Solid State Bonding of Graphite to SUS304 Steel*

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Graphite was bonded to SUS304 steel under a compressive stress of 25 MPa in a vacuum over a temperature range from 873 to 1023 K using a RF-induction furnace. The bending strength of the graphite/SUS304 steel joint, and changes of microstructure and hardness near the joining interface of SUS304 steel, were investigated. Thermal stress induced in the joint was estimated with a finite element method. On the basis of these results the influence of thermal stress on the bending strength of the joint was examined. Good solid state bonding becomes feasible when the joining temperature exceeds 923 K. Axisymmetric thermoelastic finite element analysis suggests that maximum tensile thermal stress is induced at a distance of 0.64 mm from the joining interface on the surface of the graphite and is increased with increasing joining temperature. The position of fracture in a bending test specimen corresponds approximately to that of the maximum tensile thermal stress. A part of the thermal stress is released with the deformation of SUS304 steel and graphite. The bending strength of the joint increases with decreasing residual tensile stress on the surface of graphite. Relaxation of thermal stress depends on the amount of carbon atoms which diffuse into SUS304 steel. This may be related to the changes in plasticity of SUS304 steel and graphite, that is, the changes in the amounts of Cr₂₃C₆ precipitated in SUS304 steel and point defect introduced in graphite.

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1. Introduction

Carbon materials have excellent neutron moderating power, radiation damage resistance, abrasion resistance, strength, elastic modulus, bio-affinity, thermal conductivity and chemical reactivity, and are therefore widely used in various fields such as nuclear power, space development, electronics and environmental protection. However, hybrid structures, in which graphite or C/C composites are combined with metallic materials, are adopted for various devices and machinery because graphite and C/C composites are brittle. Dissimilar materials can be joined by mechanical, material and chemical methods. Hybridization of carbon materials to metals is usually performed by mechanical joining. Brazing is also employed in the manufacture of nuclear fusion reactors.¹⁾

Recently, joining technologies for dissimilar materials using the joining method with insert materials such as brazing and the direct joining method have been developed. In addition, fundamental and application data on the joining of metals to ceramics have been collected.²⁾ A joining method that would enable the desired characteristics of the graphite or C/C composites and the metal to be maintained may allow the development of various devices and machinery having high performance. However, few studies have examined the joining of graphite or C/C composites to metals.

The present authors reported³⁾ previously that austenite phase greatly contributes to solid-state bonding of graphite to S45C steel. Thus, in the graphite/carbon steel system, good bonding becomes feasible only when the joining temperature exceeds the A₁ transformation temperature. However, in high-temperature joining, a large thermal stress is induced during subsequent cooling, resulting in a decrease in the strength of the joints.^{3,4)} Austenitic stainless steel is com-

posed of austenite at room temperature. Therefore, this metal may be bonded to graphite at lower temperatures. Moreover, the resultant thermal stress can be expected to decrease. The purpose of the present study is to obtain a fundamental knowledge of the solid-state bonding of graphite to austenitic stainless steel.

2. Experiment Method

As test materials, a graphite rod (produced by Mechanical Carbon Co. Ltd.) having a modulus of elasticity of 9.08 GPa, a Poisson's ratio of 0.18 and a thermal expansion coefficient of $5.619 \times 10^{-6} \text{ K}^{-1}$, and SUS304 steel rod having a modulus of elasticity of 205.1 GPa, a Poisson's ratio of 0.27 and a thermal expansion coefficient of $19.46 \times 10^{-6} \text{ K}^{-1}$ are used. The joining specimen of graphite is a column 5 mm in diameter and 32 mm in length, and that of SUS304 steel is a column 5 mm in diameter and 25 mm in length. The joining surface of the graphite was finished by grinding using #3000 emery paper and that of SUS304 steel was finished by polishing using 1 μm alumina. Subsequently, these surfaces were ultra-sonically cleaned.

