

Brazing Ability of an Ni-based Brazing Filler for Ferritic Stainless Steels

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Abstract

Herein, the exhaust gas recirculation (EGR) cooler is produced by brazing, which is considered suitable for joining its complicated parts. With the downsizing of these parts, ferritic stainless steels have recently been used for developing EGR coolers because of their excellent brazing ability. In this study, the effects of Ti and Nb as stabilizers and Al as a deoxidizer on the brazing ability of an Ni-based brazing filler in ferritic stainless steels were investigated. The investigation revealed that the brazing ability was reduced by adding Ti and Al. Based on these results, Nb stabilized ferritic stainless steels with low Al contents and high Ni brazing abilities were developed.

1. Introduction

Brazing¹⁾ is a metal joining method whereby a filler metal with a melting point lower than that of the base metal is placed beforehand between the surfaces to be joined, and the set is heated to have the filler metal melt so that the molten metal penetrates into the joint gap by wetting and capillarity action. Because of this joining principle, it is effective at fastening joints of complicated shapes or many joints in one action. In addition, because the base metal melts only slightly by this method, it is suitable for bonding thin materials that are difficult to join by TIG or MIG welding.

A typical application example of brazing of stainless steel is small heat exchangers used in automobiles, water heaters, etc. For example, the exhaust gas recirculation (EGR) cooler²⁾ of an automobile engine is an environmentally-friendly device that cools a part of the exhaust gas and returns it to the engine in order to reduce NOx emission and improve fuel efficiency by decreasing the pumping loss of admission air and exhaust gas, and its use is rapidly expanding. For high heat exchanging efficiency, its internal structure is complicated, and so are the joints of its components. Since joint defects lead to water leakage, good brazing bonding is essential. For reasons of heat resistance and corrosion resistance, Ni alloy is selected as the filler metal; the recently developed Ni-29%Cr-4%Si-6%P alloy^{3,4)} excellent in brazing properties and corrosion resistance is a typical example. Austenitic stainless steel such as the Type 304 steel was mainly used for the EGR cooler, but in recent years, the use of high-purity ferritic stainless steel has been increasing due to

its resistance to intergranular corrosion and costs.⁵⁾ In addition, in the trend toward lightweight and compact parts for higher fuel efficiency, cases are increasing where improved brazing properties are required for stainless steel materials.

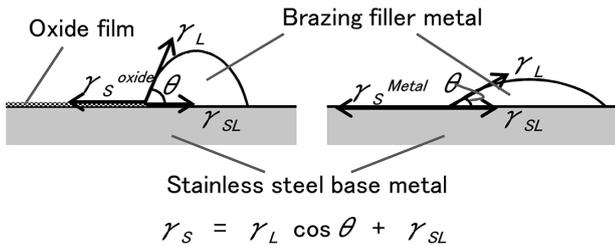
From the viewpoint of the science of brazing of stainless steel, we focused attention on easily oxidizing alloy elements, and examined their effects on the brazing properties of the material. Ti and Nb are added to high-purity ferritic stainless steel as stabilizers, and the steel stabilized by Nb addition is more suitable for brazing. In addition, we clarified through experiments that even a slight difference in the addition amount of Al, a typical deoxidizer, exerted influence on the brazing properties of the steel. Based on these findings, we have developed a steel grade excellent in brazing properties by controlling the amount of Al added to a basic high-purity ferritic stainless steel stabilized by Nb addition. The present paper reports the study of the brazing properties of stainless steel, which constituted the technical basis of the development.

