This issue describes the factors that are derived from alloy substrate and that are the basics of high temperature corrosion prevention, the coating methods that are often used as actual corrosion protection methods, and the control of environmental factors.

2. Factors derived from alloy substrate

2.1 Alloy composition

As described in the first issue, typical oxides that are used as protective scales of practical metallic materials are the three following oxides: Cr$_2$O$_3$, Al$_2$O$_3$, and SiO$_2$. Figure 2-1 shows that their parabolic rate constants are smaller than those of other oxides, indicating the above fact. Forming one of these protective scale evenly on the material surface can lower the corrosion rate, or, in other words, can prevent corrosion. Therefore, alloys with excellent high temperature corrosion resistance have a composition that can stably form these scales on alloy surfaces and can maintain them in the environment. A continuous Cr$_2$O$_3$ scale formed on the alloy surface provides high temperature corrosion resistance.
corrosion resistance to stainless steel (Fe-Cr (-Ni) based alloy), a typical heat-resistant alloy. Wagner proposed the conditions for the continuous existence of a protective oxide scale. Under the above conditions, a Fe-Cr (-Ni) alloy forms and maintains a continuous Cr₂O₃ scale basically if the amount of Cr ($J_{Cr}$) supplied from the inside of the alloy to the interface between the alloy and the Cr₂O₃ scale is larger than the amount of Cr ($J'_{Cr}$) diffusing from the Cr₂O₃ to the outside ($J_{Cr} > J'_{Cr}$) (Figure 2-2). The condition that maximizes $J_{Cr}$ is when the Cr concentration gradient in the alloy is maximized. In other words, it is when the Cr concentration on the interface between the alloy and the Cr₂O₃ reduces to zero. In this state, from the comparison between $J_{Cr}$ and $J'_{Cr}$, the following formula is derived as the conditions under which the protective Cr₂O₃ scale stably exists:

$$N^0_{Cr} > \left( \frac{\pi^{1/2}}{16Z_oC} \right) \left( \frac{k_p}{D} \right)^{1/2} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots

In this formula, $N^0_{Cr}$ is the mole fraction of the Cr in the bulk of the alloy. $Z_o$ is the atomic weight of oxygen. $Z_o$ is the valence of the Cr in the oxide. $C$ is the substance quantity of the Cr per unit volume (mole). $k_p$ is the parabolic rate constant. $D$ is the inter-diffusion coefficient of the Cr in the alloy.

Therefore, if $k_p$ (the growth rate of the oxide scale) is small, and if $D$ is large (Cr can easily be supplied from the alloy to the scale), the Cr₂O₃ scale can be maintained. Conversely, if $J_{Cr} > J'_{Cr}$, there is not enough Cr that is supplied to the interface between the alloy and the Cr₂O₃ scale. Then, the elements other than Cr (Fe, Ni, etc. for stainless steel) are oxidized, and the Cr₂O₃ protective scale cannot be maintained. The Cr content required for forming a protective scale also depends on the base material. Figure 2-3 shows the influence of the Cr content on the parabolic rate constants of Fe-Cr, Ni-Cr, and Co-Cr alloys at 1000 °C. The figure also indicates that the Cr content that lowers the parabolic rate constant is small in the Fe-Cr alloy and Ni-Cr alloys and is the largest in the Co-Cr alloy. In other words, among the practical heat-resistant alloys, Co-based alloys require the largest amount of Cr to maintain their high temperature corrosion resistance. These differences are due to differences in the inter-

![Fig. 2-1 Parabolic rate constants of several oxides](image)

![Fig. 2-2 Conditions for forming a stable Cr₂O₃ scale on the alloy surface](image)

![Fig. 2-3 Influence of Cr contents on the parabolic rate constants of Fe-Cr, Ni-Cr, and Co-Cr alloys in the air or oxygen at 1000 °C](image)
diffusion coefficient or in the solubility of oxygen between alloys.

Since Al₂O₃ and SiO₂ have a smaller parabolic rate constant than Cr₂O₃, they are expected to form a continuous scale with a lower concentration of Cr. As a corrosion-resistant oxide scale, Al₂O₃ is used at about 900 °C or more for gas turbine materials, etc. and SiO₂ is used at about 1400 °C or more.

