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Effect of Vacuum Brazing on Corrosion Resistance of SAF 2205 and Superdux64 Duplex Stainless Steel

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Duplex stainless steel has a combination of better mechanical strength and pitting corrosion resistance, but the precipitated brittle phase as σ phase formed during the cooling from the welding procedure will rapidly degrade its properties. In order to avoid the precipitation of secondary phases in the welds, the effect of vacuum brazing on the properties of the welds of UNS S31803 (SAF 2205) and UNS S31200 (SuperDux64) duplex stainless steels has been investigated. Three fillers, such as copper foil, BNi-3 and BNi-7 Ni-based alloy, were used to evaluate the influence of chemical composition on the corrosion resistance. In air quench, a cooling rate of 0.85℃/s and the precipitation of σ phase can be inhibited for those studied duplex stainless steels. Under the quenched state, the weight loss of UNS S31803 DSS dipped in 6%$FeCl_3$ solution at 45℃ for 24 hours is low. However, the precipitation of σ phase in UNS S31803 was increased as the cooling rate decreased. When the cooling rate was decreased to 0.067℃/s, the weight loss of UNS S31803 was increased. Owing to the compositional difference between the filler and duplex stainless steel, the selective corrosion occurred at the interface of brazed joints soaked in 6% $FeCl_3$ solution for 24 hours.

Keywords : *duplex stainless steel, vacuum brazing, immersion testing, pitting, σ phase*

1. Introduction

Duplex stainless steels (DSS) may be defined as a family of steels having a two-phase ferritic-austenitic microstructure. It gets a quite practically potential stainless steel species with greater mechanical strength and corrosion resistance than conventional stainless steel. In the latest one or two decades, it was studied to approve that the duplex stainless steel not only has better full mechanical properties, corrosion resistance and weldibility better but cost less than austenitic systemic stainless steel, especially extremely fitted in the environment containing chloride, so we take it as the upgrade material of austenitic systemic stainless steel.[1-4)]

In the aspect of weldibility of duplex stainless steel, those joints by traditional joint method (GTAW, PAW and SAW...etc) will produce the heat-affected zone near the welding seam from the heating and cooling steps.[4-6)] A temperature gradient was produced by the heat source in these area, the variation in phase ratio of α phase and γ phase and some harmful phases were precipitated during cooling. There was a serious problem in mechanical and corrosion resistance properties of the welded parts near the welding area, in which undesirable phases were detectable. Therefore, a method without any produced temperature gradient will be a practical potential.

The processing parameters of the vacuum brazing including temperature, degree of vacuum, and cooling rate can suitably be controlled.[7)] When the specimens were heated at the high temperature, the temperature distribution in the brazed joint was uniform. Therefore the heat-affected zone of the cooled brazing joint under different cooling schedules was not observed. The purpose of this study is to evaluate the mechanical and corrosion properties of vacuum brazed joint of duplex stainless steel under cooling schedules. The cooling rate was chosen as fast as possible for the precipitation of harmful phase (such as σ phase) in the duplex stainless steel; furthermore, the processing conditions of vacuum brazing for duplex stainless steel are also studied in different fillers to obtain the combination of high mechanical properties and corrosion resistance.

2. Experimental

A SuperDux64 (UNS S31200) duplex stainless steel plate supplied by Nippon Steel Company and a SAF 2205 duplex stainless steels (UNS S31803) produced by Avesta Sheffield Co. were used as the experimental materials. The chemical compositions of two steels were shown in Table 1.

Table 1. Chemical compositions of two duplex stainless steels (wt)

	Fe	Si	Mn	Cr	Ni	W	Mo	V	N	Cu	P
UNS S31200	64.9	0.6	0.7	24.5	5.8	0.01	1.45	0.13	0.14	1.11	0.02
UNS S31803	65.9	0.5	1.2 2	22.4	5.1	0.8	2.5	0.11	0.18	0.27	0.04

Two duplex stainless steels were machined to a size in 20mm × 15mm × 2mm. After solution treated at 1050℃ for 10 minutes in a vacuum of 10^{-5}Torr, the DSS specimen were cooled to room temperature by two cooling schedules in the rate of 0.1℃/s and 0.067 ℃/s. To obtain the cooling rate in 0.85℃/s , the specimens were first loaded in the heating chamber of the two chamber vacuum furnace to furnish the solution that was treated and then cooled by nitrogen gas quench in the second chamber. For the reason of comparison, some samples cooled at the rate of 0.1℃/s were heated to 750℃and held for the time duration of 1 hour to furnish the aging treatment, denoted as aged.

