Effect of Temperature on Reaction Layer of Diffusion Bonded Sialon to AISI 420 Martensitic Stainless Steel

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ABSTRACT

Background: Joining sialon to steel is not an easy task due to the difference in thermal expansion of these materials. Even though it is difficult to join them, many attempts have been made because combination of the optimum properties from these materials may result in effective component design. Sialon and AISI 420 martensitic stainless steel were joined using diffusion bonding process to study the effect of bonding temperature on the reaction layer. The samples were joined at 1000°C, 1100°C, and 1200°C under uniaxial pressure of 17 MPa in a vacuum of 1x10⁻⁶ Torr. Bonding occurred when joining at 1100°C and 1200°C but it did not happen at 1000°C. Interdiffusion and reaction of the elements such as Si, N, Fe, and Cr from the joined materials created the reaction layer. Thicker reaction layer was formed when joining at 1200°C due to an increase in reactivity at this temperature. The parent steel transformed its microstructure from globular coarse carbide in ferrite matrix to large grain boundary precipitates. Joining at 1200°C produced more precipitates in the parent steel. The “peeling off” effect segregated the diffusion layer and the parent steel during grinding process in the sample preparation. The segregation was not very prominent in 1100°C sample. The concentrations of the elements in steel were decreased toward the sialon and vice versa. Si from sialon diffused deeper into the steel when joining at 1200°C. Sialon retained its hardness after joining and a sharp drop of hardness at the reaction layer was observed because these regions had extreme difference in properties. Applying pressure from the beginning of the joining process was believed to be the reason for manifestation of crack on the sialon in both joining. One of the sialons detached from the joint in 1100°C sample. In a nutshell, joining sialon to AISI 420 martensitic stainless steel at 1200°C produced better joint compared to 1100°C.

INTRODUCTION

Sialon ceramics are obtained by incorporating sintering additives (e.g. MgO or Y₂O₃) into the silicon nitride lattice. It reduces the amount of secondary phase and improves its high-temperature properties. β-sialon is softer than the α-sialon and has a structure similar to hexagonal β-Si₃N₄. Sialons are superior to other refractory materials for example alumina because they possess good properties such as low density, good thermal shock resistance, high strength, good mechanical fatigue resistance and creep resistance, modest wear resistance, and outstanding resistance to corrosion or wetting by molten non-ferrous metals (Noaman et al., 2009). Even though sialon has the advantage to operate at highly corrosive environment and temperature, it is brittle and possesses low toughness (Rosenflanz, 1999). Besides, it is not economical to utilize this material alone due to its high cost. On the other hand, steel is tough and possesses high tensile strength. Combination of these properties by joining the two materials may result in effective component design and expand the utilization of sialon in industry. However, joining sialon to steel is a quite difficult task because these materials have dissimilar thermal expansion. Upon cooling, their difference in this property causes the residual stress to develop at the joint. This stress weakens the joint by reducing its load-carrying capacity, eventually causing the component to fail.

In the past, many techniques have been developed to join ceramic and metal for example mechanical joining, indirect joining, and direct joining (Nascimento et al., 2003). Mechanical joining such riveting or bolting is not recommended due to the brittle nature of ceramics. Joints are the source of failure on the assembly because the stress is concentrated around fasteners holes or at point loading sites that cause high strain and will lead to fracture. The popular choice for joining ceramic to metal tends to be an active metal brazing. However,
the formed joints can only be used for applications that can withstand working temperature with a ceiling limit of around 400°C. Diffusion bonding is one of the methods developed to produce a good joint that can operate at high temperature (Powers et al., 2007). The aim of diffusion bonding is to obtain a joint based on solid state reactions without the occurrence of a liquid phase. The challenge for utilizing this method is, it produces inhomogeneous deformation on different region at the joint. This deformation is caused by dissimilar cooling rate due to large difference in thermal expansion of the joined materials. Therefore, utilizing this method becomes more critical since this process involves heating to cooling from a high temperature which resulted in high residual stress that may produce crack at the joint. Besides, the surfaces need to be properly prepared when joining using this method.