2.2 Influence of the alloy microstructure

As described above, an alloy with an oxide scale that grows slowly can easily supply Cr to its scale and can easily maintain its Cr₂O₃ scale. The capability of supplying Cr to the alloy surface is greatly influenced by not only the Cr concentration in the alloy but also the alloy microstructure. **Figure 2-4** shows the increase in mass when Fe- (22-25) Cr- (10-40) Ni alloys are oxidized in an Ar-H₂-H₂O atmosphere (P₀₂=1.2×10⁻¹⁹ atm) at 800 °C. The figure shows that if the amount of Cr is constant in alloys, when they contain 20 mass % of Ni or more, the increase in mass losses as the Ni content increases (the oxidation resistance is improved). This is qualitatively consistent with the result shown in Fig. 2-3, which indicates that Ni-Cr alloys have better oxidation resistance than Fe-Cr alloys.

On the other hand, the Fe-10Ni-22Cr and Fe-10Ni-25Cr alloys with a small Ni content have less increase in mass (good oxidation resistance) than the Fe-20Ni-22Cr and Fe-20Ni-25Cr alloys. **Figure 2-5** shows the cross-sectional microstructures of the oxidized Fe-25Cr-(10-40) Ni alloys. The figure shows that Fe-25Cr-(20-40) Ni alloys have a single austenitic phase, and Fe-25Cr-10Ni alloy has a ferritic phase (α) and an austenitic phase (γ). The diffusion coefficient of Cr in the ferritic phase is larger than that in the austenitic phase. Accordingly, a difference in the oxidation resistance was considered to occur because a lot of Cr was supplied from the ferritic phase to the alloy surface to form a protective scale on the surface.

An alloy grain boundary is another important factor that greatly affects the Cr supply to the alloy surface. **Figure 2-6** shows the cross-sectional microstructure of the steam oxidized scale formed on a Type 304 stainless steel surface. A thick bilayer scale is formed on the surface of a large alloy grain, while a thin oxidized scale is formed on the surface where alloy grain boundaries are concentrated. This is because since the grain boundary diffusion rate is greater than the body diffusion rate, the Cr diffusion to the alloy surface through grain boundaries was promoted. Therefore, more grain boundaries (each grain becomes smaller) promote the Cr supply to the alloy surface, allowing the Cr₂O₃ scale to be maintained easily. **Figure 2-7** shows the influence of the alloy grain size on the steam oxidation resistance of austenitic stainless steels. The larger the grain size number (the smaller the grain size), the less the mass loss (the better the
oxidation resistance). In addition, it is known that when the surface is cold-worked with a shot blast, etc., the diffusion of Cr to the alloy surface is promoted, and the oxidation resistance is improved\(^7\)-\(^10\). Note that if a heat treatment is applied to the cold-worked surface, the effect of cold-working may be lost depending on the heat treatment conditions.

Depending on the production method, heat treatment, etc., practical alloys often have a complicated microstructure. Figure 2-8 shows examples of the microstructures of a welded rolled material, sand cast material, and centrifugally cast material. In the rolled material, the grain sizes are nearly the same, but the welded part has a solidification structure. The cast material has a microstructure with complicated precipitation layers depending on the alloy composition. As shown in Fig. 2-8 (c), among the precipitated layers, a layer with poor corrosion resistance may be corroded faster. These differences in microstructure affect the corrosion process not a little. Therefore, for practical alloys, to take corrosion prevention measures, their corrosion processes must be examined taking into account not only their chemical compositions but also their microstructures.

