Effects of Vacuum Heating Conditions on the Surface Brightness of Various Stainless Steels*

By Itsuo Ishigami**, Eiji Tsunasawa**, and Kyuhiko Yamanaka**

Nine commercial stainless steels were heated at temperatures from 900 to 1150°C for times up to 250 min in vacuums of 5.33 and/or 1.33 Pa. The steels heated were die cooled in the vacuums to prevent their surfaces from being stained with quenchants. Brightness of the surfaces was measured by use of an optical microscope equipped with a silicon photocell. The effects of temperature, heating time, and vacuum were investigated. An observation of the surfaces showed that an oxide film once formed during heating disappeared again with increasing temperature and/or heating time, resulting in the marked increase in surface brightness. A mechanism of the disappearance, that is, a reduction of the oxide film by solute carbon in the steels, is presented on the basis of a thermodynamical analysis and of experimental evidence, by which the results obtained through the experiments on several stainless steels can be fully interpreted.

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I. Introduction

Atmosphere furnaces have gained wide acceptance as an effective measure for protecting steels from oxidation during heating. However, they are not very satisfactory for stainless steels, because the steels contain a large quantity of chromium and hence readily react with a little oxygen. The steels on which oxide films form must in many cases undergo finishing treatments such as grinding and acid pickling. These finishing processes cause the heat treatment of stainless steels inefficient, laborious, tedious and expensive.

Vacuum heat treatment is thought to be a powerful countermeasure for overcoming the above problems. The present study was begun with the aim of investigating the applicability of vacuum heat treatment to heat treatment of stainless steels. Up to the present, the authors have investigated brightness and properties, e.g., corrosion resistance, of surfaces of stainless steels vacuum heat treated. In this paper, attention will be paid only to the effects of vacuum heating conditions, i.e., temperature, time, and pressure, on the brightness of surfaces of several commercial stainless steels. A surface situation, namely the formation of an oxide film and surface roughening, of SUS304 was first observed in detail on an optical microscope in order to find the most suitable heating conditions which ensure the excellent brightness. During the observation, the authors happened upon an interesting phenomenon. That is, an oxide film once formed during heating disappeared again with increasing temperature and/or time, and its disappearance brought about the remarkable improvement in brightness. A possible mechanism of the disappearance is discussed thermodynamically and sufficient experimental evidence is presented to lend support to the mechanism. This mechanism is considered to be applicable to all the experimental results in this study.

II. Experimental Procedure

SUS 304 and SUS 347 of the chemical compositions listed in Table 1 were used in this investigation. In addition to the two steels, stainless steels of varied types were also used as seen in a later chapter. All the steels are commercial ones. A steel plate 4.8 mm thick was cold rolled and cut to 17 mm x 25 mm x 2.2 mm rectangular sheets. Each sheet was mechanically polished to 2.0 mm thick by grinding with emery papers and by finishing with a 0.3 μm alumina powder. Prior to the heat treatment, all specimens were degreased in acetone with a supersonic cleaner.

The heat treatment was carried out by use
Table 1 Chemical compositions of stainless steels used. (wt%)  

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<tr>
<th>Specimens</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Other elements</th>
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<tbody>
<tr>
<td>SUS 304</td>
<td>0.04</td>
<td>0.64</td>
<td>1.62</td>
<td>0.02</td>
<td>0.007</td>
<td>9.0</td>
<td>18.4</td>
<td>Mo, 0.08; Cu, 0.02</td>
</tr>
<tr>
<td>SUS 347</td>
<td>0.07</td>
<td>0.57</td>
<td>1.47</td>
<td>0.02</td>
<td>0.009</td>
<td>10.9</td>
<td>17.8</td>
<td>Nb+Ta, 0.74</td>
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of a vacuum quenching apparatus\(^{(1)}\) in which a 35 mm inner diam. by 1000 mm long, high purity alumina heating tube was mounted vertically. The procedure of heat treatment using this apparatus has been described in detail elsewhere\(^{(1)}\). In order to prevent quenchants from staining specimen surfaces, the specimens vacuum heated were cooled in a vacuum by being dropped onto a mild steel disk 35 mm in diameter and 1 mm in thickness which was set up in the water cooled, lower part of the heating tube. This "die cooling method" allowed the specimens to retain only the effects of vacuum heating remained on their surfaces.