2. Science of Brazing of Stainless Steel

Wetting of the surfaces to be bonded by molten brazing metal⁶⁾ is explained using surface tension or surface energy. **Figure 1** is a schematic illustration of a situation where the Young Dupre formula, which is generally used for explaining the relationship between the surface energy of a solid and that of a liquid in contact with each other, is applied to stainless steel and molten filler metal. The surface of stainless steel is covered with an oxide film rich in Cr, and

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since oxide is more stable than metal, its surface energy is low, and the low surface energy hinders wetting by the liquid metal. It follows therefore that, to join stainless steel by brazing, it is necessary to remove the oxide film of Cr, and for this reason, brazing work is often done in a furnace with a reducing atmosphere, that is, in a vacuum or a hydrogen atmosphere. **Figure 2** shows the equilibrium temperature of different metals and their oxides and their dew points in a hydrogen atmosphere calculated from the data of the standard free energy for the formation of the oxides.⁷⁾ The graph shows that if the dew point is -30°C or lower in brazing work at 1100°C , for



- γ_L : Surface energy of brazing filler metal (Liquid)
- γ_S : Surface energy of stainless steel surface (Solid)
- $\gamma_S^{oxide} < \gamma_S^{Metal}$
- Oxide* : Oxide film surface on stainless steel
- Metal* : Metal surface of stainless steel
- γ_{SL} : Interface energy between brazing filler metal and stainless steel
- θ : Contact angle

Fig. 1 Schematic illustration of wetting of stainless steel by molten filler metal for brazing

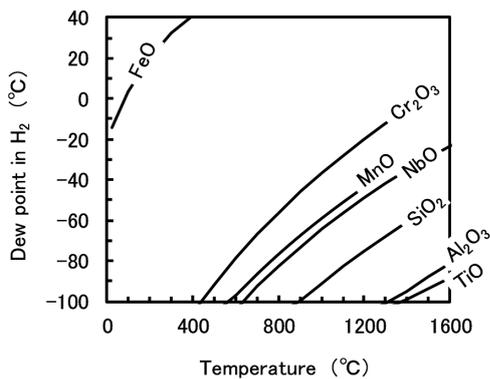


Fig. 2 Relationship between equilibrium temperature of different metals and their oxides and their dew points in hydrogen atmosphere

example, the Cr oxide film on the steel surface is considered to disappear. On the other hand, Ti and Al have extremely low equilibrium dew points, which indicates that the wettability of steel by the filler metal may be affected by the contents of these elements. The effects of Ti and Al on the brazing properties of ferritic stainless steel are examined in the following two sections.

3. Experimental Procedures

3.1 Specimens

Table 1 shows the chemical compositions of the specimens for the present tests. The effect of Ti was examined by testing of the spread of molten filler metal using specimens of Type 436L stabilized by Ti or Nb addition, and that of Al by the observation of the spread of molten filler metal and gap filling test using specimens of the Type 444 steel stabilized by Nb addition and containing 0.01 or 0.03% Al.

3.2 Heat treatment for brazing

In the present study, the brazing heat treatment was carried out using a vacuum furnace. The pressure of the brazing atmosphere was adjusted to 50 Pa by purging with nitrogen under vacuum pumping. The purpose of the nitrogen purge was to wash away the volatile gas from the binder in the Ni brazing paste and to protect the furnace body. The heat pattern of the furnace was set as follows: heating to 950°C , holding there for 20 min for soaking, heating to 1130°C , holding there for 10 min for brazing, and then cooling. A paste of Ni-29%Cr-4% Si-6%P alloy^{2,3)} described in Section 1 was used as the brazing filler metal.

3.3 Filler spread test

Test pieces, 40 to 50 mm square, were cut out from the sheets of the specimen steels, after applying 0.1 g of the paste at their center, they were subjected to the brazing heat treatment specified in the previous sub-section 3.2, after completing the heat cycle, the area covered by the spread of the filler metal, either in a circle or in an ellipse, was measured, and the wetting was evaluated in terms of the spreading ratio defined as follows:

$$\text{spreading ratio} = \frac{\text{area of filler metal after spreading}}{\text{area of applied paste}}$$

Note here that the area of applied paste was calculated as a circle 5 mm in diameter.

