Title: Bonding of Si$_3$N$_4$ to SS400 Steel with Activated Coating Layers Made by Low-Pressure Plasma Spraying (Physics, Process, Instruments & Measurements)

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Citation: Transactions of JWRI. 22(1) P.37-P.46

Issue Date: 1993-08

Text Version: publisher

URL: http://hdl.handle.net/11094/7289

DOI: 

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Bonding of Si$_3$N$_4$ to SS400 Steel with Activated Coating Layers Made by Low-Pressure Plasma Spraying†

Akira OHMORI*, Zhan ZHOU** and Katsunori INOUE***

Abstract

Bonding of Si$_3$N$_4$ and SS400 mild steel was carried out by using Cu-Ti system coatings and Cu-Mn two-layer coatings made by low pressure plasma spraying (LPPS) as interlayer materials, compared with Cu-Ti mixed paste and Cu-Ti two-layer foils. It is recognized that when the active LPPS coatings were used as insert materials Cu-Ti eutectic reaction and Cu-Mn solution reaction took place uniformly at the joint immediately after heating to the bonding temperature and improved the bondability. The mean shear strength of the joints bonded using Cu-Ti two-layer coatings at 1173 K and $5 \times 10^{-3}$ ks showed 200 MPa, and the mean shear strength of the joints bonded using Cu-Mn two-layer (Cu-40wt%Mn) coatings at 1193 K and 1.8 ks showed 175 MPa, and the joint strength bonded using Cu-22wt%Ti mixed paste was very low.

The joint strength was controlled by the eutectic reaction of Ti and Cu in the interlayer and the formation of brittle metallic compound at the interface near SS400 mild steel for Cu-Ti system. For Cu-Mn system, the joint strength was strongly affected by Cu-Mn composition in the interlayer.

KEY WORDS: (Bonding) (LPPS) (Si$_3$N$_4$) (SS400 steel) (Cu-Ti two-layer coatings) (Cu-Mn two-layer coatings) (MnSiN$_2$ compound)

1. Introduction

Ceramic materials have been considered for use as structural materials in heat engines, heat exchangers, wear parts and other applications. However, their widespread usage has limited because of the difficulty of making large or complex shaped objects and poor machinability due to the lack of ductility. Therefore, hybridization by joining ceramics and metals is considered as one of the most promising approaches to overcome these deficiencies and promote the use of ceramics.

Various methods of joining have been reported and applied, such as metallizing the ceramic surface followed by brazing, direct brazing with active metals, and diffusion bonding.1-6 Among them, direct brazing is considered to be relatively simple and reliable, and many kinds of brazing fillers including active metals of Ti and/or Zr have been developed. In addition, the eutectic alloys of Ti/Zr and Cu, Ni, Ag, Sn5-11, etc. have been used as fillers in various combinations and forms. However, there are still many problems to solve for each type of the morphology of the filler. For example, in the case of alloy filler, it is difficult to make the alloy into foils by rolling, therefore, costly amorphous foils made by melt quenching are usually used. For the binary foils, extremely high temperature and long heating times are necessary for the dissolution reaction to occur, because it takes some duration for the elements to inter-diffuse up to suitable composition.12 In the case of mixed powder, the reaction is impeded by oxides formed on the surface of fine particles. Thus, it is necessary to develop most effective method for utilizing the active metal method.

It is reported13-15 that very active Cu-Ti two-layer plasma sprayed coatings made by low pressure plasma spraying (LPPS) as a brazing aid were used in the bonding between alumina and steel, and a better joint was obtained at lower temperature and short heating times. This thermal spray bonding which uses such active coatings as insert materials considered to be simple and effective method. In this paper, brazing of two-layer coatings of Cu/Ti and Cu/Mn which produced by LPPS were used in the joining of Si$_3$N$_4$ ceramic and SS400 steel. The bondability and the factors which influences the bonding strength of Si$_3$N$_4$ and steel were examined by using two-layer coatings, compared with composite coating, mixed powder paste and two-layer foils.

