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Authors(English)	Toshi-Taka Ikeshoji, Keisuke Kuroda, Mana Katori, Akio Suzumura, Takahisa Yamazaki
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Sensitization of Braze-Pressure Welding of Stainless Steel

Toshi-Taka Ikeshoji*, Keisuke Kuroda**, Mana Katori*, Akio Suzumura*, Takahisa Yamazaki*

**Tokyo Institute of Technology, Tokyo, Japan*

2-12-1 O-okayama, Merugo-ku, Tokyo, 152-8552, Japan, E-mail: Ikeshoji.t.aa@m.titech.ac.jp

***JGC Corp., Yokohama, Japan.*

2-3-1 Minato-Mirai, Naka-ku, Yokohama, 220-6001, Japan

Abstract

Japanese Ministry of Land, Infrastructure, Transport and Tourism offers to build, so they called, the 100 years endurable house and building. Those buildings are expected to extend their lifetime and to reduce the consumption of resources for re-building. The lifetime extension of structures or skeletons of building has already accomplished. But the ordinary steel piping inside of the building withstands against the corrosion for 20 – 30 years. Therefore the stainless steel piping is expected to be installed into those long lifetime buildings. In this research, the braze-pressure welding is allied to the stainless steel pipe joining. The braze-pressure welding (BPW) is a mixed method of brazing and pressure welding. By the insertion of the low melting point brazing filler alloy, the joining interface is made clean without the oxides. It allows the following pressure welding process to join the interface without high pressure. For the BPW joint, the EPR test was conducted to measure the degree of the sensitization of stainless steel. By modifying the thermal history, the BPW joint without sensitization was obtained.

Introduction

Japanese Ministry of Land, Infrastructure, Transport and Tourism offers to build, so they called, the 100 years endurable house and building. The 100-years buildings are expected to have longer lifetime with the earthquake-proof, and, as a results, to reduce the consumption of resources for re-building. The lifetime extension and the enhancement of the strength of structures or skeletons of building have already accomplished. But the lifetime extension of the inner equipment of the building remains relatively shorter. One of the problems of the inner equipment is the piping for the steam, gas, water and sewerage. So far, the ordinary steel piping is used for them. But it withstands against the corrosion for 20 – 30 years. Therefore the stainless steel piping is expected to be installed into those long lifetime buildings.

Stainless steel pipes are jointed usually with the arc welding. But the arc welding has the problem of sensitization in the HAZ. So the solid state joining without the large heat input was expected to apply to the stainless pipes joining. Pressure welding, which is one of the major solid state joining method, cannot be applied because the high forging pressure enlarges the diameter of the pipe. To overcome the enlargement in the pipe's diameter, the braze-pressure welding (BPW) was proposed.

The braze-pressure welding (BPW) [1] is the newly developed joining method. It combined the brazing and the pressure welding. The processes of BPW are schematically shown in Fig.1. The BPW process is fundamentally the pressure welding. Different from the pressure welding, the BPW has the cleaning process. During the cleaning process, the joining surfaces are made clean by the cleaning metal. The cleaning metal is inserted between the joining surfaces. The cleaning metal has similar compositions with the base metal to join, but it is added the melting point depressant. The molten cleaning metal removes the oxides on the mating surfaces, and it is extruded from the joining interface by the pressure loaded to the mating surface and by the surface tension distribution induced by the temperature distribution, which is higher on the outer surface of the pipe than in the joining interface. Between the clean and fresh joining surface, the solid state bond can be easily made.

The cleaning process of the BPW can be considered the brazing process under the compression loading. The positive effect of compression loading during the brazing has been pointed out. For Cu/Metglas® MBF2005/Cu brazed joints, the low or moderate compression loading less than 10MPa changed the microstructure of the brazed interface, and improved the impact strength of the joints [2]. The improvement in the shear strength of the joints was reported

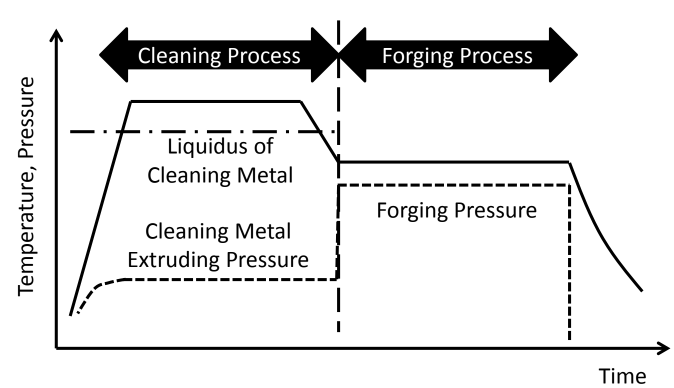


Figure 1 Schematics of BPW processes.

