1. Introduction

Additive manufacturing using metal foils enables production of a fine machine structure by solid-phase diffusion bonding that is heat-treated after foils that have been processed into a desired shape are stacked. A currently used application of this method is the manufacture of metal micro pumps. When the foil material is austenitic stainless steel, one of a challenge is a decrease in the diffusion-bonding temperature. Because the practical diffusion-bonding temperature of metal foils experience performance loss caused by a loss of yield strength due to grain growth during bonding. Accelerating the recrystallization by using pre-distorted base metals effectively decreases the bonding temperature of metal materials. Pre-distorted SUS304 contains deformation-induced martensite before bonding, and then during diffusion bonding recrystallizes with reversion of this martensite. This study evaluates the effect of bonding time on bonding state and on recrystallization with the reversion of SUS304 that has deformation-induced martensite, and discusses the relationship between bonding behavior and microstructure change. Results revealed that the bonding area (evaluated based on line profile of pixel intensity on the bonding interface in a cross-sectional image) exceeded 70% in a specimen bonded at 973 K bonding temperature, 50 MPa bonding pressure, and 60 s bonding time. Results also showed that a bonding time longer than 900 s was necessary to obtain bonding strength comparable to that of the base material. On the other hand, analysis of the bonding area of pre-distorted SUS304 that had severely deformed austenite revealed recrystallized grains at the bonded area. Recrystallization of SUS304 that has deformation-induced martensite starts homogeneously due to reversion of this martensite. Therefore the most likely effect of reversion in diffusion bonding is that diffusion is promoted homogeneously in the bonding interface because recrystallization starts homogeneously during the bonding process.

KEY WORDS: diffusion bonding; reversion; recrystallization; deformation-induced martensite; SUS304.
that has deformation-induced martensite, and discusses the relationship between bonding behavior and microstructure change. In this study, first the bonding behavior and microstructure change due to the bonding were evaluated based on cross-sectional microstructure observation, hardness test, and measured volume fraction of martensite, and then the degree of bonding was evaluated based on cross-tensile tests.

2. Experimental Procedure

2.1. Materials

Conventional blocks of SUS304 used in this study have the chemical composition as shown in Table 1. The process of introducing distortion into the material was carried out as follows and as shown in Fig. 1. First, blocks of SUS304 were cut into 40 mm×40 mm×20 mm samples (Fig. 1(a)). The samples were then compressed, cut, and rolled into a 10-mm-thick sheet so that the equivalent strain in the compression direction was 90% at 573 K (less than the recrystallization temperature) (Figs. 1(b), 1(c)). These warm-rolled samples were then rolled to 1-mm thickness at room temperature to transform the microstructure into martensite from austenite (Fig. 1(d)). To prevent the processing heat from blocking the martensite formation, a sample (hereafter called sample WC) was rolled in a single pass with up to 5% reduction and then cooled by water. Backscattered electron (BSE) image and X-ray diffraction (XRD) profile of as-rolled WC (Cu Kα radiation) are shown in Fig. 2. These indicate that the almost all microstructure consisted of deformation-induced martensite produced by rolling. The XRD profile shows some small austenite peaks, it means the sample include small amount of austenite. However, those peaks are not enough to quantitative analysis because there is little number of peaks. To evaluate the effects of the presence or absence of martensite on diffusion bonding, a sample was warm-rolled at 573 K (thus containing deformed austenite) with a reduction of 99% (hereafter called sample W99) (Figs. 1(b), 1(c), 1(e)).

| Table 1. Chemical composition of the stainless steel SUS304 (mass%). |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C       | 0.05 | 0.48 | 0.97 | 0.035 | 0.004 | 0.19 | 8.02 | 18.09 | bal. |

Fig. 1. Schematics of distortion-introduction process. Arrows show compression direction. (Online version in color.)

Fig. 2. (a) Crystallographic contrast in highly deformed SUS304 (WC) imaged with the angular selective backscattered detector and (b) X-ray diffraction pattern of WC (Cu Kα radiation).
2.2. Bonding Process

Figure 3 show the geometry and dimensions of bonding specimens for microstructure observation (Fig. 3(a)) and for the cross-tensile test (Fig. 3(b)). For the cross-tensile test, the specimen was further cut so that it fit into the testing apparatus (dimensions were 1/5 smaller than those from the original dimensions of the specimen provided in JIS Z 31377 and ISO 14272), and the geometry of grip section was modified to fit into sample holder. All the bonding specimens were cut from the 1-mm-thick sheet, and then their bonding areas were mirror polished. The surface average roughness Rα of the bonding area was 20 nm or less. The specimens removed fat with acetone and washed it with distilled water and dried before bonding.