Along with other ceramic-metal joining, joining sialon to steel becomes popular. This process has been carried out for the past twenty years. The attempt was successful with sialon-9%Cr ferritic stainless steel but failed in joining sialon to AISI 316L austenitic stainless steel since cracking occurred on sialon (Hussain and Isnin, 2001). The absence of ductile layer in joining sialon to AISI 316L was the reason behind this occurrence. The large difference in thermal expansion between sialon and steel generated high residual stress at the joint. This stress cannot be accommodated without the presence of the layer. Joining of sialon-7.5%-Cr ferritic steel and sialon-AISI 430 ferritic stainless steel were achieved by diffusion bonding process (Firmanto, 2011). Thicker reaction layers were formed when joining sialon to AISI 430 compared to joining sialon to 7.5%-Cr ferritic steel because AISI 430 contained higher Cr content that increased the reactivity during joining process. Joining sialon to these ferritic steels produced ductile reaction layers since they comprised of ferrite solid solution. The ductile layers were bridging the hard and brittle sialon to the parent steel by accommodating the residual stress that was generated during cooling. Also, they contributed to the strength of the joints. The reactivity between the joined materials can be predicted from the reaction layer thickness. Thicker layer illustrates higher reactivity occurred during joining process whereas very thin layer unable to create the joint because the joined materials will detach. The reaction layer thickness plays very important role for determining the joints strength. A thick layer does not mean it will produce a good joint and only at certain thickness, it gives the highest joint strength due to development of a strong bond. The thickness of the reaction layer was increased when joining at higher bonding temperature, pressure, and longer holding time. It was documented in the previous works that joining at a very high temperature and pressure caused the metal to deform and consequently decreasing the joints strength (Travessa et al., 2002; Lemus and Drew, 2003; Das et al., 2004; Lemus-rui et al., 2006). It is a difficult task to control the formation of reaction layer but it can be achieved by joining sialon to steel in an optimum condition which is a combination of suitable diffusion bonding parameters.

Since joining sialon to austenitic stainless steel is not possible because cracking occurred on the sialon, martensitic stainless steel could be an alternative material to propose. Among the stainless steels, martensitic stainless steels have the highest strength. This steel was chosen to be joined to sialon since no emphasis on joining these materials at combination of higher pressure and temperature (Vleugels et al., 1994; Vleugels et al., 1996). Therefore, formations of the reaction layer and the new phase at the interface of sialon-steel at these joining parameters are still not fully understood. Understanding the reaction layers is essential to obtain a strong joint. This paper aims to study the microstructure, interdiffusion of elements, and hardness across the joint of the diffusion bonded of sialon-AISI 420 martensitic stainless steel at different bonding temperature.

**MATERIALS AND METHODS**

A 20 mm diameter AISI 420 martensitic stainless steel rod (Böhler Edelstahl GMBH & Co KG, Austria) was cut into 1.5 mm thickness utilizing electrical discharge machining (EDM) wire cut. Then, both sides of the steel were ground using carbide abrasive and polished with alumina paste to mirror finish. β-sialon under the trade name of Syalon 201® (Int. Syalons Ltd., Newcastle, UK) was provided in a disk form. It was 4 mm in thickness and had the same diameter with the steel.

Before joining, the steel and sialon were submerged in acetone inside the ultrasonic chamber to remove the contaminants on their surfaces. The joining process was carried out in Korea Vac hot press furnace and Fig. 1 shows the schematic representation of the process. The sample was arranged in sandwich form (sialon-steel-sialon). It was embedded in boron nitride powder to prevent reaction with the graphite die set. Another purpose for this powder was to help in distributing the applied hydraulic pressure on the sample so that it can bond properly without deforming too much (Hussain and Isnin, 2001; Lemus-ruiz et al., 2006). Joining without boron nitride powder had caused the sample to experience imbalance pressure that profoundly deformed the samples (Nor Nurulhuda et al., 2014). The samples were joined at three different bonding temperatures namely 1000°C, 1100°C, and 1200°C. All processes were conducted in a vacuum of 1x10⁻⁵ Torr under uniaxial pressure of 17 MPa. The pressure was applied at 100°C, held for one hour when it reached the bonding temperature, and unloaded at 700°C upon cooling. Thermal shock always caused cracking on the joint and this can be prevented by heating and cooling at lower rate. Therefore, the rates were set to 5°C/min. After reached down to 750°C, the cooling rate was not controlled because it did not fully influence the sample. In addition, the equipment was
incapable to cool with a uniform rate below this temperature. The sample was left for about 18 hours in the furnace to cool down.