2.3 Addition of rare earth elements

As described above, the alloy composition and alloy
microstructure are important for the formation and maintenance of a protective oxide scale. Furthermore, to maintain high temperature corrosion resistance for a long time, the protective oxide scale (Cr$_2$O$_3$, Al$_2$O$_3$, or SiO$_2$) formed on the alloy surface must closely contact the alloy substrate. The separation of the protective oxide from the alloy substrate leads to the direct exposure of the alloy substrate to the environment. If the protective oxide is separated from the alloy substrate, the material is directly exposed to the environment. Then, since corrosion progresses at a high corrosion rate, good high-temperature corrosion resistance cannot be maintained. As a factor that affects the adhesion of oxide scales, the first issue described the thermal stress that is generated on the interface between the alloy substrate and the oxide scale. The issue also described the Pilling-Bedworth ratio (PBR), which is an index for judging the possibility of separation of an oxide scale. On the other hand, rare earth elements such as Y, La, Hf, and Zr are known to be effective for inhibiting the separation of an oxide scale that is caused by thermal stress\textsuperscript{11)-14). Figure 2-9 shows the changes in mass of two aluminized UNS N06002 alloy (Ni-22Cr-18Fe-9Mo alloy) specimens when one specimen had a small amount of Zr on its surface and the other had no Zr, and they were oxidized in air at 1100 °C and at room temperature alternately. At first, the mass of the specimen without Zr increased due to oxidation. However, in the second cooling period, the mass started to decrease due to the separation of the oxide. After that, the mass continued to decrease. In and after the third cooling, as shown in the figure, the mass continued decreasing. On the other hand, the mass of the specimen with Zr continued to increase in 23 cycles of the repeated oxidation for 750 hours, which indicates that the oxide scale had good adhesion. As a mechanism that improves the high-temperature oxidation resistance, the following is reported: the added rare earth elements affect the diffusion rate in the oxide scale or the alloy\textsuperscript{15), 16), provide the blocking and wedging effect\textsuperscript{17), 18), or suppress the void formation on the interface between the alloy and the oxide interface\textsuperscript{19), 20). As practical alloys, the materials to which these rare earths are added are available (Table 2-1).

### 3. Coating

As described earlier, to provide a high-temperature corrosion resistance to an alloy material, sufficiently concentrated Cr, Al, or Si must be added to the alloy. However, these elements are not always effective to characteristics such as high-temperature strength, workability, and weldability, which are essential to actual materials. Rather, they often deteriorate these characteristics. Accordingly, coating is used to give characteristics such as strength and high-temperature corrosion resistance to an alloy substrate and to its surface, respectively. Generally, coating is not to coat CrO$_3$, AlO$_3$, or SiO$_2$ on the alloy surface as a protective scale, but to coat an alloy layer containing a sufficiently concentrated Cr, Al, or Si on it. Coating can make a

---

**Table 2-1** Examples of commercial heat-resistant alloys including rare earth elements

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
<th>Al</th>
<th>C</th>
<th>RE</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>556 (UNS R30556)</td>
<td>bal.</td>
<td>20</td>
<td>18</td>
<td>22</td>
<td>0.2</td>
<td>0.1</td>
<td>La=0.02</td>
<td>Mo=3, W=25, Ta</td>
</tr>
<tr>
<td>230 (UNS N06230)</td>
<td>3</td>
<td>bal.</td>
<td>5</td>
<td>22</td>
<td>-</td>
<td>0.1</td>
<td>La=0.02</td>
<td>W=14</td>
</tr>
<tr>
<td>214 (UNS N07214)</td>
<td>3</td>
<td>bal.</td>
<td>5</td>
<td>16</td>
<td>4.5</td>
<td>0.05</td>
<td>Y=0.01</td>
<td>Zr, B</td>
</tr>
<tr>
<td>188 (UNS R30188)</td>
<td>3</td>
<td>22</td>
<td>bal.</td>
<td>22</td>
<td>-</td>
<td>0.1</td>
<td>La=0.03</td>
<td>W=14</td>
</tr>
</tbody>
</table>
In order to prevent these problems, the “diffusion barrier coating system” (DBC system) is proposed to establish a barrier layer containing Re between the coating and the alloy substrate. The depletion of M from the coating may affect the existence of the protective scale on the surface. On the other hand, the generated void may deteriorate the adhesion of the coating layer. In order to prevent these problems, the “diffusion barrier coating system” (DBC system) is proposed to establish a barrier layer containing Re between the coating and the alloy substrate.

Table 2-2 shows typical coating methods for high-temperature corrosion protection. Since each method has advantages and disadvantages, a method and a material must be selected according to the usage environment, base material, and the characteristics required. The following sections describe the diffusion coating, thermal spraying, and combined treatment that are often applied.

### 3.1 Diffusion coating

Diffusion coating is surface modification that provides the material with functions such as corrosion resistance and abrasion resistance by diffusing other elements from the atmosphere to form the alloy layer of the diffused elements. To form the alloy layer on the substrate surface, the diffusing elements must have a certain degree of solubility against the substrate when diffusing into it. Accordingly, it is not possible to diffuse and infiltrate each element into each substrate; there are appropriate combinations. Generally, for steel materials, diffusion coating can use Cr, Al and Si, which are known as effective elements as high-temperature corrosion resistance coating.

