a neck and volume diffusion that begins from surface sources to necks. Material can also evaporate from surface sources and subsequently condense. These mechanisms are driven by differences in surface curvature. Matter transfers from regions of low curvature to regions of higher curvature. In the first stage, plastic deformation occurs. The contact area of surface asperities on the surfaces to be bonded rapidly grows due to the applied load. At some point, the local stress will decrease below the yield strength of the material and plastic deformation will slow and stop. The second stage includes the diffusion and power-law-creep processes. Additional recrystallization and grain growth may also occur during the bonding process due to long exposures in a high-temperature environment [26,27]. Further study is needed to confirm the proposed bonding mechanisms.



Figure 8. Simplified mechanism for diffusion bonding in metal-ceramic systems [26,27].

4. Conclusions

This work encompasses a preliminary study of diffusion-bonding processes as they relate to metal–ceramic joining. Two routes were explored, including HIP using bulk substrates and FAST using bulk substrates. The challenges and benefits of using each technique were identified.

For HIP bonding of Ni to Si_3N_4 and YSZ at 1200 °C for 6 h without the use of added weight, limited reaction occurred under the selected bonding conditions. For the Si_3N_4 , separation of nickel from silicon nitride and the limited size of the reaction zone indicate that the two materials were not in good enough contact to promote uniform diffusion across the entire interface and create a strong bond. For the YSZ substrate, some reaction occurred, but it was not extensive enough to produce a strong bond. Adding weight to the process increased the amount of diffusion and facilitated the bonding process for both materials. Both samples showed trace amounts of silicon in the nickel foil based on peaks in the spectrum of the EDS line scan. Poor interfacial contact is believed to be a major cause of poor bonding performance in these samples. Two conditions were tested with SiC substrates that were bonded to Ni foil at 800 °C and 1200 °C using field-assisted sintering technology. Bonding was attempted 10 min with 10 MPa uniaxial pressure applied at ambient temperature and maintained through the heating and cooling cycles. Bonding at 1200 °C resulted in melting of the nickel and showed that local silicon concentration could meet or exceed 21 at.%, leading to eutectic melting. Bonding performed at 800 °C eliminated melting and resulted in a weak bond. Cohesive failures in the samples are likely due to the formation of brittle intermetallic Ni-Si phases. Based on initial bonding trials, FAST is a promising route for further studies that will produce successful nickel–ceramic bonding.

The processes studied require optimization to allow their practical use. Consequently, future work by the authors will focus on studying the impact of time, temperature, and pressure on the bonding of Ni foil to SiC Si_3N_4 and YSZ substrates in FAST experiments. Investigating the impact of ceramic and metal surface roughness on bond strength, diffusion, and interface characteristics is also of interest to optimize these materials for UUVs and similar applications.

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