3.4 Filler spread observation

Round test pieces 7 mm in diameter were cut out from the sheets of the specimen steels, and after applying 0.02 g of the paste at the center, each of them was set in a high-temperature laser microscope. Simulating a brazing heat pattern, the atmosphere of the microscope was changed as follows: vacuum pumping, Ar blowing, heating to 950°C , holding there for 20 min, heating to 1130°C , and holding there for 10 min. Note here that the temperature was measured above the edge of the test piece. Since the real temperature of the test piece was presumed to be higher than the temperature thus measured, the test piece temperature was considered to be higher than the measured temperature by 50°C . The spreading of the molten fill-

Table 1 Chemical composition of stainless steel samples used this study

	(mass%)									
	C	Si	Mn	Cr	Mo	Nb	Ti	Al	N	
Type 436L stabilized by Ti	0.01	0.1	0.1	17.4	1.0	–	0.2	0.08	0.01	
Type 436L stabilized by Nb	0.01	0.1	0.1	17.3	0.8	0.4	–	0.06	0.01	
Type 444 with 0.01%Al	0.01	0.2	0.2	19.3	1.9	0.5	–	0.01	0.01	
Type 444 with 0.03%Al	0.01	0.2	0.2	19.4	1.9	0.5	–	0.03	0.01	

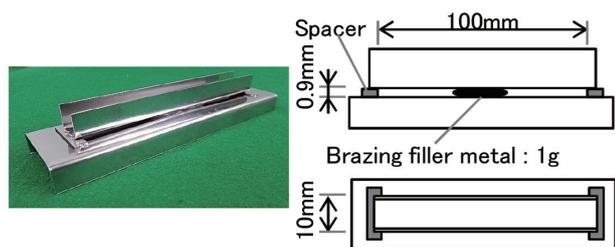


Fig. 3 Appearance and elevation and plan views of test pieces for gap filling test

er metal by wetting during the heat treatment was observed in-situ through the laser microscope from above. To keep the spreading front within the field of sight, the field was shifted following the spreading, and the spreading distance was calculated from recorded video images.

3.5 Gap filling test

Figure 3 shows the shape and appearance of the test piece for the gap filling test. It was prepared by cutting out the upper and lower pieces from the sheets of the specimen steels 0.5 mm in thickness, and arranging them to form a 0.9-mm gap 10 mm in width and 100 mm in length. After applying 1 g of the filler paste at the center of the gap, the test pieces were subjected to the brazing heat treatment described in sub-section 3.2, and the wetting was evaluated after the test in terms of the length of the filler metal in the gap.

4. Test Results and Discussion

4.1 Effect of Ti

To improve corrosion resistance and workability, the C and N contents of high-purity ferritic stainless steel are reduced to extremely low levels, and stabilizers that form carbonitrides such as Ti and Nb are added. In consideration of this, we investigated the change in the wettability of the steel due to the difference in the contents of the stabilizers.

Figure 4 shows the results of the filler spread test of the Type 436L stabilized by Ti addition and that stabilized by Nb addition. The spreading ratio was smaller with the former than with the latter, confirming poorer wettability of the former. To analyze the reason for the lower wettability of the former, the surface layer of the test pieces after the brazing heat treatment was examined in the depth direction by glow discharge optical emission spectrometry (GDS). Figure 5 shows the result. With the Ti-stabilized specimens, Ti, Al, O, and N were found to concentrate in the surface layer more significantly than with the Nb-stabilized ones, the surface of the former was oxidized and nitrated, and it was presumed that the oxides and nitrides on the surface hindered the wetting by the molten filler metal. At the filler spread test in a hydrogen atmosphere not containing nitrogen, on the other hand, a thick Ti oxide film was found to have formed on the surface of the Type 436L specimens stabilized by Ti addition, and their wettability by the filler metal was inferior to that of the Type 444 specimens stabilized by Nb addition.⁸⁾ This is presumably because Ti is oxidized more readily than Nb as shown in Fig. 2, it forms oxide during the brazing heat treatment to lower the surface energy of the steel, and consequently, the wettability by the filler metal. Based on these findings, it has been clarified that Nb-stabilized high-purity ferritic stainless steel containing no Ti is suitable for the applications for which high brazing performance is required.