Table 1 Compositions of specimens and the cleaning metal.

	Fe	Ni	Cr	Mo	Mn	Si	B	C	P	S	T_S	T_L
SUS304L AISI Type 304L	Bal.	9.00 −13.00	18.00 −20.00	−	≦2.00	≦1.00	−	≦0.03	≦0.045	≦0.030	1673 (1400)	1723 (1450)
SUS316L AISI Type 316L	Bal.	12.00 −15.00	16.00 −18.00	2.00 −3.00	≦2.00	≦1.00	−	≦0.03	≦0.045	≦0.030	1648 (1375)	1673 (1400)
Cleaning Metal	Bal.	10	20	1	−	3	2.5	−	−	−	1480 (1207)	1498 (1225)

Compositions in mass%. T_S: Solidus and T_L: Liquidus in K and (ºC)

for the brazing of Inconel 718 with Ni-based brazing filler [3]. Both works pointed out the microstructure in the brazing interface changed to cease the eutectic layer in the center of brazed interface. This is considered due to the expulsion of the liquid brazing filler metals. The BPW's cleaning process is intended to eject the liquid metals out of the joining interface. So the similar improvements in the joint strength could be taken place. But BPW's microstructure reveals no residual layer of brazing filler in the joining interface. This microstructure might be achieved during the following forging process.

The ordinary pressure welding process make the joining surface clean and fresh by breaking the oxide layer with the large deformation. And the ordinary pressure welding requires the high forging pressure. Unlike the ordinary pressures welding, the BPW can be conducted without the high forging pressure. In this way, the BPW's joint has similar properties with the pressure welding but without large deformation.

When the stainless steel is joined by the BPW, the sensitization was expected to be reduced, because the highest temperature through the BPW process was much lower than that of the arc welding. Even if the sensitization occurred, the location of the sensitized zone was considered in a distant part from the joint interface. The BPW joint of the austenitic stainless steel SUS304 (AISI Type 304SS) showed that almost all parts of the joint were not sensitized, but that, in the vicinity of the joint surface, the degree of the sensitization became high[4]. The major factor for the sensitization is considered to be the formation of the chromium carbides. The chromium carbides mainly precipitate in the temperature range 773 – 1073K (500 – 800ºC). But the vicinity of the joining interface of BPW experiences the temperature range for very short time. Therefore, it is necessary to examine the effect of the carbon content in the austenitic stainless steel to the sensitization of BPW joint.

In this research, the two types of the austenitic stainless steel with lower carbon content is jointed with BPW; SUS304L (AISI Type 304L) and SUS316L (AISI Type 316L). Their carbon composition is lower than the SUS304, and they can reduce the sensitization in the arc welding process. The BPW joining was conducted with various heating time and heating temperature. For their BPW joints, the electro corrosion chemical test was conducted using the EPR (Electrochemical Potentiokinetic Reactivation measurement) method standardized in JIS G.0580.

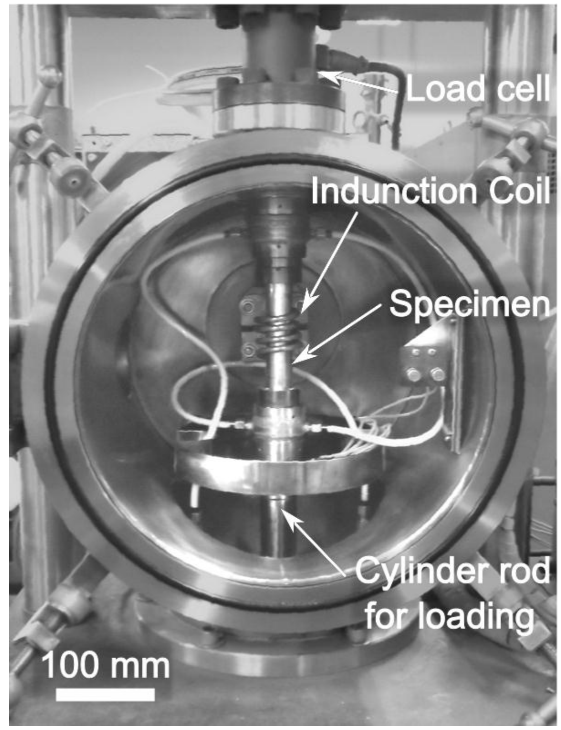


Figure 2 Vacuum furnace with the induction heater.