Pack cementation and slurry coating methods are

<table>
<thead>
<tr>
<th>Method</th>
<th>Coating material</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion coating (Pack cementation, Slurry coating)</td>
<td>Cr, Al, Si, Cr-Al, Cr-Si, Al/Si, etc.</td>
<td>• Since a diffusion layer is formed providing good adhesion to the alloy substrate, the coating growth is hard to separate from the material.</td>
<td>• Processable elements are limited. • Controlling the film thickness and concentration is difficult. • Since the entire base material is processed in a furnace, a large-sized furnace is required depending on the size of the material to be processed, and a problem such as the deformation of the processed material may arise.</td>
</tr>
<tr>
<td>Thermal spraying</td>
<td>MCrAlX (M: Co, Ni, Fe- X: Y. Hf, Zr, etc.), Ni-Cr, Ni-Cr-Al, etc., ceramics</td>
<td>• Various types of alloy and ceramic films can be formed. • The film formation rate is high.</td>
<td>• The film is porous. • Depending on the thermal spraying method, the film adhesion may not be good, resulting in the separation of the film. Note: A self-fluxing alloy may be used to obtain a dense film.</td>
</tr>
<tr>
<td>Overlay welding</td>
<td>Ni, Co, Fe-based heat-resistant alloys, etc.</td>
<td>• A thick film can be formed. • A minute film with fewer pores can be formed. • A film with good adhesion can be formed.</td>
<td>• Because of the large heat input, preheating or postheating treatment may be required to prevent the deformation or hardening of the alloy substrate. • A thin film is hard to form.</td>
</tr>
<tr>
<td>Electron beam physical vapor deposition (EB-PVD)</td>
<td>Ceramics (Thermal barrier coating like YSZ)</td>
<td>• Even ceramics whose melting point is close to 3000 °C are capable of vapor deposition. • The structure can be controlled in a nano-order. • The film growth is much faster than that of conventional vapor-deposition methods. • Because of its columnar structure, the film has good thermal shock resistance.</td>
<td>• Since the equipment is extremely expensive, this method is not suitable for general industrial products with low added-value. This method is applied only to high added-value products such as jet engines. • Because of its columnar structure, the film’s thermal barrier performance is inferior to that of the film formed by thermal spraying.</td>
</tr>
<tr>
<td>Combined treatment (plating + diffusion coating, or thermal spraying + diffusion coating)</td>
<td>Pt plating + Al diffusion coating, or NiCr thermal spraying + Al diffusion coating</td>
<td>• Additional diffusion coating can compensate for the disadvantages of each coating method, providing new functions.</td>
<td>• Due to a two-step process, more work time is required.</td>
</tr>
</tbody>
</table>
known as typical diffusion coating methods. Figure 2-10 shows a schematic diagram of the pack cementation. In this method, the substrate is immersed in the powder consisting of the metal to be diffused, a halide, and a sintering inhibitor, and then is subject to a high temperature treatment.

Mr. Harada et al.\(^{25}\) examined the precipitation reactions caused by the diffusion of Cr into Fe or Ni in detail. According to their examination, the possible precipitation reactions of Cr on the metallic surface of the substrate are an exchange reaction, hydrogen reduction reaction, and thermal decomposition reaction. However, the Cr precipitation due to thermal decomposition cannot be expected, because the rate of Cr precipitation caused by the thermal decomposition of CrCl\(_2\) is \(3.85 \times 10^{-10}\) %\(^{25}\) at 1000 °C. In contrast, the Cr precipitation rates due to exchange reactions are as shown in Figure 2-11\(^{25}\). In other words, Cr precipitation can be expected on Fe surfaces in the order of percentage, while the precipitation rate on Ni surfaces is less than 100 ppm, which means that Cr precipitation due to an exchange reaction cannot be expected. On the other hand, as shown in Figure 2-12\(^{25}\), in a hydrogen reduction reaction, the precipitation rate in the order of percentage can be expected even in a relatively low temperature range. Therefore, for Fe, both an exchange reaction and a hydrogen reduction reaction can be thought of as main Cr precipitation reactions, and for Ni, a hydrogen reduction can be thought of as a main Cr precipitation reaction. Accordingly, to obtain a sufficient Cr layer on Ni alloy or Ni-based alloy, treatment in a hydrogen gas atmosphere is required. Figure 2-13\(^{26}\) shows the cross-section of the Cr layer formed on the surface of UNSN07001 alloy (Ni-20Cr-13Co-4Mo alloy) by the pack cementation. On the surface, there is a Cr precipitation layer of approximately 10 μm, and underneath that is a Cr diffusion layer approximately 5 μm thick is formed. The thicknesses of the surface precipitation and diffusion layers vary depending on the pack agent composition, processing temperature, processing time, and the additive rate of the carrier gas (H\(_2\)).