2. Experimental Procedures and Materials

The process of thermal spray bonding is shown in

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Transactions of JWRI is published by Welding Research Institute, Osaka University, Ibaraki, Osaka 567, Japan
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![Diagram showing bonding process](image)

Fig.1 Schematic diagram of thermal spray bonding for ceramic-metal.

Fig.1, where plasma spraying is firstly carried out on SS400 steel substrate in a low pressure atmosphere with LPPS apparatus as shown schematically in Fig.2. Subsequently, the coated surface of the metal, which is also a bonding surface, and the ceramic surface are polished with metallographic paper. Then the assembly is heated up to joining temperature in a high vacuum atmosphere of about 10⁻³ Pa.

The combination, composition and the particle size of powders of the coatings as insert materials are shown in Table 1. The spraying conditions are listed in Table 2. LPPS was carried out in a low pressure Ar atmosphere of 13.33 kPa. Joints were also fabricated using a stack of Ti and Cu foils, which we call two-layer foils. The ceramic material is pressureless sintered silicon nitride (Si₃N₄) which was joined to a mild steel of JIS SS400. All joints were fabricated using a pair of cylindrical tablets with different diameter of 10 and 15 mm.

Heating rate of the assembly was 0.833K/s. After holding for appointed time at the jointing temperature it was cooled at cooling rate of 0.333K/s until 873K, then the cooling rate was changed to about 0.025K/s from 873K until room temperature. Structure of joint part and distribution of elements were examined by means of optical microscope, SEM and EDX or EPMA analysis, while the joint strengths were estimated by shearing tests using a holder as shown in Fig.3. Shear strength of the joints was measured at tensile rate of 8.33 mm/ks. Fracture surfaces were also examined by X-ray diffraction tests.

### Table 1 Composition and diameter of spray powders.

<table>
<thead>
<tr>
<th>Coating Materials</th>
<th>Diameter of Powder (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.99Cu</td>
<td>45~90</td>
</tr>
<tr>
<td>99.99Ti</td>
<td>10~44</td>
</tr>
<tr>
<td>72Cu-28Ti Mixed Powder</td>
<td>-</td>
</tr>
<tr>
<td>99.9Mn (Bal: Cr, Ca, Mg, Al, Cu)</td>
<td>40~90</td>
</tr>
<tr>
<td>98.0Mn-0.18Mn oxide (Bal:Cr,Ca,Al)</td>
<td>40~74</td>
</tr>
</tbody>
</table>

3.1 Effect of bonding conditions on joint structure
3.1.1 Cu-Ti eutectic system as insert material

Figure 4 shows microstructure and EDX analysis results of Cu-Ti two-layer coatings and a 72Cu-28Ti com-
Table 2 Low pressure plasma spray conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray apparatus</td>
<td>METCO 7MB</td>
</tr>
<tr>
<td>Spray atmosphere (Ar)</td>
<td>13.33 kPa</td>
</tr>
<tr>
<td>Plasma gas (Ar) pressure</td>
<td>0.686 MPa</td>
</tr>
<tr>
<td>Plasma gas (Ar) flow rate</td>
<td>0.712 M³/ks</td>
</tr>
<tr>
<td>Auxiliary gas (Hz) pressure</td>
<td>0.686 MPa</td>
</tr>
<tr>
<td>Auxiliary gas (Hz) flow rate</td>
<td>0.152 M³/ks</td>
</tr>
<tr>
<td>Plasma output</td>
<td>25 kW</td>
</tr>
<tr>
<td>Spray distance</td>
<td>300 mm</td>
</tr>
<tr>
<td>Rotation of workpiece holder</td>
<td>200 rpm</td>
</tr>
<tr>
<td>Feed rate of stroker</td>
<td>66.67~166.67 mm/ks</td>
</tr>
</tbody>
</table>

Composite coating sprayed under the condition shown in Table 2. It can be recognized that the Ti coating is much dense and oxidation of Ti during spraying is suppressed compared with atmospheric spraying. It is considered that titanium of the coating sprayed under controlled atmosphere will be much active because of suppression of oxidation. Clearly, the coatings also adhered well to the substrate, as shown in Fig.4. All those characteristics will be beneficial during bonding.