Figure 1 shows a schematic diagram of the joining system used in the present study. The graphite and SUS304 steel rods were placed in the center of the RF-induction coil, as shown in Fig. 1. Bonding was performed under a compressive stress of 25 MPa in a vacuum of $1 \times 10^{-4} \text{ Pa}$ at various temperatures for different keeping times. The fracture strength of the joint (a rod of 5 mm in diameter and 57 mm in length) was then measured by the four-point bending test (distance between the upper fulcrums: 10 mm, distance between the lower fulcrums: 30 mm, crosshead speed: 0.05 mm/min). In order to investigate the reaction products of the joining interface, X-ray diffraction was performed on the cross section near the joining interface of a joint that graphite remained slightly after the bending test. The longitudinal section was first pol-

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Fig. 1 Schematic diagram of the joining system using a RF-induction.

Fig. 2 Schematic illustration of axisymmetric thermoelastic finite element analysis.

ished using $1\text{ }\mu\text{m}$ alumina, followed by ultrasonic cleaning. The carbon and chromium concentrations near the joining interface in SUS304 steel were then measured by $\text{CK}\alpha$ -ray and $\text{CrK}\alpha$ -ray line analyses using an electron probe micro-analyzer. The distribution of Vickers hardness (Load: 0.49 N) was also measured in the direction of depth from the joining interface on the same longitudinal section.

Thermal stress induced by cooling from the joining temperature to room temperature was calculated by axisymmetric thermoelastic finite element analysis. The general-purpose program I-DEAS was used for this analysis. The joining model was a column of 5 mm in diameter and 30 mm in length (graphite: 15 mm , SUS304 steel: 15 mm). Figure 2 shows the schematic element division of the axisymmetric model (ele-

ment number: 15087). Concentration of the thermal stress on the surface near the joining interface resulted in fine division of elements near the joining interface.

3. Results and Discussion

3.1 The bending strength of graphite

Since graphite is a brittle material, the scatter of strength is large. The bending test of graphite specimens, which have very few surface cracks, was performed. Statistical mean bending strength was estimated by the Weibull Plot used for the estimation of fracture strength in brittle materials such as ceramics. Figure 3 shows the results (F of the vertical axis is the cumulative fracture probability). The Weibull coefficient was 19.34. The scatter of the strength of graphite used in the present study was small. The mean bending strength was 53.97 MPa .

3.2 The bending strength of the joint

Graphite/SUS304 steel couples were annealed under a compressive stress of 25 MPa in a vacuum at four different temperatures (873 , 923 , 973 and 1023 K) for three keeping times (1.8 , 3.6 and 7.2 ks). As mentioned above, austenite contributes greatly to solid-state bonding in the graphite/carbon steel system. Therefore, good joints are obtained only when the joining temperature exceeds the A_1 transformation temperature (1000 K). In the graphite/SUS304 steel system, joining was difficult at 873 K . However, good joints were obtained at temperatures higher than 923 K .

Figure 4 shows the relationships between bending strength of graphite/SUS304 steel joints and keeping time. The dashed line in Fig. 4 shows the bending strength of monolithic graphite. In the bending test, fracture occurred in graphite near the joining interface in every joint, suggesting that bonding at the interface is strong. As shown in Fig. 4(c), the bending strength of the joint obtained by annealing at 923 K was close to that of monolithic graphite. The bending strength decreased as the joining temperature increased, *e.g.* at 973 and 1023 K . In addition, for every joining temperature, the bending strength decreased as the keeping time increased.

Fig. 3 Estimation of the bending strength of graphite in the Weibull plot.

Fig. 4 Relationship between the bending strength of graphite/SUS304 steel joints and joining conditions. The dashed line shows the bending strength of graphite.

3.3 Changes in microstructure near the joining interface in SUS304 steel

Figure 5 shows the optical microstructure of the longitudinal section of a graphite/SUS304 steel joint obtained by annealing at 973 K for 7.2 ks. The black area on the left side is graphite, and the lighter area on the right side is SUS304 steel. An area (from the joining interface to a depth of 20 μm) that was difficult to etch existed in the SUS304 steel near the joining interface. Twin deformations were found in the inner region.