Two duplex stainless steel plates were cut by a laser machine into the brazed specimens by 55mm × 15mm × 2mm. The fixture made by graphite was used to furnish the vacuum brazing in a gap of 0.2mm. The nickel-based alloy powder (BNi-3 and BNi-7) and copper foil were chosen as brazing fillers, the chemical compositions and brazing temperature were shown in Table 2. Nickel-based filler powder was mixed with the Nicrobraze S-binder in the ratio of 3:1 to form a paste, and used in the vacuum brazing.

By using the Groesbeck etching solution (4g NaOH + 4g $KMnO_4$ + 100g H_2O) as the chemical etching solution, the ground and polished specimens were dipped in the heated solution (90℃) for 150 seconds. Microstructures were conducted in an optical microscopy in the BHM-12B type produced by Olympus Co. Metallographic samples were also taken from the vacuum brazed joint, ground, polished and then etched with a nieromuriatic acid solution.

Table 2. Chemical compositions and brazing range of filler metals

Filler	Chemical Compositions								Solidus/ Liquidus M.P. (℃)	Brazing range (℃)
	Cr	B	Si	Fe	C	P	Ni	Cu		
BNi-3	-	3.13	4.5	0.5	0.06	0.02	Bal.	-	982/ 1038	1010~ 1177
BNi-7	14.0	0.01	0.10	0.2	0.08	10.1	Bal.	-	888/888	927~ 1093
Cu foil	-	-	-	0.1	-	-	0.2	Bal.	1083/ 1083	

In order to evaluate the pitting corrosion resistance, the samples were cut as the dimension of 20mm × 15mm × 2mm and 15mm × 10mm × 4mm from the heat-treated samples and the vacuum brazed joint, respectively. The surfaces of samples were ground, polished and then ultrasonic rinsed in an acetone for 5 minutes. The corrosion tests were conducted by the immersion the samples in a 6% $FeCl_3$ solution kept at 47.5℃ for the time duration of 24 hours. The weight loss of the corroded sample was measured by using an ER-182A electronic balancer.

3. Results and discussion

3.1 Microstructure studies and phase analysis

The microstructure etched by Groesbeck's etchant was used to estimate the amount of the σ phase precipitation by an image analyzer. The microstructures of SAF 2205 duplex stainless steel specimen solution treated and cooled at various rates were shown in Figure 1. From these figures, the microstructure of SAF 2205 duplex stainless steel solution treated and cooled at the rate of 0.85℃/s was a band structure compromising the ferrite and austenite phases. The dark area, precipitates of sigma phase, was observed at ferrite-ferrite and ferrite-austenite boundaries and inside ferrite grain. The area of the dark region was quantitatively analyzed to calculate the amount of the σ phase by the image analyzer. The quantities of the σ phase precipitated are 0%, 2.9%, 12.1% for specimen solution treated and cooled at the rate of 0.85℃/s, 0.1℃/s and 0.067℃/s respectively. The amounts of the chromium and molybdenum atoms solved in the ferrite phase were higher than those of the austenite phase. Therefore, the formation of sigma phase preferentially occurred in the ferrite phase. The compositions of the ferrite and austenite phases which existed in two duplex stainless steels solution and treated at 1050℃ as determine by EPMA are shown in Table 3. It is observed from Table 3 that there is an enrichment effect of chromium and molybdenum the ferrite phase and of nickel and manganese in the austenite. The composition of individual phases is still adequate to give excellent resistance to corrosion.

Table 3. Chemical compositions of α phase and γ phase in two DSSs (wt)

		Fe	Cr	Ni	Mo	Si	Mn
SuperDux64	α phase	66.3	26.9	3.9	1.4	0.67	0.38
	α phase	69.6	20.6	7.7	0.77	0.55	0.72
SAF2205	α phase	65.7	25.1	4.0	4.1	0.41	1.2
	α phase	68.3	20.9	6.9	2.2	0.32	1.6

