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Effect of the Molten NaCl-$MgCl_2$ Salt on the Corrosion of 316 Stainless Steel

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1. Introduction

Stainless steel has excellent corrosion resistance to various environments even at relatively high temperatures and has excellent strength and ductility. It has good workability such as welding, is relatively inexpensive, and does not show a distinct ductile-brittle transition behavior, it is widely used as a structural material for nuclear systems[1].

In this study, a multi-purpose molten salt experimental loop[2] was utilized for evaluating the corrosion and thermodynamic properties of molten salt. The experimental loop was manufactured using austenitic 316 stainless steel, and the molten salt used NaCl-$MgCl_2$ as eutectic chloride salt. 1/8-inch thermocouples were installed to measure the temperature of molten salt in the 1-inch pipe. 1/4-inch austenitic 316 stainless steel tubes into which a 1/8-inch thermocouple is installed, were welded by gas tungsten arc welding to the 1-inch pipe surface. The loop configured in this way was operated for more than 400 hours at an average of 600 °C or more. A problem occurred in that the welded part was corroded and the molten NaCl-$MgCl_2$ salt leaked. In order to find the cause of the corrosion, the main corrosion phenomena were analyzed by SEM-EDS focused on the welding part connecting the pipe.

2. Methods and Results

2.1 The corrosion of the welded part

The 1/4-inch tube was fillet welded above the perforated 1-inch pipe with gas tungsten arc weld (GTAW) using a 308 stainless steel welding rod. Fig. 1. shows the schematic of the fillet weld used GTAW.

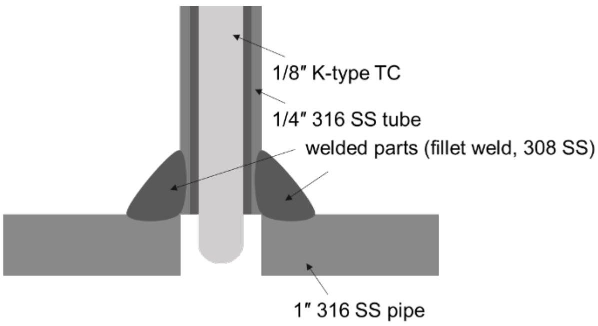

Fig. 1. the schematic of the fillet weld used GTAW.

About 6 days after exposure to high temperatures, the welded part was cut. As welding was not performed totally to the inside, the corrosion is thought caused by the penetration of molten NaCl-$MgCl_2$ salt into the gap(or crack). Fig.2. explains the penetration of the molten NaCl-$MgCl_2$ salt to the crack by the weld defects.

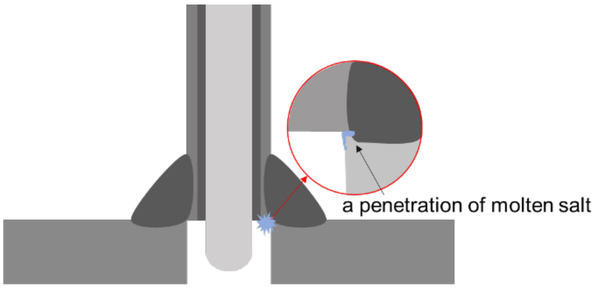

Fig. 2. the penetration of the molten NaCl-$MgCl_2$ salt to the crack(or gap) by the weld defects.

After that, 1/4 inch was repaired using a 308 stainless steel welding rod. Unlike the previous welding method, the repair welding was welded by inserting a part of 1/4 inch pipe into the 1-inch pipe and welding the boundary all around. At this time, the effect of the heat affected zone (HAZ) was observed on the surface of the repaired welded area like as Fig.3.

Fig. 3. the broken part by corrosion(left), the repair weld of a broken part, and the heat affected zone(right).

The problem occurred again in the repair welded part. The repair welded part was broken after several hours had elapsed in high-temperature operation. The shape of the broken part was the re-welded part connecting the pipe and the tube to the previous welded part.