Experimental Details

Materials & Specimens

The provided materials were the austenitic stainless steel pipes, JIS SUS316L (AISI Type 316L) and JIS SUS304L (AISI Type 304L). They had the dimensions of ø 25.4×t4 mm. They were chopped into the length of 50 mm and their end faces were lathed by the turning machine and polished using the abrasive paper with #1000 grit standardized in JIS R 6252.

The cleaning metal used in this research was the iron based alloy (Fe-20Cr-10Ni-3Si-2.5B-1Mo). This cleaning metal had the similar compositions with the austenitic stainless steels of SUS316L and SUS340L, but the silicon and boron were added to make its liquidus lower than those stainless steels. The cleaning metal's solidus was 1207ºC and liquidus was 1225ºC. The compositions, solidus and liquidus are compared in **Table 1**. This cleaning metal was provided in the powder with the average diameter of 40µm.

Braze-Pressure Welding Tests

On the side surface of a specimen in the vicinity of the mating surface, the K-type thermocouple was spot-welded. On a mating surface of specimen, acrylic adhesive (3M Type55

Table 2 Conditions for BPW tests

#	Material	Total Heating Time, s	Cleaning Process Temp. ºC	Cleaning Process Time, s	Forging Process Temp. ºC	Forging Process Time, s
A	316L*	130	1280	70	-	-
B		180		120	-	-
C		240		180	-	-
D		360			1150	60
E		360	1180			
F		480	1230			180
G		660				
H	304L**	360	1280			60
I		660	1230			180
J	316L* w/o CM+	360	1280	180	1150	60

* AISI Type 316L, ** AISI Type 304L
\+ BPW without the cleaning metal, *i.e.* pressure welded.

spray) was spayed, and the cleaning metal powder was dusted uniformly.

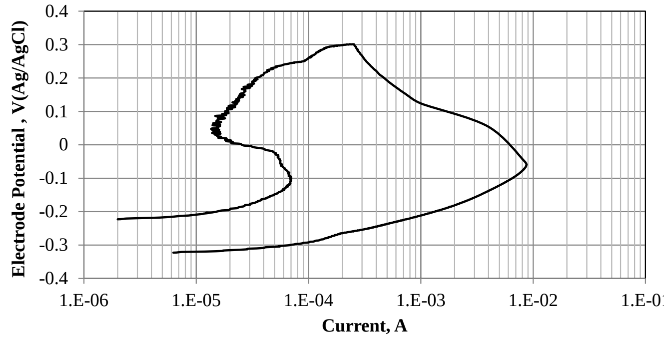
The braze-pressure welding tests were conducted in the vacuum chamber with induction heater (Fig.2). The induction coil was made from the copper tube of Ø6 mm, and the internal diameter of the coil was Ø 32mm. Its number of turn was 4, and the heating range was approximately 40 mm. The specimen pipes were placed clamped by the oil hydraulic cylinder. The joining interface was made coincide with the center of the heating range. The inside of the chamber was evacuated to approximately 2.6×10^{-3} Pa.

The specimen was heated to the cleaning temperature by 60s. The temperature during the cleaning process was 1180º – 1280ºC. The keeping time during the cleaning process was 70 – 120s. After the cleaning process, the specimen was cooled down to the forging temperature by 60 s. The forging temperature was 1150ºC. The forging time was 60 – 180s. After the forging process, the specimen was cooled down in the vacuum atmosphere. The combinations of the cleaning process and forging process are listed in **Table 2**. The total heating time is the time from the onset of the heating to the end of the forging process. The pressure during the cleaning process was 5 MPa, and the forging pressure was 10 MPa.