An important observation is that the precipitation behavior of sigma phase can be strongly influenced to a large extent by changing the heat history. When the cooling rate offered by the specific cooling schedule is larger than that of the critical cooling rate obtained from the temperature-time-transformation curve of SAF 2205 stainless steel, the precipitation of σ phase is inhibited. Therefore, there is no detection of precipitation of σ phase in the one that is cooled at the rate of 0.85℃/s. This is an agreement to the experimental investigation of the SAF 2205 by the report of Yang et al.,[8] in which the critical cooling rate to avoid the precipitation of sigma phase is 0.25 ℃/s when a solution temperature was used in the range of 1020-1080 ℃. Besides that, the microstructure of the sample aged at 750 ℃ for 1 hour was also illustrated in Figure 1. The amount of σ phase precipitated was in the aged specimen by 17.9%. The holding duration was increased at 750 ℃ falling into the temperature range from 600℃ to 1000℃ and the C curve of σ phase precipitation comes out in an isothermal transformation curve of the SAF 2205 duplex stainless steel. Therefore, the amount of σ phase was increased as the duration of holding was increased.

From the estimation of the image analysis, similarly, the amounts of the σ phase precipitated in the SuperDux64 steel were 0%, 1.4% and 4.2% for the samples cooled at the rate of 0.85℃/s, 0.1℃/s and 0.067℃/s respectively. The amount of σ phase precipitated was obtained in the aged specimen by 6.2%. From the results, the quantity of σ phase precipitated in the SAF 2205 specimen is larger than that of the SuperDux64 specimen. It is worthy to note that both the precipitation rate and the volume fraction of σ phase are increased as the increasing of the atoms of chromium and molybdenum in a large number of duplex stainless steels. In addition to the effect of chromium and molybdenum, it is noted that the tungsten, like molybdenum, increases the precipitation rate of σ phase and expands the corresponding C curve towards higher temperatures.[9] Since the 2205 duplex stainless steels are rich in the elements such as molybdenum and tungsten, they are inherently more sensitive than SuperDux64 steel and therefore require faster cooling to suppress the precipitation of σ phase.

3.2 Hardness test

To determine the hardness of two duplex stainless steels, Vickers's hardness tests were conducted. The average values of ten tests in each sample as a function of cooling

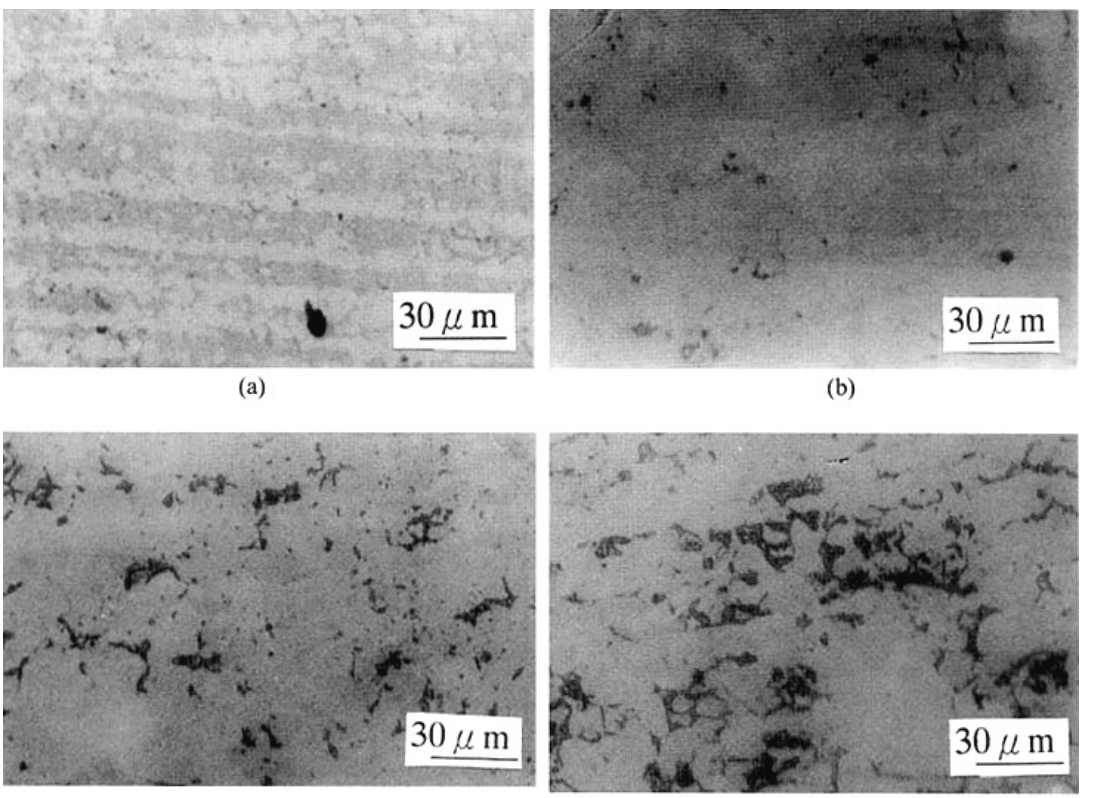

Fig. 1. Microstructures showing the distribution of σ phase of SAF 2205 duplex stainless steel after solution treatment at different cooling rates, (a) 0.85℃/s, (b) 0.1℃/s, (c) 0.067℃/s, (d) 750℃ for 1 hour.