It is estimated that hot cracking, which is known as a problem in welding austenitic stainless steel, and weld decay caused by sensitization are the causes of the problem. It mainly occurs in HAZ, which appears inevitably during welding, and a Cr-depleted zone near the grain boundary is created in the base material that is subjected to a temperature range of about 500 to 750 °C.

The surface and cross-section of the part where the problem occurred were analyzed by SEM.

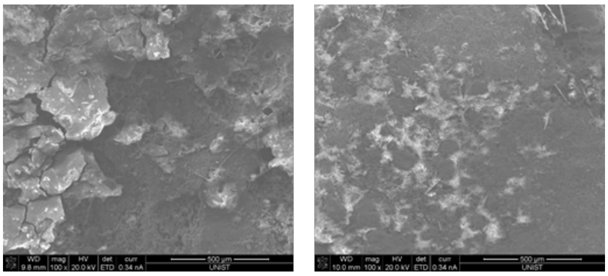

Fig. 4. the surface SEM images of the broken part. (left: top edge, right: bottom edge)

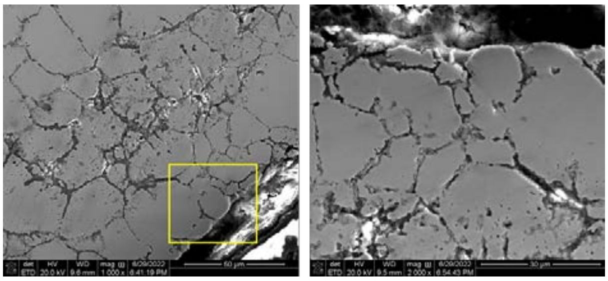

Fig. 5. the cross-section SEM images of the broken part.

A clear intergranular corrosion pattern was observed in the cross-sectional SEM image of where the corrosion occurred in the weld. Its length is about 100 μm or more, and in fact, the welded part was continuously exposed to a high-temperature condition during welding and operation.

As a result, chromium at the grain boundary combines with carbon and precipitates at the grain boundary, resulting in a chromium depleted layer, which deteriorated the corrosion resistance of this part and causes corrosion. As is known, this sensitization occurs in the temperature range of 550 to 800°C, and since the operating temperature in this experiment was 600°C on average, it can be seen that it was the cause of intergranular corrosion.

2.2 Effect of the molten NaCl-$MgCl_2$ salt on corroded weld part

The SEM results of the broken welded part due to corrosion can be confirmed that serious intergranular corrosion occurred compared to the operating time. That means that the effect of the molten NaCl-$MgCl_2$ salt on the corrosion of welded part must be considered.

$MgCl_2$ of the molten salt has strong water absorption in the atmosphere and easily forms $MgCl_2 \cdot 6H_2O$[3]. As the result, the hydrogen chloride and chlorine gas produced in molten salt can be the other cause of corrosion. At a high temperature of 150°C or higher, the thickness of the oxide film of stainless steel increases to several μm, and the passivation characteristics deteriorate, it makes vulnerable to chloride ions. Therefore, it can be considered that the oxide film with deteriorated passivation characteristics is attacked by hydrogen chloride and chlorine gas generated by the molten NaCl-$MgCl_2$ salt and has an effect of accelerating corrosion.

Additionally, the EDS analysis was performed on the broken part. The surface EDS result of the broken part of the weld and pipe was analyzed to be an average Cr ratio is about 5wt% or less, which is unreasonably low compared to the generally known Cr composition ratio. As a result, it can be seen that Cr ions are depleted and Mg ions are deposited at the depleted sites.

3. Conclusions

In the corrosion tests on 316 stainless steel using the molten NaCl-$MgCl_2$ salt, the welding without weld defects and the use of purified NaCl-$MgCl_2$ are important. In the case of a welded part of a metal that is already corroding due to HAZ, when it comes into contact with molten salt for a long time, the corrosion is accelerated. Therefore, austenitic stainless steel shows excellent corrosion resistance and mechanical properties even at a relatively high temperature of 650 °C, but when the molten NaCl-$MgCl_2$ salt is used in a nuclear environment, material deterioration or damage should be considered when selecting or using a material.

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