In order to clarify the behavior of the coated layer as brazing fillers for joint of Si₃N₄ and steel, joint structure made under various conditions were compared. Figure 5 shows silicon nitride to steel joints made with two-layer coatings, where the thickness of the coated Ti layer is about 15 μm, while the Cu layer is about 40 μm. The effects of the bonding temperatures on the joint structures made by heating at each temperature for 0.6 ks are shown in the figure. In the joint made at 1123 K in Fig. 5a, the eutectic reaction has not occurred and the coated layer remained as sprayed. The eutectic reaction occurred at 1173 K in Fig. 5b, where the joint was brazed without any defects in the joint area, which shows that it is necessary to braze at temperatures above the Cu-Ti eutectic point of 1153 K. In contrast, in the joint made at 1273 K in Fig. 5d, comparatively large voids are formed in the joint area, because the eutectic liquid flows out due to the decrease in viscosity. In addition, cracking occurred in the ceramic specimen by the thermal stress due to the mismatch of thermal expansion coefficients between the ceramic and the metal. These results show that adequate joining temperatures are restricted to a comparatively narrow range around 1173 K.

Figure 6a shows SEM image and EDX line analysis of a Si₃N₄-steel joint made with the Cu-Ti two-layer coatings, heated at 1173 K for 0.6 ks, a homogeneous eutectic structure is obtained at the joint, and there seems to be no voids or cracks. Close observation reveals that a Ti-rich layer exists at the Si₃N₄ side of the joint interface, while an iron diffusion layer exists at the steel side of interface.

![Fig. 3 Specimen holder used in shear strength tests.](image_url)

![Fig. 4 SEM image and EDX line analysis results at a cross-section of Cu and Ti coating sprayed by LPSS on SS-400 mild steel. (a) Cu-Ti two-layer coatings; (b) 72Cu-28Ti composite coating.](image_url)
some diffusion time to cause the eutectic reaction in this brazing condition, and that in the case of powder paste, the oxide films or some contaminations on the powder surface are interfering with smooth reaction. In contrast, the Cu-Ti reaction can occur immediately after heating to 1173 K in LPPS coating layers.

3.1.2 Cu-Mn solid solution system as insert material

Figure 7 shows microstructure of Cu-Mn (purity of 98% Mn) and Cu-Mn (purity of 99.9% Mn) two-layer coatings sprayed under the conditions shown in Table 2. It is recognized that the structure of Mn coating with low purity Mn powder has remarkable structure of lamella particle because of the existence of Mn oxide at the side or the surface of Mn particle. Figure 8a shows microstructure and EPMA line analysis results of Si3N4 steel joints made with Cu-Mn (purity of 99.9% Mn) two-layer coatings. It can be recognized that the structure of joint made with Cu-Mn two-layer coatings consisted of Mn-Cu solid solution phases with Cu-rich as white area and Mn-rich as dark area, and the Si-N-Mn layer exists at the interface of Si3N4 side of the joint while Fe, Mn and Cu were mutually diffused at the interface of steel side of the joint. Structure of joint made with Cu-Mn (purity of 98% Mn) two-layer coatings are compared in Fig.8b. Similar structure was recognized, and there seems to be some voids and Si-N-Mn layer at the interface of Si3N4 side of the joint was thinner than that with Cu-Mn.
Fig. 7  SEM image at cross-section of Cu-Mn two-layer coatings sprayed by LPPS on SS400 steel. (a), Mn powder purity used is 99.9\%Mn; (b), Mn powder purity used is 98.0\%Mn.

