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Development of Metal Dusting Resistant Alloy for Synthesis Gas Production Plants

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Abstract

Metal dusting, a type of corrosion resulting from carbonaceous atmosphere, is a prominent cause of damage for high temperature components of synthetic gas production plants in a process of producing clean fuel. A novel approach to resist against metal dusting has been newly proposed based on the non-dissociative adsorption of CO gas on the metal. Excellent metal dusting resistant alloy NSSMC™696 has been developed with a hybrid-suppression technique; formation of protective oxide scales and the reduction of reactivity with CO gas. The developed alloy also has excellent high temperature strength, good thermal stability and good weldability, leading to enhanced reliability and high-efficiency plants.

1. Introduction

R&D for new energy technologies and energy-saving technologies has been conducted vigorously with the aim of reducing CO_2 emissions in order to curb global warming, and ensuring stable energy supplies. For example, growing attention has been paid to clean fuels, such as GTL[1)] (gas to liquids) and hydrogen. **Figure 1** schematically shows one GTL manufacturing process, involving the reformation and synthesis of natural gas or shale gas/oil. Ammonia, methanol and DME (dimethyl ether) are also produced by similar processes. The feedstock is reformed at a temperature of 1,000°C or higher and converted into a synthetic gas containing CO, H_2, etc. When the gas temperature descends from 800°C to 400°C, pit-formed corrosion called metal dusting (MD) occurs on metallic materials at synthetic gas production plants (**Fig. 2**).[2, 3)]

MD not only shortens the life of the material by markedly reducing its thickness but also reduces the efficiency of plant operations because carbon rapidly precipitates in the plant, with metal dust detached from the material surface serving as a catalyst. (Therefore, the corrosion is called metal dusting.) For these reasons, plant equipment design has been subject to certain limitations (e.g., the necessity to rapidly cool the reformed gas in order to narrow the temperature range in which MD occurs easily). From the standpoint of improving equipment reliability and enhancing plant operation efficiency, a new material with superior resistance to MD is strongly

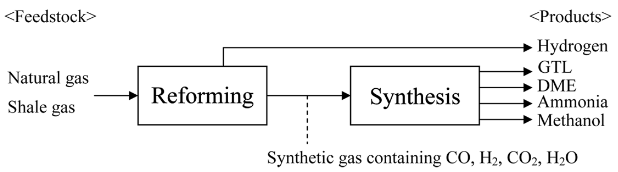

Fig. 1 Production flow of hydrogen and clean fuels

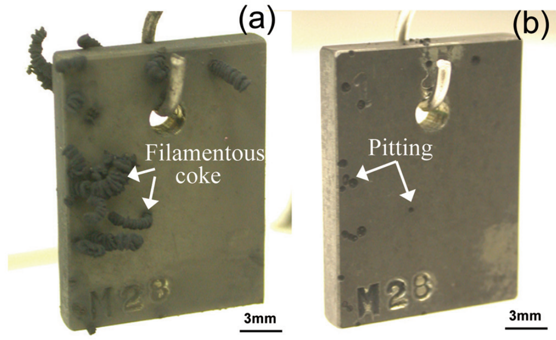

Fig. 2 Example of MD corrosion on the alloy containing 23%Cr-60%Ni-1.5%Al
(a) As exposed in a carbonaceous environment and (b) After removing coke on the test specimen

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called for. Recently, the author and collaborators developed a new technique to prevent MD, and came up with an MD-resisting alloy, NSSMC^{TM}696, whose composition design takes advantage of the technique.