The diffusion bonding between WC and WC was performed using an oil pressure servo examination machine that has a maximum load capacity 50 kN (developed by Shimadzu Corporation, EHF-EA5T) and has a radio-frequency heating apparatus in a high-vacuum chamber. In the microstructure observation, the two specimens (Fig. 3(a)) were placed on cross-wise to each other with their polished surfaces facing each other, and then pressurized to a gage pressure of 50 MPa by 20-mm-diameter Inconel-HX pressurizing rods as shown in Fig. 4. In the cross-tensile test, two specimens (Fig. 3(b)) were again placed cross-wise on a φ50 mm × 10 mm Inconel-HX base with their polished surfaces facing each other, and then pressurized to a gage pressure to 50 MPa by using a 5-mm-diameter pressurizing punch. For both the microstructure observation and cross-tensile test, the temperature was then increased at a rate of approximately 3 K/s to 973 K and held at that temperature for different bonding time tBond of 0 s, 30 s, 60 s, 120 s, 240 s, 480 s, 900 s, 1 800 s, 3 600 s, and 7 200 s. The pressurization and heating were then stopped promptly and the specimens were cooled in vacuum to less than 573 K, after which the vacuum chamber was depressurized to atmospheric pressure. For the microstructure observation, temperature was measured using an R thermocouple welded at the edge of a pressurizing rod (Fig. 4(a)). For the cross-tensile test, the temperature was measured using an R thermocouple that had been welded to the back of the sample holder (Fig. 4(b)).

2.3. Characterization of Mechanical Properties and Microstructure

The degree of bonding was evaluated based on cross-tensile tests and cross-sectional microstructure observation of bonded specimens. The cross-tensile test was performed at 0.01 mm/s at room temperature using the same oil pressure servo examination machine as in the bonding processes. For the cross-tensile test, a bonded specimen was fixed to the sample holder by screws through holes in the specimen. Fracture surface was observed by scanning electron microscopy (SEM).

The bonding behavior and microstructure change due to the bonding were evaluated based on cross-sectional microstructure observation, hardness test, and measured volume fraction of martensite. In preparation, the bonded specimens were cut along the centerline of the bonding area, and then the cut surface of each specimen was first mechanically polished and then further polished into a mirror finish by electro-polishing at 40 V (HClO: CH₃COOH = 1: 9). The polished surface of the bonded specimen was observed by using Carl Zeiss Ultra Plus SEM or Hitachi SU-70 SEM, and orientation analysis was performed by using EDAX Digi View IV electron backscatter diffraction (EBSD). The bonding area was measured from a binary image of the cross-sectional SEM image (Fig. 5) as follows. First, the threshold of the brightness level of the SEM image was set to separate the bonded and unbonded parts (Fig. 5(a)),

![Fig. 3. Schematics of bonding specimen for microstructure analysis (a) and cross-tensile test (b) (all dimensions in mm).](image-url)

![Fig. 4. Schematics of bonding jig for microstructure analysis (a) and cross-tensile test (b).](image-url)
and then used to binarize the SEM image. Then, from the line profile of the pixel intensity on the bonding interface of the binarized image (Fig. 5(b)), the bonding area was calculated as the ratio of the number of white pixels (pixel intensity = 255) (corresponding to the bonded parts) to the total number of the line profile. This bonding length ratio $BL$ is expressed as percentage as shown in Fig. 5. The subgrain boundary ratio $L_{subGB}$ was defined as the ratio of the sub-grain boundary length to the grain boundary length in the measurement area using EBSD. The micro-hardness of the bonded specimen $HV$ was measured at 12 locations per specimen on the cross-sectional surface using the Vickers hardness test at a load of 2.94 N and a loading time of 10 s. The volume fraction of martensite $V_{\alpha'}$ was measured using the magnetic induction method with FERITESCOPE (developed by Fischer). It is necessary to make a calibration curve to do quantitative analysis of the $V_{\alpha'}$. However, the $V_{\alpha'}$ was an uncalibrated read value of the FERITESCOPE because it is enough if a degree of reversion is evaluated from this value.