![Fig. 2-10 Schematic diagram of diffusion coating (pack cementation)](image)

![Fig. 2-11 Cr precipitation rates due to exchange reactions on Fe and Ni surfaces\(^{25}\)](image)

![Fig. 2-12 Cr precipitation rates due to hydrogen reduction\(^{25}\) (m is a ratio to the mass of CrCl\(_2\))] (image)

![Fig. 2-13 Cross-section of the Cr layer formed on the surface of UNSN07001 alloy (Ni-20Cr-13Co-4Mo alloy)\(^{26}\)](image)
3.2 Thermal spraying

Thermal spraying is used to form a coating layer by heating a metal or ceramics to melt or half-melt and spraying it at high speed\(^2\). Figure 2-14 shows a schematic diagram of high velocity oxy-fuel (HVOF), which is typical thermal spraying. Thermal spraying is used for applications such as thermal barrier coating (TBC) on gas turbine engines and jet engines, and heat transfer tubes for waste disposal power generation. Unlike diffusion coating, there are advantages as follow: There are fewer restrictions on processing materials, and the coating layer formation rate is so high that a thick coating layer (100-500 μm) can be formed in a relatively short time. On the other hand, note that since there are essentially pores in the coating layer, corrosive elements may reach the substrate surface through the pores, corroding the substrate.

According to the type of the heat source, thermal spraying is classified into the gas type and the electric type: the former includes flame spraying and HVOF, and the latter includes spraying and plasma spraying. Table 2-3 lists the features of typical thermal spraying. The values such as particle velocities and heat source temperatures are just guidelines because they vary depending on documents and manufacturers. Ni-Cr alloy thermal spraying or the like based on atmospheric plasma spraying are often used for preventing the high temperature corrosion of heat transfer tubes for power generation boilers. Also, to reduce the porosity, pressure reduction plasma spraying or HVOF may be used. If molten salt is produced, or if the temperature on the environmental side such as the boiler tubes is high and that on the alloy substrate side is low, the concentration of corrosive substances or a condensed phase are likely to occur in the coating layer, which may allow the pores

![Fig. 2-14 Schematic diagram of high velocity oxy fuel (HVOF) spraying](image)

<table>
<thead>
<tr>
<th>Heat source</th>
<th>Method</th>
<th>Particle velocity</th>
<th>Heat source temperature</th>
<th>Thermal spray materials</th>
<th>Adhesive strength (MPa)</th>
<th>Porosity (%)</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas type</td>
<td>Flame spraying</td>
<td>Relatively slow (around 200 m/s)</td>
<td>Relatively low (around 2000 °C)</td>
<td>Metals, oxides</td>
<td>20 to 40</td>
<td>10 to 20</td>
<td>- A film is formed by thermal spraying with compressed air of the thermal spray particle produced by melting the thermal spray material continuously supplied to the combustion flame whose heat sources are oxygen and acetylene.</td>
</tr>
<tr>
<td></td>
<td>High velocity oxy fuel spraying (HVOF)</td>
<td>Fast (around 700 m/s)</td>
<td>Relatively low (around 2000 °C)</td>
<td>Metals, cermet</td>
<td>Not less than 70</td>
<td>1 to 5</td>
<td>- Since the thermal spray particles collide with the base material surface at a speed exceeding the speed of sound, a highly adhesive and dense film is formed.</td>
</tr>
<tr>
<td></td>
<td>Arc spraying</td>
<td>Middle (around 300 m/s)</td>
<td>Middle to relatively high (around 5000 °C)</td>
<td>Metals</td>
<td>20 to 40</td>
<td>10 to 20</td>
<td>- Arc discharge between two metal wires generates discharge energy that melts the wires. - The volume of the film formed by thermal spraying per unit time is large. - The thermal spray materials are limited to materials with electrical conductivity.</td>
</tr>
<tr>
<td>Electric type</td>
<td>Atmospheric plasma spraying</td>
<td>Relatively fast (around 500 m/s)</td>
<td>High (5000 to 10000 °C)</td>
<td>Metals, ceramics, cermet</td>
<td>20 to 70</td>
<td>1 to 20</td>
<td>- In a gas such as Ar, arc discharge generates a high-temperature, high-speed plasma jet to melt the thermal spray material and accelerate the spray speed. - Thermal spraying can be used for almost all materials including metals, cermet, and ceramics with a high melting point.</td>
</tr>
<tr>
<td></td>
<td>Low pressure plasma spraying</td>
<td>Relatively fast (around 500 m/s)</td>
<td>High (5000 to 10000 °C)</td>
<td>Metals, ceramics, cermet</td>
<td>Not less than 70</td>
<td>1 to 5</td>
<td>- Since this process is performed in a chamber in which the atmosphere is controlled by purging inert gas under reduced pressure, the characteristics of the thermal spray material cannot be impaired. - A film can be formed on active metals such as Ti. - The film adhesion is good.</td>
</tr>
</tbody>
</table>
to play a big role in corrosion acceleration. In such a case, in order to suppress the porosity to as low as possible, the pores may be sealed by spraying a self-fluxing alloy or a low melting metal such as Al after thermal spraying. A self-fluxing alloy contains B or Si as a flame coating material. After thermal spraying is performed, heating and melting the coating layer at a temperature of approximately 1000 °C eliminates pores, which results in the formation of a minute coating layer. As self-fluxing alloys, there are Ni-based alloys and Co-based alloys. B combines with Ni, Co, or Si to form an intermetallic compound, which hardens the coating layer and reduces the melting point to promote fusion. To provide slurry erosion resistance in addition to high temperature corrosion resistance, Cr carbide-based cermet is often processed with HVOF.