2. Problems in Conventional Technology, and Proposed New Method for Preventing MD

2.1 Formation of a protective oxide scale to shut out CO

The mechanisms that cause MD on Cr-containing stainless steels and Ni-based alloys are as follows.[4)]

(a) C in the form of atoms dissociated from CO enters (carburizes) the metal.
(b) The C that has entered the metal combines with Cr to precipitate carbides of Cr.
(c) When carbon-supersaturated texture γ' occurs near the metal surface, lamellar graphite precipitates as a result of a eutectoid reaction (Formula 1).

$$\gamma' + \text{Cr carbide} \rightarrow \gamma + \text{graphite} + \text{Cr carbide} \quad (1)$$

(d) With the growth of graphite, the parent phase (composed of Fe and Ni) between the lamellar graphite becomes thin and some falls off from the base material, to become fine particles. As this process is repeated, the thickness of the material continues to decrease.
(e) The Fe and Ni that have fallen as fine particles become catalysts, causing filamentous coke to accumulate in MD-affected areas.

The conventional method used to restrain MD attempts to form a protective oxide scale on the metal surface in a synthetic gas atmosphere, thereby preventing the entry of carbon into the metal. A Ni-based alloy containing a large proportion of Cr forms protective Cr_2O_3 scales.[5)] And, with the aim of reinforcing this protection, Si is added to form SiO_2 in the interface between the Cr_2O_3 scale and the base metal.[6)] An alloy which is added with Al to form Al_2O_3 instead of Cr_2O_3 has been proposed.[7, 8)] However, if the protective oxide scale forms cracks or flakes, carbon immediately diffuses into the metal from the exposed surface and forms MD on the metal surface. Thus, although the protective oxide scale improves resistance to MD, this improvement is limited since it is virtually impossible to completely prevent the oxide scale from cracking and spalling. Therefore, in order to establish a guiding principle for designing an entirely new method of preventing MD, the author and collaborators carried out basic studies using model alloys, with the ultimate aim of applying the knowledge obtained from their basic studies to practical alloys.

2.2 Restraining dissociative adsorption of CO on metal surfaces

Paying attention to reactivity between metals and CO, the author and collaborators examined the behavior of reactions of various transition metals in a synthetic gas. **Table 1** shows the amount of carbon precipitation on, and the change in mass of, each transition metal specimen heated at 650°C for 100 hours in the simulative synthetic gas 60%CO-26%H_2-11.5%CO_2-2.5%H_2O (in vol%).[9)] It can be observed that specimens of Cr and Mn precipitate only a small amount of carbon because they form oxides in the gas atmosphere. On the other hand, Fe, Co, Ni, Cu, Ag and Pt form no oxides, and hence directly indicate their reactivity with CO. The amount of carbon precipitation on Cu, Ag and Pt is minimal, whereas Fe, Co and Ni react with CO and precipitate larger amounts of carbon. Therefore, paying attention to the reaction behavior of Cu, the author and collaborators prepared Ni-Cu binary alloys and subjected them to a similar test. In the test gas atmosphere, the binary alloys did not form oxide scale either. **Figure 3** shows the relationship between the amount of carbon precipitation and the concentration of Cu in Ni. When the Cu concentration is 20 at% or more, the amount of carbon precipitation is minimal. From this it was confirmed that when Cu is added to an alloy, it helps restrain the reaction of the alloy with CO.

The reaction between CO and a metal is influenced by a combination of the *d*-orbital electronic state of the metal and anti-bonding orbital of CO. **Figure 4** shows the change in electronic density of state caused by the surface reaction between CO and the metal, using the DV-Xα method. When CO is brought near the bcc-Fe (100)

Table 1 Amount of coke deposition and mass change of the test specimen for transition metals exposed in a 60%CO-26%H_2-11.5%CO_2-2.5%H_2O gas mixture at 650°C for 100 h

	Cr	Mn	Fe	Co	Ni	Cu	Ag	Pt
Amount of coke in g·m^{-2}	0.6	<0.1	14,340	65.5	119.5	0.3	<0.1	<0.1
Mass change in g·m^{-2}	1.4	22.2	-371.5	-8.3	-1.5	0	0	0

* Specimens of Cr and Mn formed oxide scale on the surface in the test gas environment.