![Image](image_url)

**Fig. 1:** Schematic diagram of diffusion bonding process in a hot press furnace (not drawn to scale).

After joining, the samples were cut into half using diamond disc cutter since sialon has high hardness. Then, their surfaces were ground with diamond abrasive having roughness of 30 µm grit followed by polishing with 0.05 µm alumina paste. Nital reagent with a mixture of 100 ml ethanol and 5 ml nitric acid was used to etch the samples. They were immersed in the etchant for about 30 seconds to reveal the microstructure. The micrograph of the joint was captured and analysed using Zeiss Supra 55 variable pressure field-emission scanning electron microscope (SEM). The average thickness of the reaction layer was used in the analysis. Energy-dispersive x-ray (EDX) spectroscopy that attached to SEM was used to perform the elemental analysis across the joint; starting from sialon, reaction layer, and parent steel. Micro Vickers hardness test utilizing LECO LM247 AT tester was employed to measure the hardness across the joint. This technique was suitable to measure the hardness of the reaction layer since it produced small indentation on the surface. A small test load of 50 g with a dwell time of 15 seconds was selected to ensure the indentation was within the region of the interface layer.

**RESULTS AND DISCUSSION**

Joining at 1000°C did not produce any joint and no significant transformation on the microstructure of the steel was observed because it still contained globular coarse carbide in ferrite matrix. No bonding was achieved at 1000°C because when joining utilizing diffusion bonding, the temperature should be three quarters of the steel melting temperature (Nicholas, 1998). Therefore, the bonding temperature should be at least 1088°C to obtain the joint since the melting point of this steel is approximately 1450°C. Besides, sialon starts decompose at 1053°C (Vleugels et al., 1996). Hence, no interdiffusion and reaction occurred when joining at 1000°C. Joining at 1100°C and 1200°C produced reaction layers. The cross-sectional views of the joint are shown in Fig. 2a and 2c. The layer consists of interface and diffusion layer that are represented by region I and II, respectively. Diffusion layer did not contain any precipitate and this zone was a few times thicker than the interface layer. Instead of growing into sialon, the diffusion zone grew toward the steel because atomic diffusion was harder in the sialon compared in the steel (Suganuma, 1990). Sialon only decomposed at the initial surface contact with the steel and when interdiffusion of elements occurred, the new interface was created. Therefore, formation of the interface layer had shifted the original sialon-steel interface and it overlapped with this new layer. Microstructure of the sialon at other region was retained after bonding. Joining at 1100°C produced a thin and irregular interface layer as depicted in Fig. 2b. The possible reason behind this irregularity might be due to inhomogeneous diffusion of the steel’s elements into the sialon. The average thickness of the interface and diffusion layer for joining at 1100°C was 4.45 µm and 19.20 µm, respectively. On the other hand, joining at 1200°C produced 17.96 µm and 50.49 µm of interface and diffusion layer, respectively. Joining at higher temperature produced thicker reaction layer because sialon decomposed more rapidly at this temperature. Hence, more N and Si could diffuse into the steel. This caused the joined materials to have higher reactivity and led to development of a thicker reaction layer. For both samples, the steels were no longer containing globular coarse carbide in ferrite matrix after joining. Their microstructures transformed to α-ferrite with precipitates and the grain size enlarged. More precipitates were observed when joining at higher temperature. The precipitates were concentrated nearly the diffusion layer and in the grain boundary of the parent steel.

The following describes the formation of reaction layer; the first stage of achieving the interfacial contact was influenced by the pressure. At 17 MPa, this pressure was adequate to produce appropriate mating on the joined surface especially when joining at 1200°C. The surface asperities were plastically deformed and followed by closing the voids. The process of closing the voids by flattening them was driven by creep deformation. Then, they were spherodized when vapor phase transport and diffusion occurred (Suganuma, 1990). The atomic and dislocations movements in the steel were increased when joining at higher temperature because they have more energy. At high temperature, sialon decomposed by liberating its element such as Si, Al, O, N, and Y. Then, interdiffusion of the elements between the joined materials took place and formed the reaction products in
the reaction layer. The interface layer was a porous zone due to the existence of voids or known as Kirkendall voids in this region. Diffusion rate among the atomic species across the interface played significant role in voids formation. The non-equilibrium diffusion rate of the elements especially iron and silicon was the most likely reason for the voids to be formed (Tang et al., 2002). The porosity weakened the joint and consequently, increasing the possibility for cracking because it tended to follow the porous zone once it was initiated. Voids were formed on the metal side due to incomplete diffusion and they were presumed to be the fracture origins (Tomsia, 1993). A few crack lines were observed on the sialon due to long applied pressure even though 5°C/min of cooling rate was employed. One of the sialons in 1100°C sample detached from the joint during the cross-sectioning process whereas sialons in 1200°C sample stayed intact.