For thermal spraying, the development of new thermal spraying guns and thermal spray materials has rapidly advanced recently, enabling the formation of coating layers with higher performance. Therefore, it can be said that thermal spraying is an effective means for coating for high temperature corrosion resistance. On the other hand, even if the processes are the same, the coating properties may greatly differ depending on the type of thermal spraying gun used or the processing conditions. Therefore, before applying thermal spraying to actual equipment, it is important to evaluate the fundamental characteristics of the processing method to be used and of the coating.

3.3 Combined treatment
In the coating formation process, because sprayed coating and plating are generally not accompanied by a diffusion reaction and chemical reaction between the substrate and the coating layer, the coating layer adhesion is lower than that of diffusion coating. In addition, since sprayed coating inevitably has pores, corrosive substances can easily reach the surface of the alloy substrate. To compensate for these disadvantages, a combined treatment\(^{29-31}\) that combines diffusion coating with thermal spraying or plating has been developed. If Al diffusion coating is performed after Pt or Rh is electrically plated, the high-temperature oxidation resistance is better than that of Al diffusion coating alone. This method has been applied to jet engine components for a long time. In addition, if Al diffusion coating is performed after the application of Ni plating on Ni-40Cr alloy, the α-Cr layer\(^{32}\), is formed as diffusion barrier between the Ni-Al coating layer and the alloy substrate. Other than the above, the following method\(^{33}\) has also been developed: After Ni plating on a TiAl alloy, if Al diffusion coating is performed on the alloy to use up-hill diffusion, a layer having a higher Al concentration is formed on the alloy side rather than the outermost surface to improve the high-temperature oxidation resistance of the Ti alloy for a long time. As shown above, combined treatments can achieve higher performance coating than any single method can provide, and arouse expectations for further research and development.

4. Control of environmental factors

4.1 Gas atmosphere
Chapters 1 through 3 described the concept of corrosion prevention from a viewpoint of materials, and the coating as actual measures. However, corrosion behaviors are determined by not only material factors but also interactions of environmental factors. This chapter mentions the possibility of corrosion prevention through the control of environmental factors.

For example, to inhibit oxidation, reduction in oxygen partial pressure is a possible dynamic measure. However, in many cases, even though the oxygen partial pressure is low, corrosion may not be reduced more than with high oxygen partial pressure. Figure 2-15 shows the cross-section images of the Fe-19Cr-10Ni model alloys, which were oxidized in a heat cycle of 800 to 250 °C for 144 hours: one was in the air (\(P_{02}=10^{-0.7}\) atm) and the other in a mixed atmosphere of N₂-H₂-H₂O (\(P_{02}=10^{-17.0}\) atm). In the air, a uniform oxide scale with a thickness of several microns is formed; on the other hand, in the mixed atmosphere of N₂-H₂-H₂O, a thick bilayer scale with a thickness of around 100 μm is formed. Since these corrosion reactions are oxidation, the oxygen partial pressure is an important factor. However, other factors (in this case, the behaviors of H₂ and H₂O) that affect the scale behavior and mass transfer may create a more severe corrosive environment. Such a phenomenon is observed in
multiple oxidant gas such as SO \(_2\) and CO\(_2\). In the case of SO\(_2\), even if the oxygen partial pressure is high and the oxide is stable, the following formula is obtained in an equilibrium state:

\[
\text{SO}_2 + 2M \rightarrow 2MO + \frac{1}{2} \text{S}_2 (g) \quad \quad \quad \quad \text{(2-2)}
\]