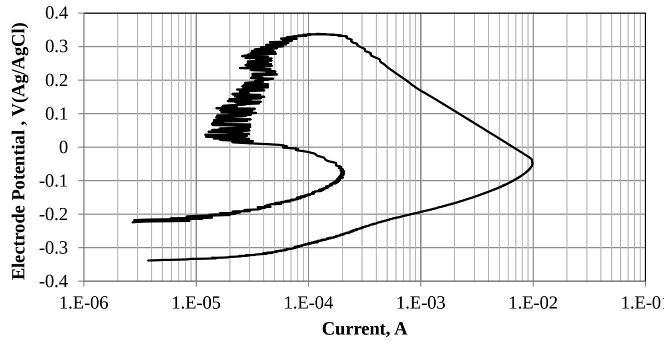
Electro Corrosion Chemical Tests

From the center part of the obtained BPW joint, the electro corrosion chemical test specimen was cut out. The specimen was cut in its middle where coincided with the joint interface. The specimens' dimensions were L5×W10×t4 mm. The area of this end face was 34.6 mm^2. It was embedded in the acrylic resin. The end face of the former joint interface was polished using the abrasive paper with #1000 grit.

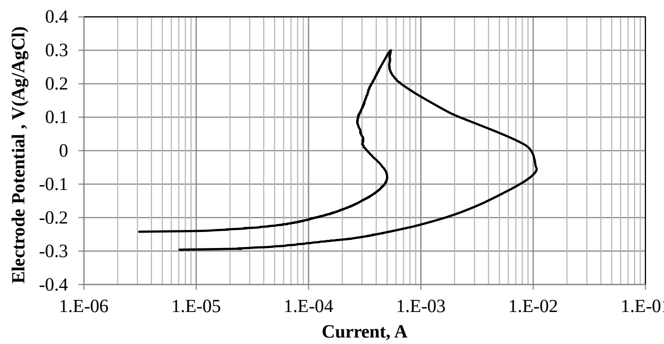
The EPR test was performed according to JIS G 0580. The EPR cell had an austenitic stainless steel counter electrode and a saturated Ag/AgCl reference electrode. The specimen was mounted as the work electrode. The cell was poured with 500



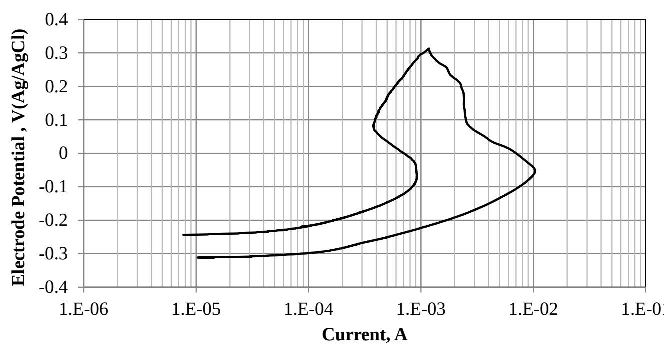
(a)



(b)



(c)



(d)

Figure 3 I-V curves of EPR tests for the BPW joint specimens. (a)Specimen A, Total heating time 130 s, (b) B, 180 s, (c) C, 240 s, (d) F, 360 s.

ml of 0.5M H_2SO_4 solution containing 0.01M KSCN. The N_2 gas purged for 300s. The open-circuit potentials (OCP) were measured first. For all of the specimens, OCP was lower than 350mV. Then, the specimen was anodically polarized from −300 mV to +300 mV and then cathodically polarized to OCP from +300 mV(SCE) at a scan rate of 1.667 mV/s (100 mV/min). For each specimen, the ratio of reactivation current

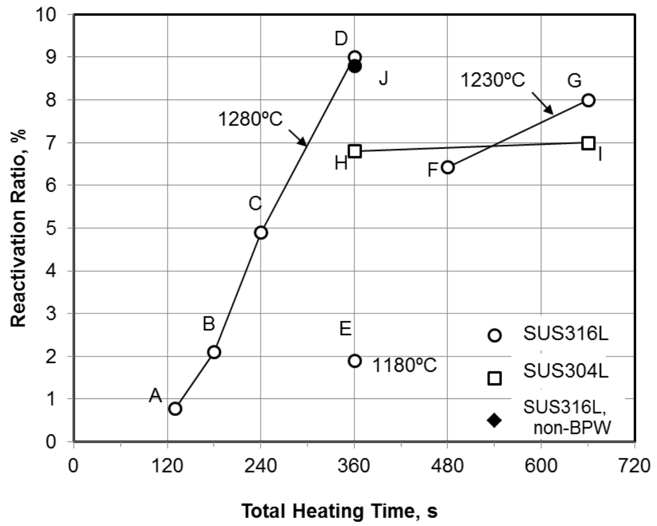


Figure 4 Reactivation ratio of EPR tests for the BPW joint specimens.