Brightness was measured by use of the optical microscope equipped with a N-P junction type silicon photocell\(^{(2)}\). A 6 V-15 W tungsten lamp was used as the light source. The beam of light emitted from the source is directed to the specimen surface and then reflected into the photocell. The silicon photocell generates an electromotive force proportional to illuminance\(^{(2)}\). The brightness of the surface of the treated specimen is defined by the equation

\[
B = \left( \frac{E_T}{E_U} \right) \times 100\%, \tag{1}
\]

where \(E_T\) is the electromotive force for the surface of the treated specimen and \(E_U\) is that for the untreated specimen.

III. Experimental Results

1. Brightness of SUS 304

To study the effect of temperature experiments were done at temperatures within the range of 900 to 1150°C; the heating time was maintained constant for 30 min and the vacuum was kept at 5.33 and 1.33 Pa. The results are shown in Fig. 1. In the case of heating at 5.33 Pa, below 970°C the brightness is very low, for example, only about 20% at 900°C, whereas it increases with increasing temperature and reaches 100% at 1050°C. However, an excess increase in temperature decreases the brightness, it being 72% at 1150°C. The appearance of the specimen surfaces is made clear in Photo. 1(a)~(f). At 950°C, as shown in Photo. 1(a), a dark green oxide film is observed on all parts of the surface. However, one finds the disappearance of the film occurs near grain boundaries on increasing temperature (see Photo. 1(b) and (c)). Eventually, at 1050°C the film vanishes away without leaving a trace from any part of the surface as shown in Photo. 1(d). A further increase in temperature brings about a surface roughening due to the formation of grain boundary grooves\(^{(3)}\) and surface relieves illustrated in Photo. 1(e) and (f). The width of the boundary grooves is also plotted in Fig. 1. In the case of heating at 1.33 Pa, a remarkable improvement in brightness takes place below 970°C, which may be accounted for by the reason mentioned above. A comparison of Fig. 1 with Photo. 1 shows that the brightness of one surface reflects accurately the appearance of its own surface. It is worth noting that the temperature which provides the maximum brightness for SUS 304
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Photo. 1 Optical micrographs of surfaces of SUS 304 heated for 30 min under a pressure of 5.33 Pa at (a) 950°C, (b) 980°C, (c) 1030°C, (d) 1050°C, (e) 1070°C, and (f) 1150°C. Brightness: (a) 27%, (b) 51%, (c) 89%, (d) 100%, (e) 71%, and (f) 72%.

coincides with that accepted widely to dissolve carbides.

The effect of heating time was studied at constant temperatures (950, 980, and 1050°C) and vacuum (5.33 Pa). The results are plotted in Fig. 2. Increasing heating time results in disappearance of the oxide film and hence the brightness is improved. This indicates that for the optimum selection of heating time it is necessary to take into account not only the solution of carbides but also the improvement in brightness.

Fig. 2 Changes in brightness with heating time. SUS 304 was heated under a pressure of 5.33 Pa.

2. Brightness of SUS 347

Experiments similar to those on SUS 304 were made on SUS 347. Prior to the experiments, specimens were prepared by austenitizing under argon atmosphere at 1300°C for 60 min and water quenching. A higher vacuum, 1.33 Pa, was selected, since it was difficult to obtain a bright surface on SUS 347 compared to that on SUS 304. The results are shown in Figs. 3 and 4. Heating in the vicinity of 1100°C gives the maximum brightness,

Fig. 3 Changes in brightness and width of groove with temperature. SUS 304 and SUS 347 were heated for 30 min under a pressure of 1.33 Pa.
Fig. 4 Changes in brightness with heating time. SUS 347 was heated under a pressure of 1.33 Pa.

about 90%. The growth rate of boundary grooves on SUS 347 is smaller than that on SUS 304. This seems to be intimately related with the microscopic observation in that oxide films disappear more slowly on SUS 347 than on SUS 304. Fine grains of SUS 347 lead to an immense amount of boundary grooves. This supplies a reason for the result that SUS 347 is inferior in brightness to SUS 304, even if both the surfaces are free from oxide films. Figure 4 shows that below 1000°C the brightness decreases with increasing heating time contrary to the expectation from the results of SUS 304 (see Fig. 2).