In order to investigate the microstructure of SUS304 steel near the joining interface, X-ray diffraction was performed on the cross section near the joining interface of a graphite/SUS304 steel joint that graphite remained slightly after the bending test. Figure 6 shows the diffraction pattern

Fig. 5 Optical microstructure of the longitudinal section of a graphite/SUS304 steel joint bonded by heating at 973 K for 7.2 ks.

Fig. 6 X-ray diffraction pattern of the cross section near the joining interface of a graphite/SUS304 steel joint bonded by heating at 973 K for 7.2 ks.

of the joint obtained by annealing at 973 K for 7.2 ks. The diffraction peaks of the slightly graphite, austenite, Cr_{23}C_6 produced during joining and strain-induced martensite produced by thermal stress during the cooling process after bonding were detected, suggesting that Cr_{23}C_6 and strain-induced martensite coexist in austenite near the joining interface.

In order to examine further details on the change in microstructure near the joining interface, $\text{CK}\alpha$ -ray and $\text{CrK}\alpha$ -ray line analyses using an electron probe micro-analyzer and the measurement of hardness distribution using a micro-Vickers hardness tester were performed on a longitudinal section of the same specimen, as shown in Fig. 5. Figure 7 shows the results of $\text{CK}\alpha$ -ray and $\text{CrK}\alpha$ -ray line analyses using a beam of 1 μm in diameter as well as the hardness distribution of the section. It is generally assumed that the information obtained is actually taken from an area of approximately 10 μm in diameter even when the beam is 1 μm in diameter. Therefore, information from both sides of the joining interface is detected as the beam approaches the joining interface. Figure 7 shows the carbon and chromium profiles in a region in which neither the carbon intensities nor the chromium intensities are influenced by graphite. According to Fig. 7, the chromium concentration was almost unchanged. This is because the increase in chromium concentration due to the pre-

Fig. 7 CK α -ray and CrK α -ray line analyses and Vickers hardness of the longitudinal section of a graphite/SUS304 steel joint bonded by heating at 973 K for 7.2 ks.

cipitation of Cr_{23}C_6 is cancelled by the resultant decrease in chromium concentration in austenite matrix. However, the chromium concentration decreased slightly near the joining interface due to the remarkable increase in carbon concentration near the joining interface. Both carbon concentration and hardness decreased with depth from the joining interface and became nearly constant at the depth of more than about 120 μm . As shown in Fig. 7, the change in carbon concentration corresponded to the change in hardness. According to the phase diagram of 18Cr–8Ni steel,⁵⁾ the solubility of carbon in austenite is very low at 973 K (0.05 mass%). Considered together with the results of the X-ray diffraction shown in Fig. 6, the reason for the increase in carbon concentration near the joining interface shown in Fig. 7 is that carbon atoms diffuse from the graphite to the SUS304 steel, and the excess carbon atoms beyond the level of solubility reacts with chromium to produce Cr_{23}C_6 . The increase in hardness in this area is thought to be due to the double effects of hardening by the precipitation of Cr_{23}C_6 , that is, precipitation hardening, and work hardening by strain-induced martensite, as shown in Fig. 6. Both carbon concentration and hardness were almost unchanged when the depth was greater than approximately 120 μm . Thus, it is reasonable to speculate that carbon atoms do not diffuse beyond this depth. Since carbon diffusion depends on joining temperature and keeping time, the amount of Cr_{23}C_6 may vary according to the joining conditions.

3.4 Thermal stress analysis by finite element method

Thermal stress induced in the joint was examined by axisymmetric thermoelastic finite element analysis. In the present study, we postulate direct bonding of graphite to SUS304 steel without a change in microstructure near the joining interface.