(I_R) to activation current (I_A) was calculated which will be referred to as reactivation ratio (R). All EPR tests were performed at the room temperature.

Results

The I-V curves of the EPR tests are shown in Fig.3. The left side of the I-V curve is the reactivation curve and its peak, which appears around the -0.1 V, is the reactivation current (I_R). The right side of the curves in the plots is the anodizing curve and its peak is the activation current (I_A). For almost of all specimens, the I_A values were constant and approximately 1.0×10^{-2} A. On the other hand, the I_R values increased with the total heating time. When the total heating time was 130 s, the I_R value was 7.0×10^{-5} A. The I_R value increased to 9.0×10^{-4} A when the total heating time was 360 s.

The change in the I_R values reflected directly in the variation of the reactivation value, R (Fig.4), because the values of I_A were almost constant. The specimens A, B, C, and D experienced the same cleaning temperature, 1280º C, but the total heating time was changed. Their values of reactivation ratio R increased linearly from 1% at 130s of the total heating time to almost 9% at 360s.

Even the total heating time was larger than the 360 s, the reactivation rate R was lower, when the total heating time lowered. The joining conditions of D and E shared the same total heating time, 360 s, but the cleaning temperature of E was 100º C lower than D. The R value of E was approximately a quarter of that of D. The joining conditions of F and G were with much longer total heating time, 480s and 660s, but the cleaning temperature was 50 ºC lower than D. The R values were comparable with that of D.

From these results, it is suggested that the degradation in corrosion through the BPW process could be avoided by making the total cleaning time shorter and the cleaning temperature lower.

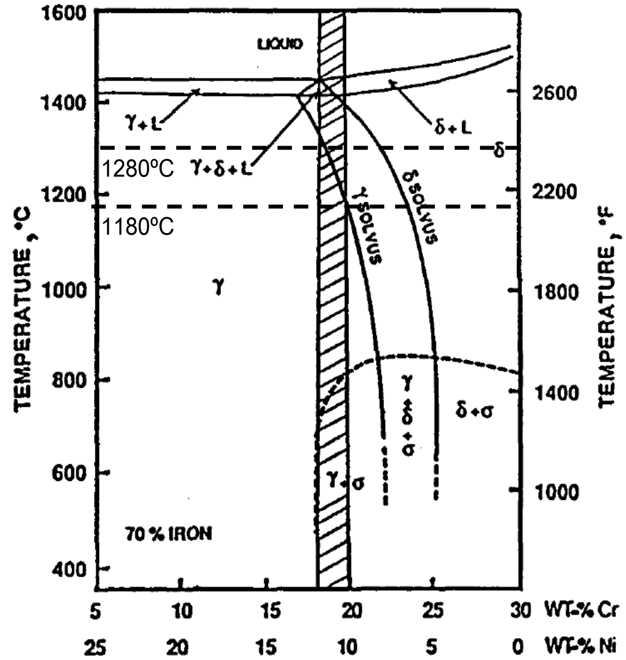


Figure 5 70％Fe-30%(Cr, Ni) phase diagram. (Tseng, CC *et.al.*[5], The dashed lines were added by the author.)

The BPW joints of SUS316L and SUS304L were compared with the joining conditions of D, G, H, and I. When the cleaning temperature was 1280º C, the R value of SUS304L (H) was lower than that of SUS316L (D) by 2%. When the cleaning temperature was lower, 1230ºC, the difference in R values between SUS304L and SUS316L became smaller. Therefore, at the high cleaning temperature, the difference in the R values by the stainless steel grade might appear larger.

Discussion

Conventionally, it has been said that the degradation in corrosion resistance of the stainless steel was mainly by the chromium carbide formation. Around the chromium carbides, the chromium depleted layer is formed which leads to the insufficient formation of the chromium oxides passive layer. To avoid the chromium carbides precipitation, the austenitic stainless steels with lower carbon content, SUS304L and SUS316L, were chosen for the specimens in this research. The continuous-cooling-precipitation (CCP) diagrams for the SUS304 indicate that the chromium carbide precipitation is expected to precipitate during the cooling process of the BPW joining. But on the case of the SUS304L, according to its CCP diagram, the chromium carbides would not precipitate along the cooling curve of the BPW joining process. Therefore, the chromium carbides precipitation might not be major factor of the degradation of corrosion resistance in this research.