3. Results

3.1. Bonding Behavior

Cross-sectional BSE images showing the bonding interface of the diffusion-bonded WC are shown in Fig. 6. Metal areas appear white to gray, and pores (i.e., unbonded parts) are black because electrons do not reflect from pores. These images clearly show that the bonding area increased with increasing $t_{bond}$, and that bonding started at $t_{bond} = 0$ s. On the other hand, pores were elongated along the bonding interface when $t_{bond}$ was short (< 60 s), and then separated into small equiaxed pores that decreased in number while increasing in size when $t_{bond}$ was increased. Figure 7(a) shows change in $BL$ with $t_{bond}$. The $BL$ was 33% at $t_{bond} = 0$ s, then rapidly increased to 70% at 60 s, and then gradually increased to 89% at 7 200 s.

Figure 7(b) shows the change in fracture load $F$ with $t_{bond}$ and Fig. 8 show the fracture surface after cross-tensile tests. In Fig. 7(b), open square symbols indicate base material fracture and closed squares indicate both base material fracture and interfacial debonding. $F$ at $t_{bond} = 0$ s and 30 s were not measured because the bonded specimens had peeled before the cross-tensile tests could be performed. The $F$ apparently increased with increasing $t_{bond}$, although it widely varied. In comparison with the $F$ of the specimen bonded at 973 K and $t_{bond} = 900$ s, that of it in this study is approximately twice as large as that of it in the previous study. It is thought that this difference is due to presence or absence of degreasing bonding surface. An acetone removal of fat and distilled water washing were performed in this study whereas a tap water washing was performed in the
previous study. The fracture surface (Fig. 8) showed interfacial debonding and base material fracture, and the amount of the base material fracture increased with increasing $t_{\text{bond}}$. Change in the $F$ does not indicate an increase in bonding directly because the $F$ does not represent bonding strength. Figure 6 suggest, however, that bonding does increase with increasing $t_{\text{bond}}$.

3.2. Recrystallization Behavior with Reversion of Deformation-induced Martensite

Specimens bonded at $t_{\text{bond}} = 0$ to 60 s show recrystallized grains and a highly strained region where the contrast of the BSE image is heterogeneous (Figs. 6(a)–6(c)). Specimens bonded at $t_{\text{bond}} \geq 900$ s show only recrystallized grains (Figs. 6(d)–6(g)). To evaluate the process of recrystallization with reversion of deformation-induced martensite, three parameters of bonded SUS304 were measured, namely, volume fraction of martensite $V_{\alpha'}$, length fraction of sub-grain boundary $L_{\text{subGB}}$, and hardness $HV$. Figure 9 show the measurement results. All three parameters changed when $t_{\text{bond}} \geq 900$ s. Figure 9(a) shows the change in $V_{\alpha'}$ as a function of $t_{\text{bond}}$. The $V_{\alpha'}$ was 3.7% at $t_{\text{bond}} = 0$ s, and decreased with increasing $t_{\text{bond}}$ until $t_{\text{bond}} = 900$ s, and then suddenly decreased to almost 0% at $t_{\text{bond}} = 900$ s. Microstructure at $t_{\text{bond}} = 0$ s (Fig. 6(a)) was austenite (confirmed by EBSD) and consisted of recrystallized grains and a highly strained region. Figure 9(b) shows the change in $L_{\text{subGB}}$ of bonded WC as a function of $t_{\text{bond}}$. The $L_{\text{subGB}}$ rapidly decreased until $t_{\text{bond}}$ reached 900 s, and then leveled out. Figure 9(c)
shows the change in $HV$ as a function of $t_{\text{bond}}$. The $HV$ of the bonded WC at $t_{\text{bond}} = 0$ s was almost the same as the base material, but rapidly decreased until $t_{\text{bond}} = 900$ s, then remained relatively unchanged from $t_{\text{bond}} = 900$ s to 3 600 s, until it finally decreased at $t_{\text{bond}} = 7200$ s. The results for these three parameters suggest that recrystallization with reversion was complete when $t_{\text{bond}} \leq 900$ s, after which the grains grew.

4. Discussion

Compared to the diffusion bonding conditions commonly used in current manufacturing processes (1 200 K for 10 h), bonding of the SUS304 in this study (WC) occurred at lower temperature at a shorter $t_{\text{bond}}$. The bonding area of WC suddenly increased at $t_{\text{bond}} = 60$ s and reached 70%. The behavior of an oxide film on the SUS304 and microstructure transformation during the bonding process is an important factor in obtaining a bonding area at low temperature within such a short $t_{\text{bond}}$.