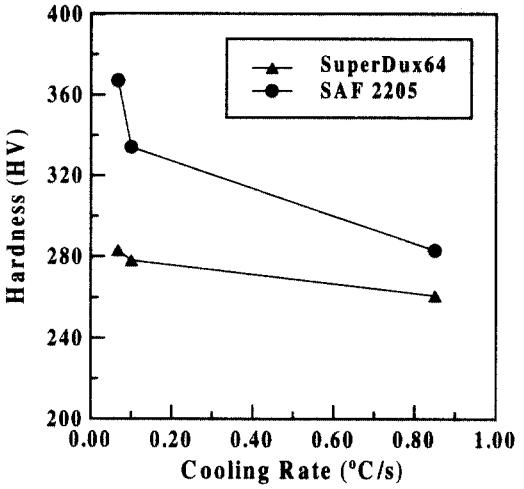

Fig. 2. Hardness as a function of cooling rate for two steels

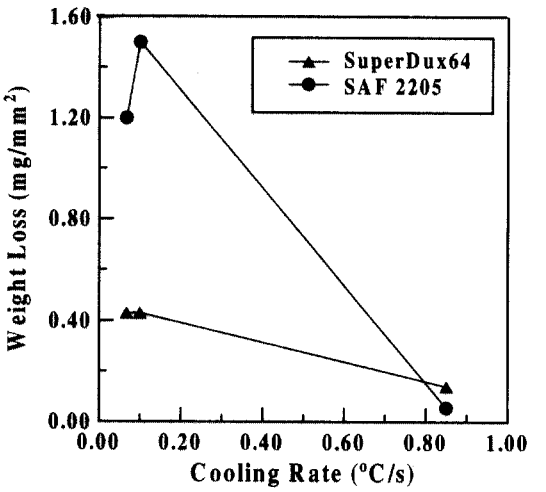

Fig. 3. Weight loss of DSS specimen solution treated and cooled from different cooling rates after specimens were immersed in the 6 $FeCl_3$ solution at 47.5℃ for 24hours

rate for two steels were shown in Figure 2. The hardness of the as-received SuperDux64 and SAF 2205 duplex stainless steels were 422 and 395 HV respectively. The hardness of the solution treated SuperDux64 (261HV) and SAF 2205 (283 HV) duplex stainless steels were lower than those of the as-received one. The decreasing of effect on the hardness of steels was arisen from the stress relaxation offered by the high temperature of solution treatment.

The hardness of SAF 2205 duplex stainless steels was 283, 334 and 367 HV for specimen cooling from the rate of 0.85℃/s, 0.1℃/s and 0.067℃/s, corresponding to the quantity of sigma phase of 0%, 2.9%, 12.1% respectively. Because the σ phase was a chromium-rich phase with hard and brittle character, there was a reinforced function to duplex stainless steel. When the quantity of σ phase was raised, the value of hardness was also increased for the duplex stainless steel.

The hardness of SuperDux64 duplex stainless steel, processed at various cooling rates was 261, 278 and 283 HV respectively. It should be noted that the quantity of theσ phase contained in SuperDux64 duplex stainless steel was 4.2% as cooled at 0.067℃/s. The quantity of the σ phase for SuperDux64 DSS was not sufficient to affect the hardness of bulk substrate. For this reason, the hardness of SuperDux64 was not strong influenced by the cooling schedule. Nevertheless, it also showed a similar trend in increasing hardness as the quantity of σ phase increased.