However, the heat treatment temperature of those CCP diagram is around 1000ºC. The cleaning temperature during

BPW joining of this research was more than 1200ºC. As shown in Fig.4, the reactivation rate *R* of EPR tests increased with the cleaning temperature. So the corrosion resistance would be degraded with the increase in the cleaning temperature. The formation of chromium carbides might precipitate at this high temperature, but it is generally said that the temperature range of the precipitation is 500 – 800ºC. The other microstructural change could be considered to affect the corrosion resistance during the BPW process in this research.

To examine the precipitates in the austenitic stainless steels, SUS316L and SUS304L, the Fe-30%(Ni,Cr) cross section of Fe-Cr-Ni ternary diagram is shown in Fig.5 [5]. Assuming that the compositions of nickel and chrome in SUS316L and SUS304L are 13%Ni-17%Cr and 11%Ni-19%Cr, which are the middle values of the range of nickel and chrome compositions in **Table 1**, SUS316L and SUS304L fall on the hatched part in Fig.5. At the higher temperature than 1200ºC, the delta ferrite phase precipitates in the gamma phase. The mixture ratio of the delta ferrite becomes larger at the higher temperature. When the austenitic stainless steels are cooled down, a part of this delta ferrite phase changed into the sigma phase. The BPW joints heated up to 1280ºC during the cleaning process might have the delta ferrite phase, and after cooling down, they changed into the sigma phase remained in the gamma phase [6]. When the cleaning temperature was 1180ºC, almost no delta ferrite phase might precipitate and almost no sigma phase might remain at low temperature. In the lower temperature range around 800ºC, the sigma phase precipitation requires more than 100 hours [7]. The sigma phase in the austenitic stainless steels is considered to enhance the sensitization and lower its strength [8,9]. Comparing the reactivation rate values with the cleaning temperature, the amount of the sigma phase originated from the delta ferrite precipitation at high temperature can have the effect to the degradation of the corrosion resistance.

For the SUS316L stainless steel, the minor addition of molybdenum is said to enhance the precipitation of sigma phase. So, the reactivation rate values of BPW joint interface are compared between the SUS316L and SUS304L which does not contain the molybdenum (Fig.4, D, G, H, and I). The comparison between the pairs of the same cleaning temperature and the total heating time, D and H, and G and I shows that the *R* values for the SUS304L were lower than those of SUS316L. But the differences among those values were not so large, and the further accumulation of *R* value data is necessary.

On the other hand, although the arc welding processes expose the vicinity of the weld metal to the higher temperature than 1200ºC, the degradation against the corrosion by the sigma phase has not reported as far as the authors' knowledge. This is considered due to the shortness in time that the arc welding's joint experience such the temperature, and the temporary precipitation of delta phase and the following formation of sigma phase in the delta phase might be suppressed.

The cleaning metal used in this research contains 2.5%B. The boron is well known that they easily diffuse into the stainless steel at high temperature, and segregate the borides along the grain boundary. This segregation could occur during the BPW process and could lead to the degradation of the corrosion resistance of the BPW joints. In this research, the reactivation ratio value for the BPW joint with the cleaning metal (D in Fig.4) was a little bit larger than the value of joint without the cleaning metal (J in Fig.4), but their difference was small. The BPW with the cleaning metal might raise the reactivation ratio value and degrade the corrosion resistance. But if the difference is considered to be negligible, the borides might not segregate so much to cause the degradation in corrosion resistance. For example, the ejection of the cleaning metal might prevented the diffusion of the boron into the stainless steel. The experiment results of this research are not enough to explain the effect of the boron in the cleaning metal, so that the further investigation is required.

Conclusions

Braze-pressure welding tests with the induction heating were conducted for the austenitic stainless steel SUS316L and SUS304L. The sensitization at the vicinity of the joining surface was measured using the EPR tests.

(1) When the total heating time was shorter, the sensitization at the joint interface could be reduced.
(2) The suppression of the cleaning temperature could reduce the sensitization of the joint interface.
(3) The major factor of the sensitization of the BPW joint interface of the austenitic stainless steel might be the delta ferrite precipitation at higher temperature than 1200ºC, which changed into the sigma phase after cooling down.

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