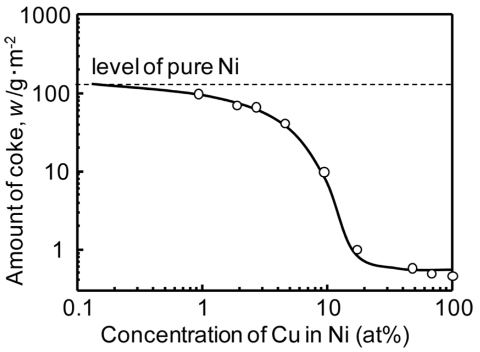
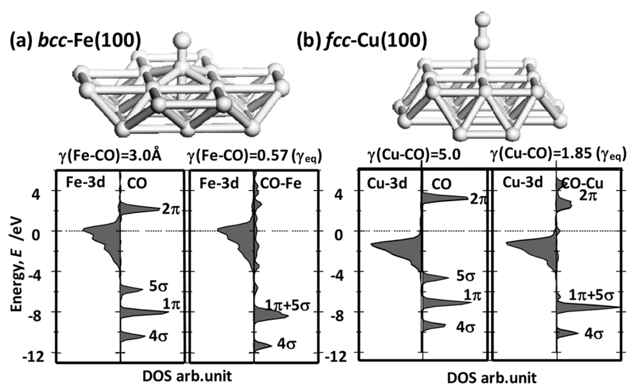


Fig. 3 Amount of coke deposited on the Ni-Cu binary alloys exposed in a 60%CO-26%H_2-11.5%CO_2-2.5%H_2O gas mixture at 650°C for 100 h



Remarks: The partial DOSs projected to 3d states of metal elements (left panels) and to total ones of CO molecule (right panels) are shown. Energy is measured from the Fermi level, which is denoted by horizontal broken line.

Fig. 4 Electronic density of states (DOS) for the cluster models which mimic the adsorption of CO (a) On bcc-Fe (100) and (b) On fcc-Cu (100) surfaces as a function of r (M-CO), the distance between CO and metal (M) surfaces in Å

plane, electrons are back-donated from the *d*-orbital of Fe to the 2π anti-bonding orbital of CO. As a result, the bond between C and O becomes weak and the dissociative adsorption of CO (separation of CO into C and O in the form of atoms) occurs.[9] On the other hand, it can be seen from Fig. 4 that even when CO comes near Cu whose *d*-orbital is full of electrons, the interaction between them is so small that dissociation can hardly occur.

The phenomenon of dissociative adsorption of gas is related to the surface tension (energy) of the metal concerned. Elements having only a small surface tension restrain dissociative adsorption. When those elements are added to an alloy, after the alloy is heated to a high temperature they segregate to the surface layer which is several atoms thick. The surface of a Ni-Cu binary alloy heated in a hot vacuum (oxide scale not formed) was observed using X-ray photoelectron spectroscopy (XPS).[10] It was found that the surface layer of a Ni-18 at% Cu alloy, which was several atoms in thickness, was Cu segregation of about 65 at%. Thus, when any element that restrains the gas dissociative adsorption is added to an alloy, it segregates in the alloy surface (or the interface between the oxide scale and the parent phase) in an amount that is more than what is added. This explains why it is effective in preventing MD.

3. Development of MD-Resisting Alloy "NSSMC™ 696"

3.1 Composition design concept

The above basic studies found that restraining the dissociative adsorption of CO requires adding about 20 at% of Cu. However, adding an excessive amount of Cu to a high temperature structural material must be avoided since this would deteriorate the high temperature strength, thermal stability, and weldability of the material. Therefore, the author and collaborators decided to use the conventional method of forming a protective oxide scale, but in combination with the new technique described above.[11] **Figure 5** shows the concept of the newly developed method for preventing MD. In a hot synthetic gas atmosphere, a scale composed of oxides of Cr and Si is formed to act as a barrier against CO molecules. Once the scale that is formed breaks or flakes off, the metal surface is exposed. However, on the exposed surface, Cu restrains the dissociative adsorption of CO. In the meantime, the damaged protective oxide scale heals (repairs) and starts shutting out CO again. According to this concept, it should be possible to maintain the desired resistance to MD on a lasting basis, without concern for any damage to the oxide scale.