3.3 Corrosion behavior

The corrosion tests were conducted in the present work by a modified ASTM G48 method.[10] The weight loss of the corroded sample was calculated by immersing the samples in the 6% $FeCl_3$ solution kept at 47.5℃ for the time duration of 24 hours. The weight loss of immersed specimen of SuperDux64 and SAF 2205 steel solution treated and cooled at 0.85℃/s were 0.14 mg/mm^2 and 0.06 mg/mm^2 respectively. As reported in preceding section, the σ phase precipitation was not obvious in the cooling schedule when the cooling rate of 0.85℃/s was applied. According to the contents of Cr, Mo and N in two duplex stainless steels used to calculate PRE (Pitting Resistance Equivalent) value, the PRE value for SuperDux64 and SAF 2205 steels were for 32.1 and 34.7 respectively. The results of corrosion tests were in agreement to the PRE value of two duplex stainless steels.

Weight loss of specimen for two steel solutions heated and cooled from different cooling rates after specimens were immersed in the 6 $FeCl_3$ solution at 47.5℃ for 24hours was shown in Figure 3. From Figure 3, the weight loss of SuperDux64 duplex stainless steel cooled from different cooling of 0.85℃/s, 0.1℃/s and 0.067℃/s was 0.14 mg/mm^2, 0.43 mg/mm^2 and 0.43 mg/mm^2 respectively. And those for SAF 2205 duplex stainless steels by various cooling rates were 0.06 mg/mm^2, 1.5 mg/mm^2 and 1.2 mg/mm^2 respectively. These results of corrosion tests show that the pitting resistance of the SuperDux64 steel does not fall down rapidly as the cooling schedule varies. On the contrary, the weight loss of SAF 2205 steel was obviously raised to 1.5 mg/mm^2 as the cooling was decreased. According to the research of Potgieter,[11] the σ phase was harmful to the corrosion resistance of duplex stainless steel. When the σ phase contained in duplex stainless steel was increased, the pitting resistance of duplex stainless steel was decreased. Therefore, when the amount of sigma phase precipitation in 2205 steel speci-

men was increased, the degradation of pitting resistance of 2205 duplex stainless steel was easier than those of the SuperDux64 duplex stainless steels.

The CPT data for high alloy austenitic parent and weld metals were reported by Walker,[4] which indicates the lower corrosion resistance of the weld metal while comparing with the matching composition parent materials, an effect due to segregation. These effects of segregation on the selected corrosion of weld metal for the high alloy austenitic stainless steel have been well documented by Garner,[12] who carried out the ferric chloride corrosion testing of type 254 SMO (S31254) weld metal produced by a tungsten inert gas (TIG) process in a wide range of heat inputs. Garner observed that the corrosion resistance decreased with increasing heat input, and suggested that this could be related to the higher segregation associated with the dendrite spacing.

In order to evaluate the effect of filler in the corrosion resistance of welded duplex stainless steels, the specimens cut from the vacuum brazed joints were immersed in 6% $FeCl_3$ solution at 47.5 ℃ for 24 hours, and the weight changes per unit area was also calculated as shown in Figure 4. The weight loss of the vacuum brazed joint using the copper foil was the smallest among those investigated conditions. In Figure 3, the weight loss of SuperDux64 cooled at the various rates of 0.85℃/s, 0.1℃/s and 0.06 7℃/s were 0.14 mg/mm^2, 0.43 mg/mm^2 and 0.43 mg/mm^2 respectively. Comparing of the results (Figure 4) with data (Figure 3), we can see that the weight loss of the brazed specimens after immersing test were larger than that of parent metal. It is demonstrated that the existing interface in brazed joints arising from a galvanic cell induced the decreasing corrosion resistance of the SuperDux64.

Microstructures of vacuum brazed joint for SAF 2205 DSS brazed at 1020℃/10^{-5} torr by using the BNi-7 filler under different cooling rates were shown in Figure 5. The interaction layers between the parent metal and filler in the interface cooled at 0.85 ℃/s were thinner than those in the joint cooled at 0.1℃/s and 0.067℃/s. Because the interaction between the parent metal and filler was decreased in fast cooling schedule at 0.85℃/s, the reaction distance crossing the joint could not be as sufficient as the slow cooling one, the corrosion resistance would be higher than those specimens cooled from the rate of 0.1℃/s. However, this phenomenon can be improved by extending the holding timer at higher temperature and it's also worthy of further discussion.