Figure 8 shows the longitudinal thermal stress distribution on the surface of the joint obtained by annealing at 973 K. Figure 8(a) shows the stress distribution near the joining interface, and Fig. 8(b) shows an enlarged picture of the graphite

Fig. 8 Thermal stress distribution on the surface of a graphite/SUS304 steel joint bonded by heating at 973 K. σ_{zF} shows the longitudinal stress calculated using a finite element method.

Fig. 9 Relationship between the maximum longitudinal stress on the surface of graphite and joining temperature.

side. Tensile stress was induced in the graphite, whereas compressive stress was induced in the SUS304 steel. As shown in Fig. 8(b), the maximum tensile stress was located 0.64 mm from the joining interface. This position remained almost unchanged, even when joining temperature was varied. In the bending test, the position of fracture corresponded to that of

maximum tensile stress, suggesting that the bending strength of the joint is closely related to the thermal stress.

Figure 9 shows the relationship between the maximum longitudinal stress on the surface of graphite, $\sigma_{z\text{FMAX}}$, and joining temperature. $\sigma_{z\text{FMAX}}$ increased with increasing joining temperature. This is likely due to a more pronounced difference between room and joining temperatures.

3.5 Relaxation of thermal stress

In Fig. 4, the difference between the bending strength of monolithic graphite and that of the joint is regarded as the residual thermal stress on the surface of graphite in the joint. Figure 10 shows the changes in the maximum longitudinal stress calculated by the finite element method, $\sigma_{z\text{FMAX}}$, and residual thermal stress, $\sigma_{z\text{R}}$, according to the joining conditions. $\sigma_{z\text{R}}$ was smaller than $\sigma_{z\text{FMAX}}$ under every joining con-

dition. This suggests that thermal stress is released by some mechanism during this bonding process.

Figure 8 indicates that a compressive thermal stress of approximately 300 MPa is induced at a position of 100 μm from the joining interface. The proof stress of SUS304 steel is 205 MPa, so SUS304 steel is plastically deformed by this compressive stress. As shown in Fig. 7, the increase in Cr_{23}C_6 near the joining interface results in an increase in the strength of SUS304 steel. The thermal stress also increases near the joining interface (refer to Fig. 8). Thus, the probability of plastic deformation near the joining interface may be large. However, in Fig. 8, compressive thermal stress shows the largest value at a distance of 20 μm from the joining interface, and decreases at locations closer to the joining interface. In contrast, hardness increases near the joining interface, as shown in Fig. 7. As a result, plastic deformation is not feasible near the joining interface. The reason why the area from the joining interface to a depth of about 20 μm in the optical microstructure shown in Fig. 5 was difficult to etch may be a result of this phenomenon. In contrast, in the region deeper than 20 μm , etching was easy due to plastic deformations such as twin deformation.

In the solid-state bonding of graphite to carbon steel, relaxation of thermal stress due to deformation of carbon steel is not expected to occur because the yield stress of carbon steel near the joining interface is larger than the maximum compressive thermal stress. But, thermal stress is released by deformation of graphite. Graphite is anisotropic because hexagonal graphite has an a -axis, that is, a basal plane consisting of covalent bonds and a c -axis consisting of small van der Waals bonds. The diffusion rate of carbon also indicates anisotropy. As a result, point defects are formed between the basal planes. When the amount of carbon atoms that diffuse from graphite to carbon steel is relatively small, large iron atoms are difficult to diffuse into graphite. In such a case, the greater the number of carbon atoms that diffuse into carbon steel, the greater the number of point defects that are formed in graphite. The increase in point defects allows graphite to be deformed easily, resulting in the relaxation of thermal stress. Conversely, when large amounts of point defects are formed in graphite, iron atoms are able to diffuse into graphite. Therefore, the point defects in graphite decrease in proportional to the number of such iron atoms. It follows that the relaxation of thermal stress is lowered. In this way, the optimum amount of carbon atoms that diffuse into carbon steel exists for relaxation of thermal stress.