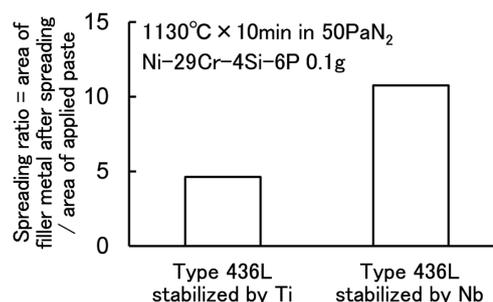


Fig. 4 Spreading ratio of filler metal on specimens heated at 1130°C for 10 min in N_2 atmosphere at 50 Pa

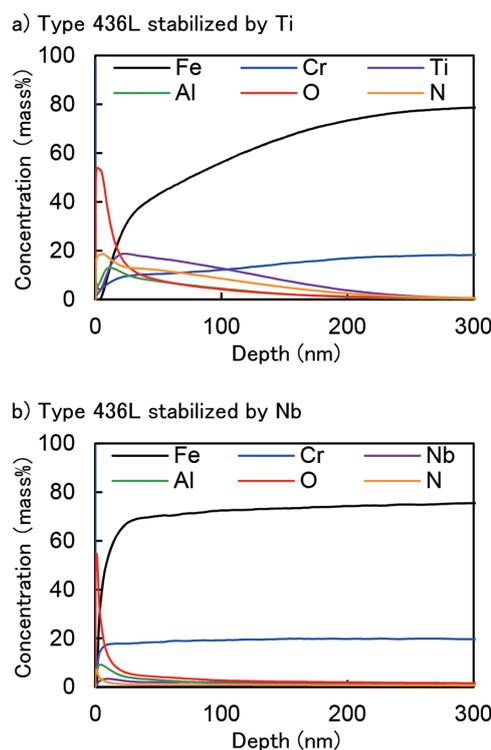


Fig. 5 GDS profiles of specimens heated at 1130°C for 10 min in N_2 atmosphere at 50 Pa

4.2 Effect of Al

Regarding the effect of Al on the brazing properties of ferritic stainless steel, it has been reported that, when Al is added by a few percent, an Al_2O_3 film forms on the steel surface, and as a result, the spreading of molten filler metal due to wetting is hindered.⁹⁾ However, the amount of Al added to high-purity ferritic stainless steel as a deoxidizer is very small, and it is difficult to evaluate the change in the brazing performance within the limited range of the Al addition amount. In fact, regarding especially the effect of Al addition on the performance of vacuum brazing with Ni-based filler metal, it was difficult to detect a significant difference in the filler spread test. In a real brazing process, the filler metal does not simply spread, but it spreads by wetting and fills the joint gap. In consideration of the above, we studied the effect of Al addition by a very small amount on the behavior of the filler metal in an early stage of its wetting and spreading by the spread observation method mentioned in sub-section 3.4, and the same on the gap filling behavior by the gap filling

test in sub-section 3.5.

4.2.1 Effect of Al on behavior of molten filler metal at early stage of spreading

As a result of the filler spread observation, **Fig. 6** shows the change over time of the distance covered by the spread of the filler metal on the specimens of the Type 444 steels with Al addition by 0.01 and 0.03% during the brazing heat treatment. The filler metal began to melt when the estimated temperature of the test piece was 980°C (the solidus temperature of the filler metal), and the distance covered by its wetting and spreading began to increase slightly. With the 0.01% Al specimens, the distance increased rapidly at roughly 1020°C and higher, and with the 0.03% Al specimens, at roughly 1100°C and higher, which indicated that the less the Al addition amount, the lower the temperature at which the wetting began to accelerate. **Figure 7** shows photomicrographs of the test pieces before and after the acceleration. The molten filler metal was seen to spread after the acceleration carrying on its surface what was presumed to be oxide that had been on the base metal surface. The process of the oxide being peeled off was seen more clearly with the specimen containing 0.01% Al. Assuming that the oxide flaked off because the filler metal dissolved its interface with the base metal, it is presumed that the interface is dissolved and the oxide film peeled off more easily with lower Al content in the steel, and the wetting