3. Brightness of other types of stainless steels

To study the effect of alloy elements the stainless steels containing 0~14 wt%Ni and 12~27 wt%Cr were heated under three conditions, that is, 970°C~30 min, 970°C~150 min, and 1050°C~30 min in a vacuum of 5.33 Pa. The condition 1050°C~30 min may ensure the brightness of the steels to be in equilibrium and free from surface roughening; on the contrary the condition 970°C~30 min leads the brightness to a state far from equilibrium. The condition 970°C~150 min is situated at a position intermediate between the conditions above mentioned. The compositions of the steels and the corresponding brightness are summarized in Table 2. The calculated solubility limits of carbon in austenite are shown in Table 2, since the solute carbon is likely to play an important role in the disappearance of the oxide film. The calculation was carried out using the experimental formula developed by Nishino and Kagawa(4); the effect of molybdenum on the solubility was neglected in the calculation using this formula, because the values calculated for 16.9Cr–14Ni steel

<table>
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<th>Table 2 Chemical compositions of stainless steels used. (wt%)</th>
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<td>Specimens*</td>
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* No. 1~No. 3, ferritic and martensitic stainless steels; No. 4~No. 10, austenitic stainless steels; No. 11~No. 13, heat resisting cast steels.

** Specimens were treated under a pressure of 5.33 Pa.
agreed quite well with the values measured for 16.9Cr–14Ni–2.7Mo steel by Deighton(5).

The composition dependence of the brightness shows that a higher content of solute carbon† and/or a lower content of chromium in the steels considerably improve the brightness. This trend is more pronounced in the case of heating at 970°C which should offer the brightness being far from an equilibrium state to the steels. A trial and error analysis of the composition dependence of brightness revealed that there exists the most intimate correlation between the (Ni+Cr) content and the brightness. To be more specific, the brightness decreases as the (Ni+Cr) content increases. The difficulty of the achievement of a bright surface by the types of steels are may be generally arranged in the order of heat resisting cast steels, austenitic stainless steels, ferritic and martensitic stainless steels.

IV. Discussion

The experimental evidence shows that the disappearance of oxide film gives rise to at least a satisfactory brightness on surfaces of any stainless steel; therefore, attention will be paid only to the disappearance of the oxide film with increasing temperature and/or heating time. The priority of discussion is due to the actual meaning of "brightness" measured in this study.

1. Physical meaning of the brightness measured by use of a silicon photocell

The luminance \( I \) of a specimen surface lit up with the daylight as being visible to the naked eye and the electromotive force \( E \) generated in a silicon photocell response to the light of a tungsten lamp reflected from a specimen surface are given by the following equations\(^6\):

\[
I = N(\lambda)D(\lambda)V(\lambda)d\lambda, \quad (2)
\]
\[
E = P(\lambda)D(\lambda)S(\lambda)d\lambda, \quad (3)
\]

where \( N(\lambda) \) and \( P(\lambda) \) are, respectively, the spectrum distributions of the daylight and the radiant flux emitted by a tungsten lamp, \( D(\lambda) \) the reflection coefficient of a specimen surface, and \( V(\lambda) \) and \( S(\lambda) \) the spectral responses of the naked eye and of the silicon photocell respectively. The suffix \( T \) is used to indicate a notation for a treated specimen and the suffix \( U \) for an untreated specimen. Then, combination of eqs. (2) and (3) yields the following relation for \( B \), the brightness defined by eq. (1),

\[
B = 100\left( \frac{E_T}{E_U} \right) = 100\left( \frac{I_T}{I_U} \right) \int_0^\infty N(\lambda)D(\lambda)T V(\lambda)d\lambda \int_0^\infty P(\lambda)D(\lambda)T S(\lambda)d\lambda.
\]