(purity of 99.9\%Mn) two-layer coatings. It is possible to be consider because Mn-Cu solid solution and Mn-Si3N4 reaction were impeded by Mn oxides and structure of lamella particle shown in Fig.8. Figure 9 shows the result of X-ray diffraction of Si-N-Mn layer at Si3N4 side of the joint made with Cu-Mn (purity of 99.9\%Mn) two-layer coatings. Existence of MnSiN2 compound can be recognized except Si3N4 for ceramic body.

Figure 10 shows the relation between Mn content and thickness of Si-N-Mn reaction layer at the interface of Si3N4 side of the joint made with Cu-Mn (purity of 99.9\%Mn) two-layer coatings, at the temperature of 30K higher than the liquidus line of the Cu-Mn compositions for 1.8ks, where the thickness of the coated Mn layers is constant and are about 50 $\mu$m, while the Cu layers are varied from 30 $\mu$m to about 150 $\mu$m. The result reveals that there is a linear relation between the thickness of the reaction layer and Mn content in the Cu-Mn insert material. From these results, it can be consider that joint of

Fig. 8  EPMA image and analysis results of Si3N4-SS400 steel joints made at 1223K for 3.6ks with Cu-Mn two-layer coatings; (a), purity of 99.9\%Mn; (b), purity of 98.0\%Mn.
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![Graph showing X-ray diffraction](image)

Fig.9 Result of X-ray diffraction of Si-N-Mn layer at SiN₄ side of the joint made with Cu-Mn two-layer coatings.

![Graph showing Mn content and thickness of reaction layer](image)

Fig.10 Relation between Mn content and thickness of Si-N-Mn reaction layer at the interface with SiN₄.

Si₃N₄ and the Cu-Mn interlayer is decided by the reaction of Mn-Si₃N₄, and the formation of the Si-N-Mn reaction layer at SiN₄ side was mainly influenced by activity and amount of Mn in Cu-Mn interlayer as insert material.

These results also indicate that Cu-Mn reaction can occur immediately at the lower temperature in jointing of Si₃N₄ and mild steel by using Cu-Mn solid solution system LPPS coatings as insert material, like LPPS coating layers of Cu-Ti eutectic system.

3.2 Variation in joint strength with joining condition

The strengths of Si₃N₄-steel joints made with various types of Cu-Ti interlayers are compared in Fig.11, and the effects of holding time for joints made with Cu-Ti two-layer coating and 72Cu-28Ti composite coating are demonstrated in Fig.12 and Fig.13, respectively. These results indicate that the joint strengths are affected by both the morphology of the interlayer and the holding time at the bonding temperature. The strength of joint made with paste of Cu-Ti mixed powder was very low, and that made with LPPS Cu-Ti coatings has been remarkably higher strength shown in Fig.11. Comparing the case of heating for a short time in Fig.12 and Fig.13, the joint made using LPPS Cu-Ti two-layer coatings reveals a considerably higher strength of about 200 MPa, and when bonding at 1173 K using LPPS Cu-Ti composite coating,
Fig. 12 Effect of joining time at 1173K on shear strength of Si3N4-SS400 steel joints made with LPPS Cu-Ti composite coating.

Fig. 13 Effect of joining time at 1173K on shear strength of Si3N4-SS400 steel joints made with LPPS Cu-Ti two-layer coatings.

Fig. 14 Effect of the composition of Cu-Mn two-layer coatings on the joint strength of Si3N4 and SS400

the joint strength increases up to about 185 MPa with increase in holding time during the first 1.8 ks. Then, the strength decreases rapidly with increase in holding time. Additionally, it is also recognized that when using LPPS two-layer coating, not only the joint strength does not decrease greatly with increase of holding time but also the scattering of the strength is significantly smaller than in the other cases. This can be related to the homogeneous eutectic reaction at the interface.

Figure 14 shows the effect of the composition of Cu-Mn two-layer coatings on the joint strength bonded for 1.8 ks. Best joint strength was obtained by using the coating containing 40~50wt%Mn. Figure 15 shows the joint strength of Cu-Mn two-layer coatings contained 60wt%Mn, where Mn powder of different purities was used, and the figure demonstrates that the strength of the joint made with Cu-Mn (low purity) two-layer coatings is lower than 1/2 of the strength of joint made using the Cu-Mn (high purity) coatings. These variations in joint strength are considered to be related to the fracture mode, as illustrated in the next figure.