Table 2 shows the standard chemical composition of the newly developed alloy. From the standpoint of forming the desired protective oxide scale, Alloy 690: 30%Cr-60%Ni was adopted as the base, to which was added Si. In addition, about 2% Cu was added to restrain the dissociative adsorption of CO. Furthermore, solid-solution hardening by Mo was applied to enhance the alloy hot strength, and the amounts of the additions of C, Ti and Fe were optimized to secure good weldability. The newly developed alloy has been registered as UNS N06696 with the American Society for Testing and Materials (ASTM), and is applicable to tubular, sheet, and plate materials.

3.2 Resistance to MD

The author and collaborators studied the MD resistance of the newly developed alloy during a long-time test. In a 60%CO-26%H_2-11.5%CO_2-2.5%H_2O (in vol%) simulative synthetic gas, test specimens were subjected to a cyclic heating-cooling test (650°C for 50 hours). The cyclic test was aimed to promote MD corrosion by causing the oxide scale to spall easily. Each specimen was removed from the furnace every 20 test cycles (1,000 hours of heating), and the development of pits was checked. For pits that were present, their depth was measured and their growth behavior was examined (**Fig. 6**).[12]

In the conventional alloys 800H and 601, pits occur early and grow rapidly. However, in the case of Alloys 690 containing 30%Cr and 160 containing 2.7%Si, some time is required before pits occur. This means that 690 and 160 have better MD resistance than 800H or 601. However, once pits do occur in them, they grow with the lapse of time, and the effect of a protective oxide scale can hardly be expected to repair the damage. On the other hand, the newly developed alloy was free of pits for 27,000 hours, demonstrating that it has excellent MD resistance. **Figure 7** shows the results of observations of pit cross sections. Characteristically, MD reveals a wide opening and forms a deep concave pit. On the alloy surface free of

Table 2 Limiting chemical compositions of the developed alloy

(mass%)

C	Si	Mn	Cu	Ni	Cr	Mo	Ti	Fe
0.15 Max.	1.0-2.5	1.0 Max.	1.5-3.0	Ramainder	2.80-32.0	1.0-3.0	1.0 Max.	2.0-6.0

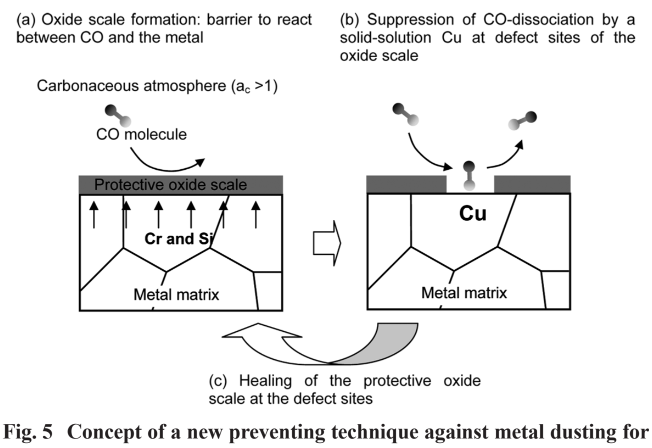


Fig. 5 Concept of a new preventing technique against metal dusting for the developed alloy

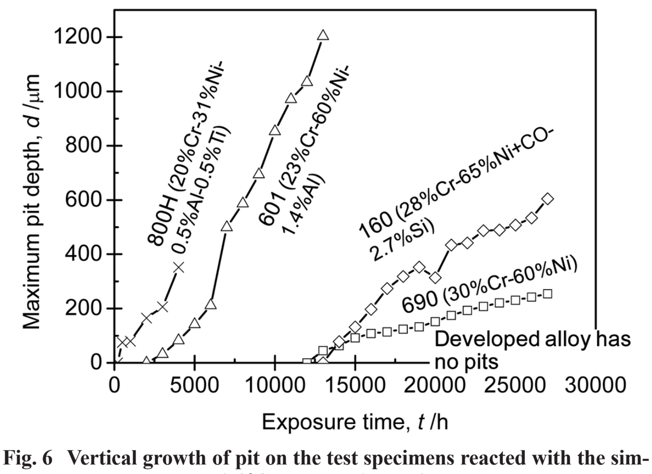


Fig. 6 Vertical growth of pit on the test specimens reacted with the simulated syngas at 650°C upon cyclic heating

pits, a protective oxide scale has formed.