This equation proves that the brightness measured by using the silicon photocell, \( 100(E_T/E_U) \), perfectly agrees with that evaluated with the naked eye, \( 100(I_T/I_U) \), only when the value of the square brackets is unity, that is, \( D(\lambda)_T = kD(\lambda)_U \). When the specimen surface is free from any oxide film, the relation may be applied; the constant \( k \) is less than unity or equal to unity, according to whether or not there exists the surface roughening on a specimen. On the other hand, when the greenish oxide film is formed on a specimen, the value of \( \int_0^\infty P(\lambda)D(\lambda)_T S(\lambda)d\lambda \) should be rather large compared to that of \( \int_0^\infty P(\lambda)D(\lambda)_U S(\lambda)d\lambda \), since compared to the peak of \( D(\lambda)_T \), the peak of \( D(\lambda)_T \) must be farther below the wavelength region in which the peaks of \( P(\lambda) \) and \( S(\lambda) \) exist\(^6\)(\(^7\)). Therefore, the value in the square brackets of eq. (4) will be fairly below unity.

† In the case of the steels whose carbon content is above their solubility limit, it may safely be assumed that a higher solubility of carbon gives a higher content of solute carbon in a steel, since an increase in a carbon content produces a less increase in a solute carbon content in an austenite plus carbide region than in the austenite single-phase region.
on the contrary, the brightness measured on a surface free from any oxide film must be in complete agreement with that evaluated with the naked eye, whether a surface roughening occurs or not.

2. Thermodynamical analysis of a mechanism of the disappearance of the oxide film

The disappearance of the oxide film fomed in heating up to about 900°C may occur during isothermal heating at higher temperatures by one or more of the following mechanisms: (1) evaporation or dissociation of the oxide; (2) reduction of the oxide by residual gases in a furnace; (3) reduction of the oxide by solute carbon in steel. Now, in investigating these mechanisms, let us assume that the oxide is \( \text{Cr}_2\text{O}_3 \), because the previous studies\(^{(8)-(13)}\) of the oxidation of Fe–Cr and Fe–Cr–Ni alloys in various atmospheres assert that at least \( \text{Cr}_2\text{O}_3 \) is a main constituent in the oxides, in addition, because \( \text{Cr}_2\text{O}_3 \) is undoubtedly most stable in all of oxides of the main alloy elements in stainless steels, i.e., Fe, Ni, Cr.

From the known vapor pressure\(^{(14)}\) and dissociation pressure\(^{(15)}\) of \( \text{Cr}_2\text{O}_3 \), its contribution is easily shown to be negligible at all the temperature used. It is rather worthy of our notice that \( \text{Cr}_2\text{O}_3 \) often reacts even with only a little oxygen to turn into highly volatile species, e.g., \( \text{CrO}_3 \), \( \text{CrO}_2 \), etc.\(^{(16)}\) However, the reviewing literature on thermodynamics\(^{(16)-(17)}\) and kinetics\(^{(18)}\) of the volatilization of the species indicates that the disappearance of the oxide cannot be due only to the formation of such species.