Fig. 2: SEM micrograph of joining sialon to AISI 420 martensitic stainless steel at: (a) 1100°C and (c) 1200°C; magnified area of the interface layer when joining at (b) 1100°C and (d) 1200°C.

The diffusion layer and the parent steel were clearly segregated by a uniform line especially in 1200°C sample as shown in Fig. 3. The segregation was not very severe when joining at 1100°C and this can be seen from Fig. 3a. On the other hand, the severity of the segregation was conspicuous when joining at 1200°C as depicted in Fig. 3b. The difference in properties between the layer and the parent steel as well as the high applied pressure might cause this segregation to be formed. Grinding during sample preparation may cause the border between these regions to experience the “peeling off” effect since diamond abrasive was used to grind the surfaces. The border might be peeled off because it was softer compared to the parent steel as shown in Fig. 5b. Therefore, the segregation was not actually a gap since the sample should be separated after the joining process. The samples were broken to verify it and instead of breaking at the gap, sialons were broken whereas the steel remained intact. It was reported in the previous work that joining sialon to steel at lower pressure such as 2.5 MPa did not produce any segregation (Vleugels et al., 1994). However, the interface layer contained numerous pores that made this layer a porous zone, causing the joint to be weakened.

Fig. 3: SEM micrograph of the diffusion layer-parent steel’s border when joining at (a) 1100°C and (b) 1200°C.

Elemental diffusion took place between the joined materials when joining was conducted at 1100°C and 1200°C. The concentration profile of the elements is shown in Fig. 4. The region is divided into four parts; sialon, I for interface layer, II for diffusion layer, and the parent steel. Analysis using EDX was started 30 µm on the sialon before the interface layer with an increment of 10 µm. The concentration of elements from both materials decreased when they reached interface layer and this showed that interdiffusions took place in this layer. At the sialon’s core which was 30 µm before the interface layer, the concentration of Si and N were significantly higher compared to other sialon’s elements such as Al and O due to their higher initial weight percentage (wt%) since no decomposition occurred at this part. Fe and Cr have nearly constant wt% in the parent steel when joining at 1100°C because less precipitates were formed. Their concentration started to diminish when they were approaching the diffusion layer and their values were almost zero when they reached sialon. Other elements of the joined materials such as Y, Mn, Ni, and V possessed very low wt%. Thus, they were not taken into consideration for the analysis. The drop of Fe and the increase of Cr concentration in the parent steel at some points were observed in 1200°C sample. These data were obtained because the analyses
were conducted on the precipitates, not on the steel matrix. During joining process, the sample was compressed and heated to achieve the reaction layer. Therefore, the original contact point of the materials had been shifted due to the applied pressure and interdiffusion of elements. The new interface between the joined materials was formed due to development of the reaction layer. The elemental diffusion took place without the presence of liquid phase since the process was carried out at much lower temperature compared to the steel melting point. Si diffused into the steel until 110 µm at 1100°C sample but in 1200°C, it was still detected beyond 130 µm due to higher rapid movement of the atoms in the crystal lattices. Hence, joining at higher temperature increased the reactivity of the joined materials.

**Fig. 4:** Concentration profile across the joint for joining sialon to AISI 420 martensitic stainless steel at (a) 1100°C and (b) 1200°C.

The size of the element’s atom in the sialon did not affect the diffusion and reaction rate of sialon’s elements into the steel but it was determined by the ionization potential. The ability of sialon’s atom to release its valence electrons to form a common electron group with the steel’s atoms is known as ionization potential. Lower ionization potential possessed by Si compared to N enabled this element to diffuse in larger volume and deeper into the steel. In addition, it was easier for element with lower ionization potential to react with the steel’s element to form new compounds. The ionization potential for Si and N were 8.14 eV and 14.51 eV, respectively (Samsonov and Vinitskii, 1980). New phases such as silicides, nitrides, and carbides may be formed at the reaction layer due to interdiffusion of elements and their reactivity between the joined materials.