The oxide scale formed on the surface of the newly developed alloy was observed under a scanning transmission electron microscope (STEM) and analyzed by an energy dispersive X-ray spectroscope (EDS). The results of the observation and analysis are shown in **Fig. 8**. The oxide scale is composed of Cr, and an oxide of Si is formed in the inner layer. Under the Cr oxide scale, fine grains of Fe, Ni and Cu are found scattered in the scale. Thus, the newly developed alloy displays excellent resistance to MD thanks to the uniform formation of a protective oxide scale on the surface, and thanks also to the ability of the alloy surface to restore damage to the oxide scale by non-dissociative adsorption of CO.

3.3 Creep characteristic and thermal stability

The author and collaborators carried out a creep rupture test of the newly developed alloy over a wide temperature range of 500°C to 1,100°C (**Fig. 9**).[13] A maximum of 40,000 hours of test data showed that at all of the test temperatures, the alloy maintained stable rupture strength for many hours. For the newly developed alloy (registered as Code Case 2652 in Section I and Section VIII, Div. 1 of ASME), tolerable stresses are specified. In addition, the alloy is registered with the Technology Inspection Association of Germany (TÜV) and can be widely applied overseas.

The alloy also maintains excellent thermal stability for many hours. Alloy specimens aged at 650°C and 800°C for a maximum of 10,000 hours were subjected to Charpy impact tests at 25°C. The test results are shown in **Fig. 10**.[13] Although the aging at 650°C causes the impact value to decline slightly, the value remains 60 J · cm^{-2}, which is sufficient. At 650°C, only $M_{23}C_6$ composed of Cr or Fe was precipitated. On the other hand, at all of the test temperatures, the reference Ni-based alloy containing 3%Al markedly declined in impact value after 1,000 hours of heating. The reference alloy was embrittled as fine particles of intermetallic compound γ' (Ni_3Al) were precipitated in it. Thus, the newly developed alloy containing Si and Cu is superior in thermal stability to the reference Ni-based alloy containing Al.

3.4 Weldability

Since the newly developed alloy contains Si and Cu, it requires suitable measures to secure good weldability. The results of an extensive study on the phenomenon of solidification cracking and cracks in heat affected zones (HAZ) were reflected in the alloy design. In addition, there are good prospects for commercializing welding materials that have the same composition as the alloy. The author and collaborators prepared the Welding Procedural Specification (WPS) containing the procedure for welding with different materials.

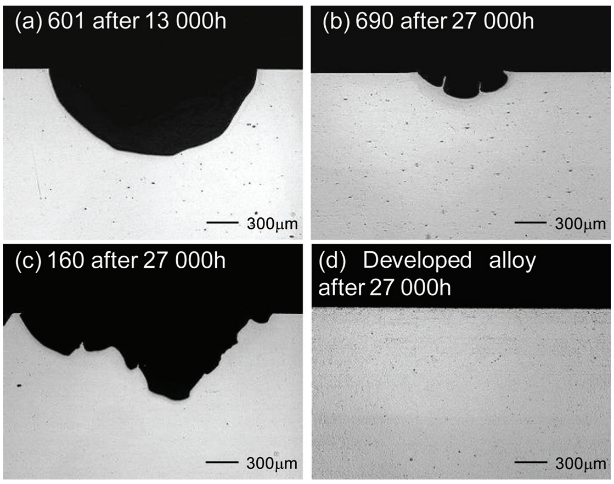


Fig. 7 Metallographic cross sections of the test specimens reacted with the simulated syngas at 650°C upon cyclic heating
The developed alloy has no pits.