3.3 Bonding mechanism and fracture morphology of joints

Various kinds of fracture morphology were observed in the joints in this investigation. They can be classified into four types as illustrated in Fig. 16a when using Cu-Ti
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System interlayer as insert material. In every case, the joint structure was fabricated with a Ti-rich layer at the ceramic side of the interface, and Cu-Ti eutectic layer in the middle area. Additionally, at the steel side of the interface, either a Ti-Fe compound layer was formed as shown in figure of (A), (C), and (D) of Fig.16a, or a Ti-rich layer was formed as shown in (B) of Fig.16a. In the Type-A of Fig.16a, voids and defects were included in the joint area.

Type-A of Fig.16a shows the case where fracture occurred at the bond layer where voids and defects are included, and the fracture of this type was only observed in the joint made with Cu-Ti mixed-powder paste. In the case of Type-B of Fig.16a, the fracture occurs at the interface between steel and Cu-Ti eutectic layer, which was observed in the joints made with Cu-Ti composite coating or Cu-Ti two-foils at short holding time. It can be considered where the reaction between the eutectic and steel is insufficient. Type-C of Fig.16a shows the case where the fracture occurred in ceramic. In this case, the joint had fairly high strength of about 185~200 MPa, like the joints made with Cu-Ti two-layer coatings or Cu-Ti composite coating at holding time of 0.6 ks, where sufficient eutectic reaction had occurred. The fracture of joints made with Cu-Ti composite coating and Cu-Ti two-layer foils at long holding time, was observed as Type-D of Fig.16a. The fracture occurred in the thick Fe-Ti compound layer formed at the interface between the bond layer and the steel and the joint strength decreased markedly. It is recognized that the brittle Fe₂Ti compound layer is detected along with Ti₂Cu₃ phase at Fe-Ti compound layer by X-ray diffraction analysis to the fracture surface of these joints. This suggests that the joint becomes brittle in this area.

These results demonstrate that when Cu-Ti system as insert material were used in joint of mild steel and Si₃N₄, a brittle layer grows through reaction between excess Cu-Ti eutectic and steel during long time heating, and the joint strength decreases markedly. This shows that the most important factor to obtain sound joints is not the simple time-temperature history but the achievement of a rapid eutectic reaction by heating at a temperature as low as possible. Such conditions could be obtained only in the case of using LPPS two-layer coatings for Cu-Ti system in this investigations.

Figure 16b shows various kinds of fracture morphology observed in the tensile test of joints made with Cu-Mn two-layer coatings contained various composition and with different Mn purities. They can be also classified into four types of (E), (F), (G), and (H). The joint structure was fabricated with a Si-N-Mn reaction layer at the ceramic side of the interface, Cu-Mn solid solution reaction layer in the middle area, and Fe-Cu-Mn reaction and/or

![Diagram](image)

Fig.16 Illustration for shear-fractal morphology of Si₃N₄-SS400 steel joints made with different types of Cu-Mn interlayer.
inter-diffusion layer at the steel side of the interface. In the Type-E of Fig.16b, voids and defects were included in the joint area, and in Type-F of Fig.16b, Si-N-Mn reaction layer is thicker at the ceramic side of the interface.

The fracture of joints made with Cu-Mn two-layer coatings used Mn powder of low purity (98 wt%) was almost occurred at the bond layer where void and defects are included much, as shown in Type-E of Fig.16b. The fracture of the joints made with Cu-Mn two-layer coatings used Mn powder of high purity (99.9 wt%) shows Type-F, G and H of Fig.16b.