Although the authors have not analyzed the residual gases in the vacuum furnace used, thermodynamic calculations\(^{(19)}\) show that the principal gaseous species in vacua above 700 K are \( \text{H}_2 \) and \( \text{CO} \). The reduction of \( \text{Cr}_2\text{O}_3 \) by \( \text{H}_2 \) may be represented by eq. (7):

\[
\begin{align*}
\text{Cr}_2\text{O}_3 + 3\text{H}_2 &= 2\text{Cr} + 3\text{H}_2\text{O}; \quad \Delta G^0_3 = \Delta G^0_1 + \Delta G^0_2, \\
\Delta G^0_1 &= -RT \ln \left( \frac{a_{\text{Cr}}^2 p_{\text{H}_2}^3}{a_{\text{Cr}_2\text{O}_3} p_{\text{H}_2\text{O}}^3} \right) = 380950 - 95.40 T \text{ J}, \\
\Delta G^0_2 &= -RT \ln \left( \frac{a_{\text{Cr}_2\text{O}_3} p_{\text{H}_2\text{O}}^3}{a_{\text{H}_2}^3} \right) = 785130 - 522.79 T \text{ J}.
\end{align*}
\]  

When the partial pressure of \( \text{CO} \) at a gas/oxide interface is lower than that calculated by eq. (12), the reduction can occur. Unless the content of solute carbon extremely decreases at an oxide/steel interface owing to its consumption by reaction (10), the reduction proceeds until the oxide completely disappears.

For 18Cr–8Ni alloy steels containing 0.004–0.08 wt% carbon, using eq. (12), \( P_{\text{CO}} \) was calculated as a function of temperature \( T \). The results are shown in Fig. 5. The dashed and solid curves indicate the results for steels of a \( \gamma + \text{M}_{23}\text{C}_6 \) phase and of a \( \gamma \) single phase, respectively. In the calculation \( a_{\text{Cr}} \) was obtained from the data of Tůma et al.\(^{(20)-(21)}\) and in the
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Fig. 5 Changes in \( P_{CO} \) and \( P_{CO} \) with temperature for 18Cr-8Ni alloy steels with different carbon contents from 0.004 to 0.08 wt%.

absence of the data for \( a_{Cr} \) in 18Cr-8Ni alloy steel, an approach would be to use the data for the Fe-Cr binary system of Kubaschewski and Heymer(22), and Jeannin et al.(23) The reduction of \( Cr_2O_3 \) on the steels occurs on the lower side of the \( P_{CO}-T \) curves in contrast to the oxidation of the steels on the upper side. The results of Fig. 1 and Photo. 1, therefore, can be interpreted in such a way that on heating the alloy steels, first oxide film appears in a lower temperature range but subsequently the reduction of the film takes place in a higher temperature range, namely, in the reduction region across the \( P_{CO}-T \) curve and eventually the oxide film vanishes away. Furthermore, on the basis of a common understanding that lowering the pressure in the furnace brings about a lower partial pressure of CO at the gas/oxide interface, \( P_{CO} \), it may be expected that a higher vacuum serves not only for suppressing the growth of an oxide film in the oxidation region but for lowering the temperature above which the reduction occurs. Figure 1 confirms this expectation. In addition, the reduction by solute carbon may be supported by the fact that the oxide film disappear near grain boundaries prior to in grains as shown in Photo. 1(b) and (c), since the carbon can diffuse at a higher rate along grain boundaries than in grains.

Contrary to the direct reduction by the solute carbon, eq. (10), the previous studies(24) of the reduction of iron oxide and carbon powder mixtures also might support the solid-gas reaction represented as follows:

\[
Cr_2O_3 + 3CO = 2Cr + 3CO_2, \quad (13)
\]
\[
3C + 3CO_2 = 6CO. \quad (14)
\]

Nevertheless, it was recognized by other investigators(25) that “true” direct reduction is possible when the gaseous products of reactions (10) and (13), i.e., CO and \( CO_2 \), are removed from the reaction system as fast as these are generated. Since vacuum can ensure the removal of the gaseous products, in the present study the direct reduction must play an important role in the disappearance of the oxide film.

In Fig. 5 is also presented the equilibrium vapor pressure of chromium in Fe-18Cr, \( P_{Cr} \), which was obtained by combining \( a_{Cr} \) in Fe-18Cr(23) with the equilibrium vapor pressure of pure chromium(15). A further kinetic treatment is necessary to foresee whether or not chromium depletion in the surface region of the steels appears during vacuum heating. However, it is presumable that there exists an annealing condition under which the reduction of the oxide and no chromium depletion can occur, because the \( P_{Cr}-T \) curve is far below the \( P_{CO}-T \) curves as seen in Fig. 5. This is quite favorable to the practical application of vacuum heat treatment to stainless steels.