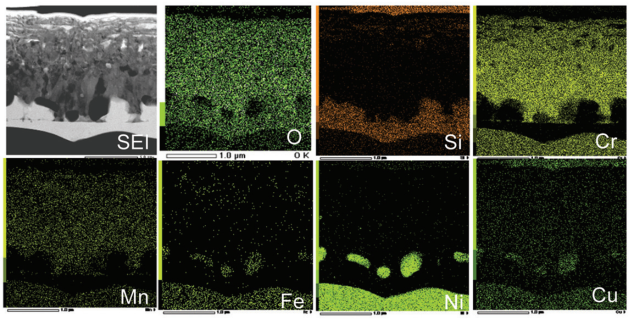


Fig. 8 STEM/EDS analysis of the cross section for the developed alloy reacted with the simulated syngas at 650°C for 17,000 h (340 cycles)

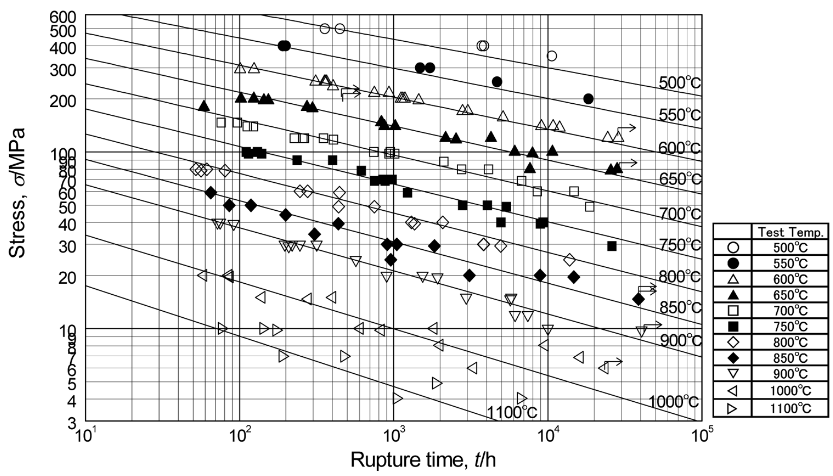


Fig. 9 Stress versus time to rupture curves of the developed tubes and plates

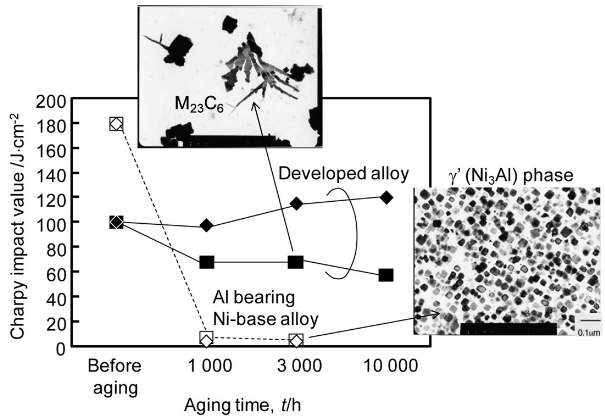


Fig. 10 Charpy impact value of the developed alloy and Al bearing Ni-base alloy aged at 650°C (■,□) and 800°C (◆,◇)

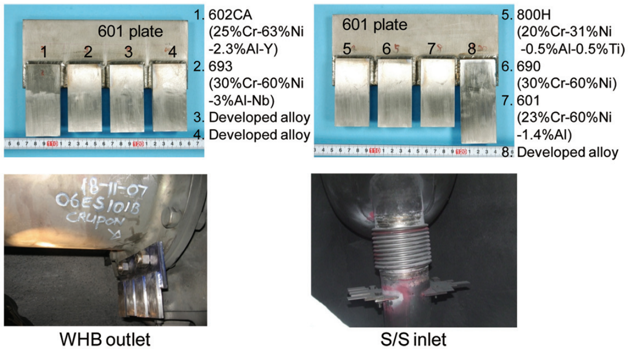


Fig. 11 Appearances of the test specimen before testing at waste heat boiler (WHB) outlet and at steam superheater (S/S) inlet in the GTL plant (Petro SA, Mossel Bay, South Africa)