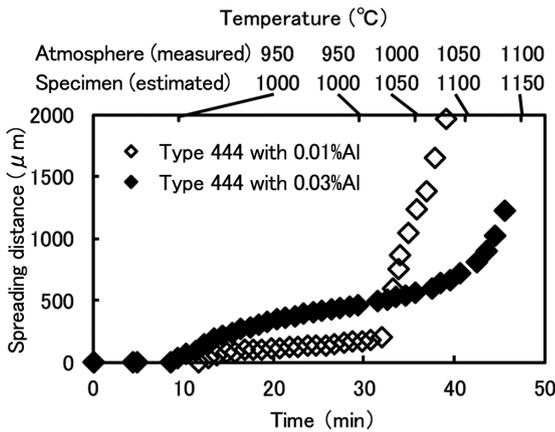


Fig. 6 Distance covered by spreading of molten filler metal

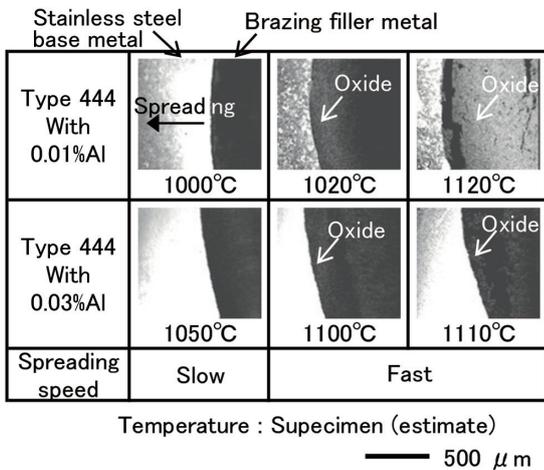


Fig. 7 Photomicrographs of spreading of molten filler metal before and after acceleration

begins to accelerate earlier.

To confirm the formation of the oxides during the heating of the brazing heat treatment, specimens of the Type 444 with 0.03% Al addition were subjected to the following heat treatments: heating to 950°C and holding there for 20 min as in the brazing heat treatment mentioned in sub-section 3.2; then heating to 1130°C (the brazing temperature), and cooling piece by piece from 950, 1040, 1060, 1080, and 1130°C during the second heating. **Figure 8** shows the appearances of the specimens thus heat-treated. Temper color was seen with the specimen cooled from 950°C without the second heating, the color lightened as the temperature of the cooling start became higher, and it substantially disappeared with the one heated to 1130°C. **Figure 9** shows the result of GDS analysis in the depth direction of the surface layer of the specimen cooled from 950°C. Cr and O were found to concentrate at the surface, which indicates that the temper color was due to Cr oxide. It became clear from the above that a film of Cr oxide is formed during the heating of the brazing heat treatment, and the molten filler metal wets and spreads on the base metal surface breaking and peeling off the oxide film even before it is reduced, and that the initial wetting and spreading progress easier with low-Al stainless steel.

4.2.2 Effect of Al on gap filling of filler metal

Figure 10 shows the result of the gap filling test using specimens of the Type 444 steels containing 0.01 and 0.03% Al. The filler metal penetrated deeper into the joint gaps of the specimens containing 0.01% Al than those containing 0.03% Al. Since the filler metal filled the gaps evenly in the width direction and did not flow out of them, the specimens were cut after the test along the width center line in the direction of the filler metal's penetration, and observed at the section surface using a scanning electron microscope