The corrosion behavior in the interface of brazed SuperDux64 duplex stainless steel plate was similar to the results of SAF 2205 duplex stainless steels. In summary,

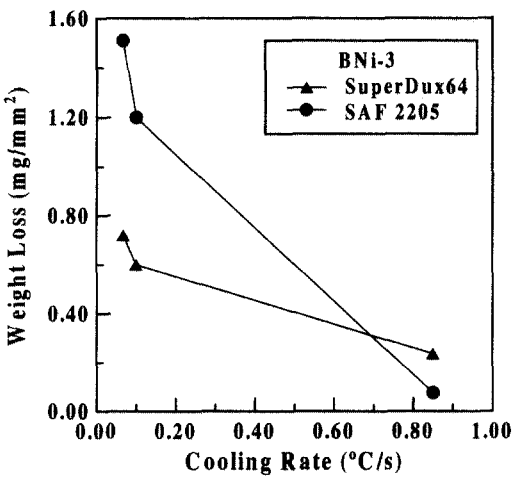

Fig. 4. Weight loss of vacuum brazed joints using BNi-3 filler immersed in 6 $FeCl_3$ solution at 47.5℃ for 24hours

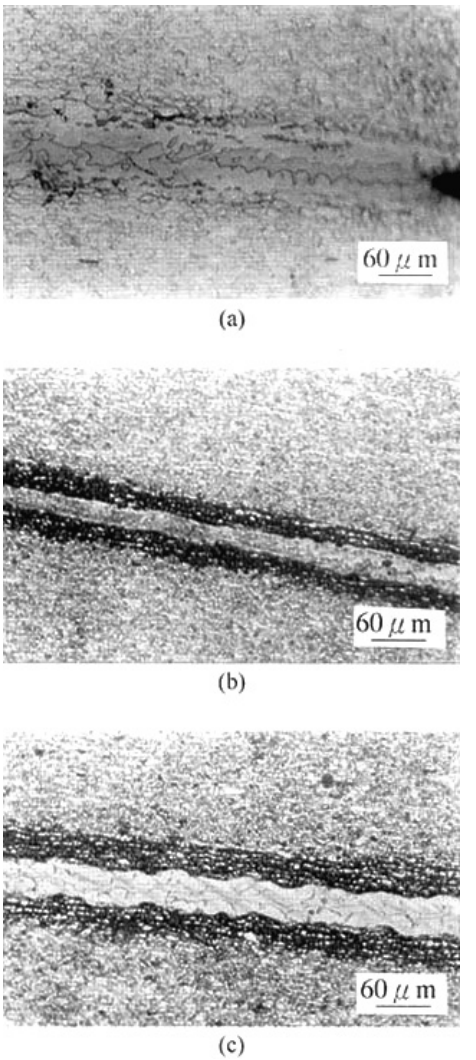

Fig. 5. Microstructures of vacuum brazed joint for SAF 2205 DSS brazed at 1020℃/10^{-5} torr by using the BNi-7 filler under different cooling rates: (a) 0.85℃/s, (b) 0.1℃/s, (c) 0.067℃/s.

the galvanic corrosion was also observed in two brazed duplex stainless steel joints using three fillers such as the BNi-3, BNi-7 and copper foil, in the chloride solution. If the galvanic cell was established, the obvious corrosion was taken place in the brazed joint, especially in interface of two steel plates. Hence, the corrosion resistance of duplex stainless steels was also decreased; it is worthy to develop the filler whose galvanic series is close to the parent metal to improve its corrosion resistance.

4. Conclusions

1) The amount of sigma phase precipitated is increased as the cooling rate was lowered. When the cooling rate was increased to 0.85℃/s, the precipitation of sigma phase was suppressed. Therefore, the precipitation of σ phase of duplex stainless steel can be avoided by using the vacuum brazing with air quench cooling.

2) The hardness of SAF 2205 duplex stainless steels was 283, 334 and 367 HV corresponding to the quantity of sigma phase of 0%, 2.9%, 12.1% respectively. When the quantity of σ phase precipitation is increased, the hardness of SAF 2205 duplex stainless steel is gradually increased.

3) The weight loss of the immersed specimen of SuperDux64 and SAF 2205 steel solution which was treated and cooled at 0.85℃/s was 0.14 mg/mm^2 and 0.06 mg/mm^2 respectively. These results were in agreement to the PRE value of the duplex stainless steel. When the quantity of the sigma phase in 2205 steel was increased, the pitting resistance of 2205 duplex stainless steel was worse than that of the SuperDux64 duplex stainless steels.

4) The galvanic corrosion was also observed in two brazed duplex stainless steel joints using three fillers such as the BNi-3, BNi-7 and copper foil in the chloride solution. If the galvanic cell was established, the corrosion was taken place in the joint, especially around the boundary.

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