According to the report by Ohashi et al., the oxide film of a bonding surface in iron-type materials coheres to the surface and forms oxide-base inclusions on the bonded region early in the bonding process, and then such inclusions cohere as bonding progresses while the number of oxide-base inclusions generated by oxygen diffusion into base materials decreases. Such inclusions were not observed in our study in inclusions generated by oxygen diffusion into base materials, but they were observed in the fracture surface of the specimen at $t_{\text{bond}} = 60$ s, although dimples were observed as shown in Fig. 8(n). Active surfaces of the base materials were apparently exposed within a short $t_{\text{bond}}$, and bonding progressed at $t_{\text{bond}} = 60$ s. The mechanisms of the active surface exposure in the early stages of bonding (short $t_{\text{bond}}$) are not well understood. Possible mechanisms, however, are the effects of diffusion acceleration in the base material by introducing strain and by eliminating the oxide film via the superplastic deformation of the base material.

In the bonding process of WC, deformation-induced martensite recrystallizes after diffusional reversion. The steps in such recrystallization are reportedly as follows. First, recovery of martensite occurs and then nuclei of austenite grains are generated. The austenite grains then increase by absorbing martensite into the recrystallized grains, and finally the grains grow. In this study, the microstructure of the specimens bonded at 973 K might have undergone recrystallization after completing reversion because the microstructure was entirely austenite, and because both $L_{\text{recrystal}}$ and $HV$ were low. To discuss effects of recrystallization with reversion of deformation-induced martensite in diffusion bonding at low temperature, we investigated both the recrystallization without reversion and the bonding behavior of W99 (SUS304 with severe deformed austenite), and then compared the recrystallization and bonding behavior between WC and W99 under the same temperature and pressure at $t_{\text{bond}} = 0$ s. Cross-sectional BSE images showing bonding interface of bonded W99 (Fig. 10) reveal that the microstructure of the bonded W99 consisted of both recrystallized and un-recrystallized grains. The bonded region contained recrystallized grains, suggesting that diffusion by recrystallization contributed to the bonding. Recrystallization of WC occurred homogeneously by reversion, leading to generation of fine grains of austenite. Therefore, the bonding area of WC apparently increased at a low temperature within a short $t_{\text{bond}}$ because diffusion occurred homogeneously via recrystallization with the reversion.

5. Conclusions

Diffusion-bonding mechanisms of SUS304 that has deformation-induced martensite were revealed by evaluating the bonding behavior and recrystallization in reversion of deformation-induced martensite. Conclusions of this study are as follows.

If the SUS304 sample having deformation-induced martensite was bonded in 50 MPa at 973 K, the bonding area (calculated as BL) reached 70% within a short bonding time $t_{\text{bond}} = 60$ s. The $t_{\text{bond}}$ required to obtain bonded areas that have fracture strength equivalent to that of the base material, however, was more than 900 s.

The bonding area increased within a short $t_{\text{bond}}$ of 60 s at a low bonding temperature of 973 K because the microstructure had recrystallized homogeneously by a reverse transformation in highly deformed SUS304 (WC).

The most likely effect of reversion of deformation induced martensite in diffusion bonding is that diffusion is promoted homogeneously in the bonding interface because recrystallization starts homogeneously during the bonding process.

REFERENCES

1) Kikuchiseisakusho Co., Ltd.: Kikuchiseisakusho Monozukuri Mechatronics Laboratory, Micro Fluidies Device, http://www.kikuchiseisakusho.co.jp/mechatro2/MicroFluidDevice.html, (accessed 2016-03-11).
2) Y. Kabasawa: Press Working, 51 (2013), 46.
3) O. Ohashi: J. Jpn. Inst. Met., 56 (1992), 579.
4) M. Katoh, N. Sato, T. Shiratori and Y. Suzuki: Tetsu-to-Hagané, 102 (2016), 34.
5) I. Masumoto and H. Hira: J. Jpn. Weld. Soc., 50 (1981), 284.
6) T. Haramoto, Y. Yamashita, O. Ohashi and T. Ishiguro: Mater. Trans., 55 (2014), 633.
7) JIS Z 3137: 1999, Specimen dimensions and procedure for cross tension testing resistance spot and embossed projection welded joints.
8) ISO 14272: 1994, Specimen dimensions and procedure for cross tension testing resistance spot and embossed projection welds.
9) M. Katoh and Y. Torisaka: Tetsu-to-Hagané, 80 (1994), 249.
10) M. Katoh and Y. Torisaka: Tetsu-to-Hagané, 91 (2005), 694.
11) O. Ohashi: J. Jpn. Weld. Soc., 62 (1993), 512.