In the solid-state bonding of graphite to SUS304 steel, we also examined the relaxation of thermal stress from the viewpoint of diffusion of carbon atoms. Assuming that the carbon concentration is maintained at constant concentration in the region from the joining interface to a depth z_m , z_m is expressed by the following equation:³⁾

$$z_m = 1.1\sqrt{Dt} \quad (1)$$

where D is the diffusion coefficient of carbon, t is the keeping time. The ratio of relaxation of thermal stress to $\sigma_{z\text{FMAX}}$ is given by the following relationship:³⁾

Fig. 10 Changes in the maximum longitudinal stress on the surface of graphite, $\sigma_{z\text{FMAX}}$, and $\sigma_{z\text{R}}$, with respect to the joining conditions.

Fig. 11 Relationship between stress relief ratio R , $(\sigma_{z\text{FMAX}} - \sigma_{zR}) / \sigma_{z\text{FMAX}}$, and diffusion distance from the interface, z_m .

$$R = \left(\frac{\text{the magnitude of relaxation of thermal stress}}{\sigma_{z\text{FMAX}}} \right) \times 100$$

$$= \left(\frac{(\sigma_{z\text{FMAX}} - \sigma_{zR})}{\sigma_{z\text{FMAX}}} \right) \times 100 \quad (2)$$

where R is the stress relief ratio (%). Figure 11 shows the relationship between R and z_m . Although the scatter of the results is large, the relation shown in Fig. 11 is similar to that of the graphite/carbon steel system. That is to say, R reaches a maximum at a certain amount of carbon atoms (a certain value of z_m in Fig. 11) and then decreases with increasing z_m . As mentioned above, this suggests that the relaxation of thermal stress is closely related to the point defects formed in graphite.

In the solid-state bonding of graphite to SUS304 steel, however, the thermal stress is also released by plastic deformation of SUS304 steel. As shown in Fig. 4, the bending strength of the joint decreases as the keeping time becomes very long. This is because carbon atoms diffuse not only into the neighborhood of the joining interface but also into very deep positions. The area of high strength spreads into the inner region as the amount of Cr_{23}C_6 increases and the relaxation of thermal stress due to the deformation of SUS304 steel is consequently lowered. In this way, the relaxation of thermal stress in solid-state bonding of graphite to SUS304 steel is related to the deformation of both graphite and SUS304 steel. The scatter shown in Fig. 11 may be due to the interrelation of these behaviors.

4. Conclusions

Graphite was bonded to SUS304 steel in the solid-state under a compressive stress of 25 MPa in a vacuum of 1×10^{-4} Pa at various temperatures for different keeping times, and the bending strength of the joint, the microstructure and the hardness of SUS304 steel near the joining interface were investigated. The thermal stress induced in the joint was estimated by the finite element method. Based on these results, the influence of thermal stress on the bending strength of the joint was examined. The following conclusions are obtained based on the results of the present study:

(1) Good joints are obtained by annealing at temperatures higher than 923 K.

(2) Axisymmetric thermoelastic finite element analysis revealed the following: Compressive thermal stress is induced on the surface of SUS304 steel. The maximum tensile thermal stress is induced on the surface of graphite 0.64 mm from the joining interface, and this stress increases with increasing joining temperature. The position of maximum tensile thermal stress corresponds to that of fracture in the bending test.

(3) The maximum residual tensile thermal stress in practical joints is less than the maximum tensile thermal stress calculated by finite element method because the thermal stress is released by the deformation of SUS304 steel and graphite. The smaller the maximum residual tensile thermal stress, the higher the bending strength of the joint.

(4) The relaxation of thermal stress is closely related to the amount of carbon atoms that diffuse from graphite to SUS304 steel. This is because the amounts of Cr_{23}C_6 in SUS304 steel and the number of point defects in graphite vary and those influence the deformabilities of SUS304 steel and graphite, respectively.

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