Type-F of Fig.16b shows the case where fracture occurred at thin Si3N4-Mn reaction layer of the interface between ceramic and Cu-Mn coating interlayer, where Si3N4-Mn reaction was not sufficient. The case was observed in the joints made with Cu-Mn two-layer coatings which the composition is about Cu-20 wt% Mn. Type-G of Fig.16b shows the case where fracture occurred partially at the Ni-N-Mn layer between ceramic and Cu-Mn solid solution interlayer, and in the ceramic. The case was observed in the joints made with Cu-Mn two-layer coatings with the composition of Cu-30 wt% Mn. The fracture of joints made with Cu-Mn two-layer coatings with the composition of Cu-40~60 wt% Mn was occurred in ceramic, as shown in Type-H of Fig.16b, where Si3N4-Mn reaction had occurred sufficiently at the interface between the ceramic and Cu-Mn interlayer. In the case of the joints made with the Cu-Mn two-layer coatings with 60 wt% Mn, The existence of micro-crack in ceramic was observed by SEM image of cross-section of the joints, and the micro-crack can be considered to be caused by thermal stress, produced by different thermal expansion between ceramic and metal, when the joints cooled. In the case of the joints made with the Cu-Mn two-layer coatings containing 40 and 50 wt% Mn, the joints had most high strength of about 165~170 MPa. It may be considered that when the joints cooled, the stress existed in ceramic was relaxed by the Cu-rich phase in Cu-Mn interlayer, which has some ductility and was continuously distributed in the interlayer like network frame as shown in Fig.8, where Cu-rich phase contained little Mn is more than that contained much Mn.

These results also demonstrate that when Cu-Mn solid solution system coatings used as insert materials, some similar results as the case of Cu-Ti system coatings were obtained, but, the interface between Cu-Mn interlayer and steel has a enough strength, and thermal stress in ceramic can decrease in some degree through suitable selection of the composition of Cu-Mn in the interlayer.

From the results mentioned above, it is suggested that the thermal spray bonding using Cu-Ti eutectic and Cu-Mn solid solution system two-layer coatings produced by LPPS is superior to the conventional brazing using other type interlayers in the bonding of Si3N4 and steel.

4. Conclusions

The bonding of Si3N4 ceramic and steel was investigated by using insert-material of Cu-Ti binary system coatings produced by LPPS, compared with paste mixed powder and Cu-Ti two-layer foils, and by using that of Cu-Mn solid solution system produced with different purities of Mn powder by LPPS. From the joint strength and elements behavior in the joint part, the factors controlling the joint strength were examined. The results obtained in the present study are summarized as follows.

(1) The joints of Si3N4 and SS400 mild steel made by using the Cu-Ti two-layer coatings and Cu-Mn two-layer coatings at short holding time and low temperature showed the mean shear strengths of 200 and 170 MPa respectively.

(2) For Cu-Ti binary system interlayer, the joint strength is affected by such factors as: (a) Cu-Ti eutectic reaction in the interlayer, (b) the reaction between ceramic and interlayer, (c) the reaction between steel and interlayer, and (d) the occurrence of thermal stress between ceramic and the metal.

(3) For Cu-Mn binary system interlayer, the joint strength is affected by such factors as: (a) reaction between ceramic and interlayer, (b) the occurrence of thermal stress between ceramic and the metal, controlled in some degree by Cu-Mn composition in the interlayer. In the case of the composition of Cu-(40~50) wt% Mn, the sound joints obtained.

(4) It was recognized that the bonding of Si3N4 and SS400 mild steel using Cu-Ti two-layer coatings was more efficient owing to easiness of the eutectic reaction, compared with the Cu-Ti two-layer foils and the Cu-22wt%Ti mixed powder paste.

(5) The bonding of Si3N4 and steel using Cu-Mn two-layer coatings carried out by the reaction between Si3N4 and Mn, where MnSiN2 compound was formed, and the thickness of the reaction layer was increased linearly with increase of Mn content in Cu-Mn interlayer.

Acknowledgement

The authors would like to thank Dr. A. Suzumura and Prof. Y.Y. Qian for the valuable advice and suggestions.
References