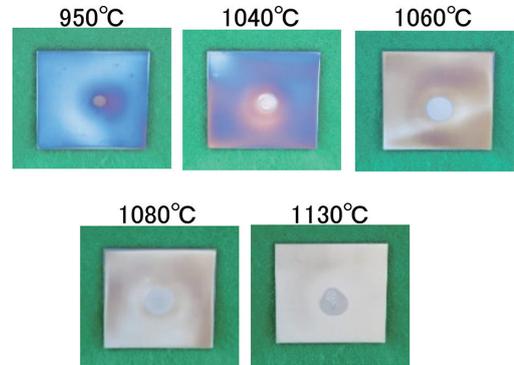


Fig. 8 Appearances of Type 444 with 0.03%Al specimens cooled from different temperatures during brazing heat treatment

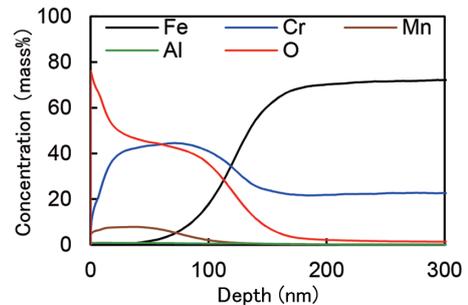


Fig. 9 GDS profiles of Type 444 with 0.03%Al specimen heated to 950°C in N₂ atmosphere at 50 Pa

(SEM) and a digital microscope. **Figure 11** shows sectional micrographs of the specimens taken through the SEM. The gap of the specimen containing 0.01% Al filled with the Ni filler metal was confirmed to be narrower than that of the other. This is presumably because the penetration force of the filler metal was stronger with the low-Al base metal, and the negative pressure in the gap was stronger. From the fact that the area ratio of the primary crystal, which appears white in the SEM micrograph, was smaller with the 0.01% Al specimen than with the other, it is presumed that the temperature range of the filler metal where the solid and liquid phases coexist is narrow, and its solidification contraction is small. **Figure 12** shows the result of measuring the thickness of the base metal sheets through the digital microscope. The sheet thickness was con-

firmed to have decreased from initial 0.5 mm, and the decrease of the 0.01% Al specimens was larger than that of the 0.03% Al. This is presumably because the stainless steel base metal dissolved in the filler metal, and the dissolution of the 0.01% Al sheets was quicker than that of the 0.03% Al sheets, and consequently, the total amount of the filler metal increased more with the former. The above result to the effect that the 0.01% Al base metal dissolves in the filler metal more readily than the 0.03% Al also corroborates the finding stated in the previous paragraph 4.2.1.

When the driving force of the wetting by the molten filler metal is explained based on surface energy, the surface of the filler metal is slightly exposed in the gap filling test, the effect of its surface energy on the wetting was therefore small, and it is presumed that the filler metal penetrates into the gap owing to the difference between the surface energy of the base metal and the interface energy between the molten filler metal and the base metal. The surface layers of the specimens after the brazing heat treatment were analyzed in the depth direction by Auger electron spectroscopy (AES); **Fig. 13** shows the result. It is seen from the graphs that the depth range where the concentrations of Al and O are high is shallower with the 0.01% Al specimen than with the 0.03% Al. Since the dew point at which Al and its oxide are in equilibrium is extremely low as seen in Fig. 2, it is presumed that while Cr oxide is reduced during the vacuum brazing heat treatment, oxidation of Al advances at the same time, but the Al oxidation is limited with the 0.01% Al sheets, and the decrease in the surface energy of the base metal is restricted. The above finding that the 0.01% Al material is dissolved more easily by the filler metal than the 0.03% Al material is possibly due to the low interface energy of the 0.01%Al stainless steel; this is likely related to the oxidation of Al. It is considered from the above that the gap penetrating force of the filler metal was greater with the 0.01% Al steel than with the other because the surface energy of the

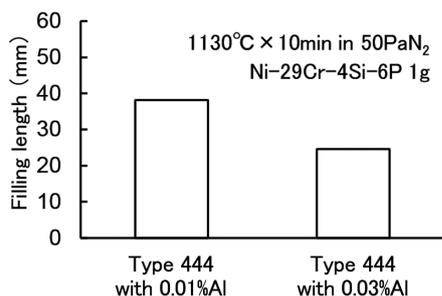


Fig. 10 Gap filling length of filler metal brazed at 1130°C for 10 min in N₂ atmosphere at 50 Pa