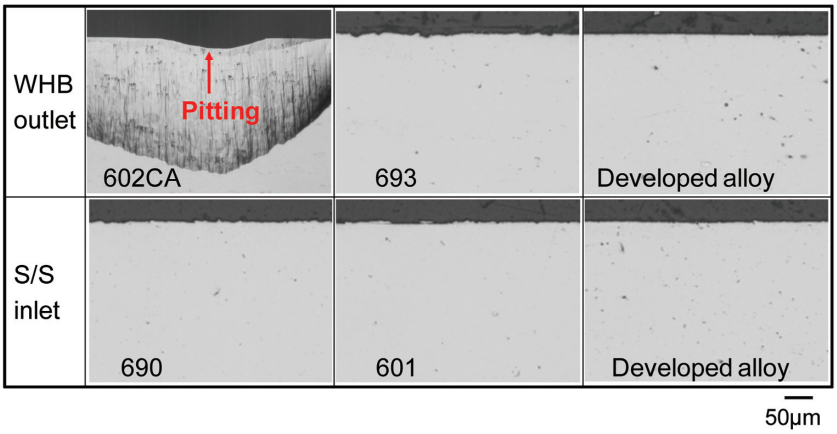


Fig. 12 Cross section of the test alloys exposed at 520°C for 15,000 h in the synthetic gas of the actual GTL plant

4. Evaluation of the Developed Alloy in an Actual Furnace

In order to determine the applicability of the newly developed alloy in actual environments, the author and collaborators carried out an MD test of the alloy in Petro SA's world-class GTL plant in South Africa. Test pieces were set near the outlet of a waste heat recovery boiler installed at the rear stage of the reforming furnace, and near the outlet of steam superheater piping located beyond the furnace (**Fig. 11**). A synthetic gas as hot as about 520°C passed through those parts. The composition of the synthetic gas used was 48.2%H_2-16.6%CO-6%CO_2-26.8%H_2O-1.1%CH_4. The test was conducted for a cumulative total of 15,000 hours.[14] **Figure 12** shows cross-section structures of the specimens observed after the test. Specimens of 800H disappeared completely as a result of violent MD. In a 602CA specimen containing 2.3% Al, a pit 30 μm in depth occurred. In addition, MD occurred on 601 plates to which various types of specimens had been fitted. On the other hand, the newly developed alloy was completely free of pits, showing superior resistance to MD. After this test, the specimens were subjected to Charpy impact tests. They confirmed that the developed alloy has excellent thermal stability.

Similar tests to evaluate the developed alloy have been carried out at the facilities of customers who operate not only GTL plants but also ammonia, methanol, or hydrogen production plants. The developed alloy is highly respected by the synthetic gas industry, and there are good prospects for its application in diverse fields.

5. Conclusion

With regard to mechanisms that restrain metal dusting (MD) caused by CO, the author and collaborators developed a new technique to restrain the dissociative adsorption of CO, and applied it to the composition design of a practical alloy. Application of the newly developed alloy makes it possible to prolong plant equipment life and enhance plant operation efficiency. The new alloy is expected to dramatically improve the efficiency of reforming equipment of the heat-exchange type. This type of reforming equipment has not yet been commercialized because of the absence of alloys having good MD resistance. The development of the new alloy will spur the practical use of heat-exchange type reformers.

MD poses a thorny problem affecting direct reduction iron-making equipment and natural gas reforming equipment utilizing concentrated solar rays as its heat source (called solar chemistry). When the newly developed alloy is used in such equipment, it will significantly facilitate equipment maintenance. Thus, the developed alloy is one of the new materials that can support new energy technologies and new energy-saving technologies that are needed to reduce CO_2 emissions and thereby curb global warming.

Controlling surface/interface reactions in accordance with the electronic theory of organic chemistry could possibly be applied to techniques that restrain not only MD but also other types of corrosion. Therefore, there are excellent prospects for further similar developments in the future.

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