Since \(P_{\text{SO}_2}\) increases locally to produce sulfide, the formed scale contains sulfide, and its protection performance is poorer than that of a pure oxide. Therefore, it is recommended to remove oxidizing agents other than oxygen as much as possible. Since general heat-resistant alloys are designed to form a protective oxide scale, controlling the gas atmosphere so that a stable oxide can be formed often results in the inhibition of corrosion.

### 4.2 Temperature

Since a corrosion reaction is a thermal activated reaction, basically the reaction rate varies exponentially against the temperature. This can also be presumed from the Arrhenius equation shown below, which relates the temperature and the chemical reaction rate.

\[
k = A \exp \left( \frac{-Q}{RT} \right) \quad \quad \quad \quad \text{(2-3)}
\]

In the above equation, \(k\) is the reaction rate, \(A\) is the frequency factor, \(Q\) is the activation energy, \(R\) is the gas constant, and \(T\) is the absolute temperature. By taking the logarithms of both members, the Arrhenius equation can be expressed as the following:

\[
\ln k = \ln A - \frac{Q}{R} \cdot \frac{1}{T} \quad \quad \quad \quad \text{(2-4)}
\]

Therefore, as shown in Figure 2-16, the activation energy can be estimated by plotting the logarithm of the reaction rate at each temperature against the reciprocal of the absolute temperature. The larger the activation energy of the reaction becomes, the more corrosion is reduced at a low temperature. As for TBC on gas turbine blades, a ceramic thermal barrier layer covers their surfaces to reduce the temperature on the alloy surface, resulting in corrosion prevention. On the other hand, in the case of a boiler tube, etc., a temperature gradient is formed from its external surface to its internal surface. Reducing the temperature on the external surface of the tube reduces corrosion. However, in the case of waste incineration boilers, etc., close attention is required due to the following: if the high-temperature gas atmosphere outside the tube contains low melting compounds like chlorides, conversely the formation of a low melting condensed layer on the external surface of the tube may be enhanced, resulting in the promotion of corrosion.

### 4.3 Gas flow and other factors

If the gas flow is fast or fluctuates, the protective scale may be peeled off, or partial corrosion may occur, resulting in the promotion of corrosion. In this case, it is recommended to prevent the gas flowing at high
speed from directly contacting the member by means of lowering the gas flow velocity as much as possible or by installing a protector to the part subject to a high-speed flow.

If a soot blower or the like is used to remove foreign matter deposited on the member surface, thermal shock may be given to the protective oxide scale formed on the surface, inducing the separation of the scale from the surface and promoting corrosion. In addition, it is recommended to avoid rapid heating or quenching during start/stop operation as much as possible, because such operations promote the separation of the oxide scale. In a waste incineration plant, etc., the oxide scales formed on member surfaces during operation often contain a chloride. In this case, while the plant is stopped, the oxide scales may absorb moisture producing a corrosive solution such as hydrochloric acid, which promotes corrosion (down time corrosion).

As described above, because high-temperature corrosion resistance often depends on the stability of the oxide scale formed on the alloy surface, it is recommended to eliminate as much as possible the factors that prevent the maintenance of the protective oxide scales.

5. Conclusion

This issue describes some important material factors that are related to methods for preventing high temperature corrosion, and introduces typical high-temperature protective coating methods.

An important thing for corrosion prevention is to take appropriate measures with a good understanding of the corrosion mechanism. In addition, it is necessary to take into account that the characteristics of high-temperature materials change over time. Therefore, we should know that while the coating is used at high temperatures, its characteristics change due to the reactions in the environment and the base material. The first and second issues outline the basics of high temperature corrosion and corrosion protection methods. The next and following issues will describe the concrete high temperature corrosion cases that we have experienced and the measures against those cases.

References