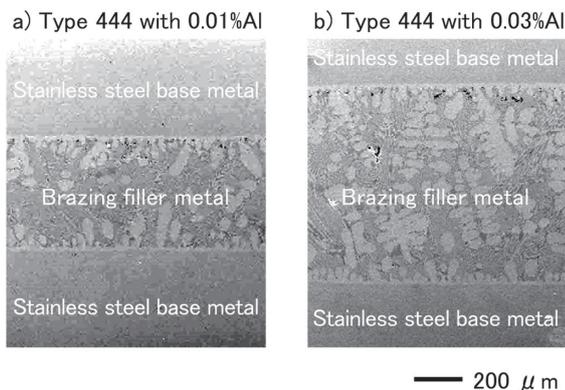


Fig. 11 Sectional SEM photomicrographs of specimens brazed at 1130°C for 10 min in N₂ atmosphere at 50 Pa

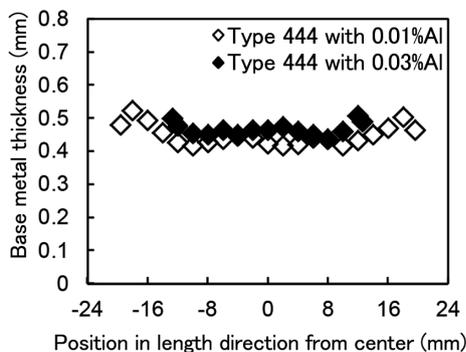


Fig. 12 Base metal thickness after gap filling test at 1130°C for 10 min in N₂ atmosphere at 50 Pa

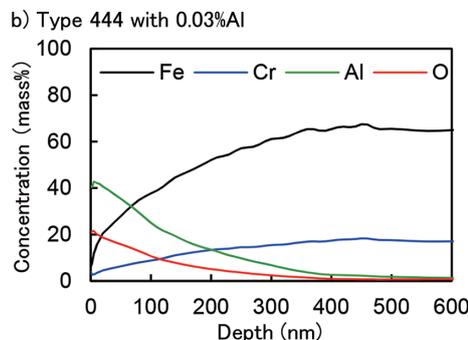
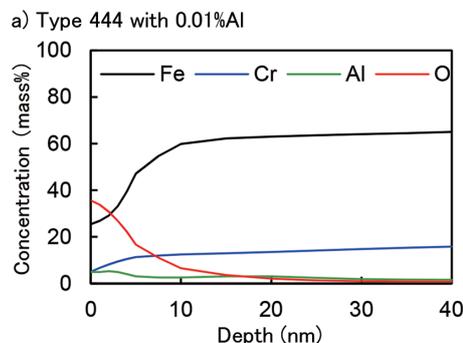


Fig. 13 AES profiles of specimens heated at 1130°C for 10 min in N₂ atmosphere at 50 Pa

base metal was higher than that of the 0.03%Al steel, and the energy of the base metal/filler metal interface was lower.

It has been clarified from the above that, in the vacuum brazing of the Nb-stabilized Type 444 steel using Ni-based filler metal, the smaller the addition amount of Al for deoxidation, the better the initial spreading behavior of the molten filler metal during the heating process, and the deeper it fills the joint gap. Stainless steel excellent in brazing properties with restricted Al addition has been developed based on the findings presented hereinabove.

5. Conclusion

The effects of Ti and Nb as stabilizers and Al as a deoxidizer on the vacuum brazing properties of high-purity ferritic stainless steel were examined in the present study using Ni-based filler metal. It was clarified that Ti deteriorates the brazing properties by forming oxide, as does Al for the same reason and by lowering the solubility of the base metal in the molten filler metal. Stainless steel excellent in brazing properties has been developed based on the findings pre-

sented herein. It is being used for EGR coolers, and its application is expected to expand in the future.

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