High concentration of C was detected in the precipitates that formed in the grain boundary of the parent steel. Thus, the precipitates might be carbides (Fe₃C and/or Cr₃C₂). Carbides sensitization at the grain boundary was detrimental since it degraded the corrosion resistance of the steel. Based on the Fe-Si binary phase diagram, joining at 1100°C and 1200°C definitely will produce silicide unless a certain measure is taken (Massalski, 1990). However, the presence of silicides cannot be concluded by utilizing this technique alone. High concentration of silicides at the interface layer posed as a risk because they increased the failure rate of the joint due to their brittleness (Firmanto, 2011).

Hardness across the joint was measured from sialon to steel and the profile is shown in Fig. 5. The interface and diffusion layer are labelled as region I and II, respectively. The measurement was carried out on the sialon, approximately 45 µm before the interface layer with an increment of 15 µm. Sialon retained its hardness after joining because it consisted of strong covalent bonding. This type of bonding provided sialon with a stable structure so that the property was not affected when subjected to high working temperatures. Hardness at the interface layer dropped really low due to decomposition of sialon and interdiffusion of elements at this part to form new phases. From this, it can be inferred that the interface layer and sialon have different properties. The interface consisted of pores that weakened this layer (Fig. 2b and 2d). Based on the data plotted in Fig. 5, the weakest part of the joint might be the border between the interface layer and the sialon. This was the region where failure always first to take place. Hardness for joining at 1100°C gradually decreased towards the parent steel and exhibited almost constant hardness in this region. On the other hand, joining at 1200°C produced the lowest hardness at the diffusion layer. The hardness slightly increased toward the core of the parent steel because the indentations were carried out on the steel matrix that possessed higher hardness compared to precipitates. The intermediate hardness possessed by the reaction layer was beneficial in achieving the joint because it connected the hard and brittle sialon to the steel. It served as a buffer zone to relieve the residual stress that was generated upon cooling down. However, crack still occurred on the sialon in this attempt. The crack was not caused by the difference in thermal expansion but rather the applied pressure. The pressure was applied for too long and the sample cannot withstand it. One side of the sialon cracked and detached from the joint in 1100°C sample. Crack was also observed in 1200°C sample but it not as severe as in 1100°C.

**Conclusion:**

Joining sialon to AISI 420 martensitic stainless steel utilizing diffusion bonding at different temperature is reported in this paper. Based on the microstructure, interdiffusion of elements, and hardness of the joint, the following conclusions can be drawn:
a. There was no diffusion and reaction occurred when joining at 1000°C because the temperature did not reach sialon’s decomposition temperature and three quarter of the steel melting point. Sialon retained its...
microstructure after joining process. Joining at 1200°C produced thicker reaction layer and more precipitates were formed in the parent steel compared to joining at 1100°C due to higher reactivity took place at higher bonding temperature. The diffusion layer and the parent steel were segregated by “peeling off” effect due to the difference in properties between these regions. This segregation was not very pronounced when joining at 1100°C. Microstructures of the steels transformed from globular coarse carbide in ferrite matrix to large grain size with precipitates.

Fig. 5: Hardness profile across the joint for joining sialon to AISI 420 martensitic stainless steel at (a) 1100°C and (b) 1200°C.

b. Interdiffusion of elements occurred between sialon and steel. The concentration of the sialon’s elements decreased toward the steel and vice versa. More Si diffused into the steel because it possessed lower ionization potential than N. It was identified that Si could diffuse deeper into the steel when joining at 1200°C compared to 1100°C because the atoms possessed higher energy. Therefore, the reactivity of the joined materials can be observed by the distance of the Si diffusion into the steel.

c. The hardness profiles across the joint for joining at 1100°C and 1200°C were similar but differed in the parent steel because joining at 1200°C produced more precipitates. Sialon retained its hardness and the reaction layer possessed very low hardness. One of the sialons detached in 1100°C sample but 1200°C, they remained intact. In this attempt, cracks were formed on the sialons for both joining due to the applied pressure from the beginning of the joining process.

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