3. Experimental confirmation of reduction of oxide film by solute carbon

In this section, first by some experiments are confirmed phenomena that are justly predicted to be involved in the direct reduction and thereafter interpretations are put upon the results of SUS 347 and of various stainless steels as shown in Figs. 3, 4, and Table 2.
Changes in pressure in the furnace with heating

It is reasonable to anticipate an increase in pressure owing to the production of CO by the reduction eq. (10). A specimen with a large surface area, 25 mm × 50 mm × 1 mm, was used in order to enhance the degree of change in pressure. The measurements were made under two conditions that the specimen was charged and was not charged. The results obtained are shown in Fig. 6. In both cases, the pressure gradually increases on heating, then reaches its peak near 600°C, and thereafter decreases with heating up to about 880°C. The increase may be attributed to the emission of gases from the furnace wall. The degree of the increase was often affected by the past run condition of the furnace and so the reproducibility of the data is invariably poor. On the other hand, only when a specimen was charged, an increase in pressure again takes place over the temperature range of 900 to 1050°C. This increase presumably is caused by the generation of CO by the reaction (10), because within the same temperature range the oxide film disappears and brightness increases (see Figs. 1, 2, and Photo. 1).

Changes in carbon content in steel with reduction

An experiment was carried out to confirm the consumption of the carbon in steel that naturally is predicted from the eq. (10). For the purpose of enhancing the change in the content of carbon in a specimen with the reduction, a thinner plate, 0.85 mm × 26 mm × 90 mm, as rolled was prepared for this experiment. The specimen was die cooled after being annealed under a pressure of 1.33 Pa at 1050°C for 30 min. The brightness of the specimen treated was first measured and then a sample weighing about 0.5 g was taken from the specimen and was subjected to analysis of carbon content with Coulomatic C manufactured by Kokusai Electric Co., Ltd. The same procedure was repeated eleven times for the remainder of the specimen. Also specimens were examined which were continuously heated for eight different times within the range of 0 to 330 min at 1050°C in a vacuum of 1.33 Pa. The results obtained are shown in Fig. 7. In case of the repeated heating, the carbon content decreases nearly in a straight line. The brightness increases up to about 125% at the first heating; this is due solely, or at any rate mainly, to a scratch smoothing effect (26). After that, the brightness remains almost unchanged till the eighth time. However, over the ninth time the formation of a gray-green oxide film brings about a rapid deterioration in brightness.

Fig. 6 Changes in pressure with temperature and heating time. SUS 304 plates as cold rolled, 25 mm × 50 mm × 1.0 mm, were prepared as specimens.

Fig. 7 Changes in carbon content and brightness with heating time at 1050°C and number of heating cycle for 30 min at 1050°C. SUS 304 plates as colled rolled, 26 mm × 90 mm × 0.85 mm, were heated under a pressure of 1.33 Pa.
This deterioration may be attributed to a shift of the heating condition used, i.e., 1050°C–1.33 Pa, from the reduction region to the oxidation region owing to the downward movement of the $P_{CO}-T$ curve in Fig. 5 with decreasing of the carbon content. In contrast to the repeated heating, the continuous heating gives a much lower rate of decrease in carbon content. In addition, its brightness deteriorates more rapidly than that of the specimen heated repeatedly. In this study, there is no indirect or direct evidence in favor of interpretation of this marked discrepancy between the two brightness changes.

(3) Brightness of SUS 347

Since most of the carbon in SUS 347 is consumed in forming niobium and tantalum carbides, the solute carbon which can move to the oxide/steel interface is little; from the data by Matsuki and Uchiyama(27) the content in the material used is roughly estimated as 0.004–0.017 wt% within the temperature range of 900 to 1150°C. The lack of the solute carbon causes the $P_{CO}-T$ curve to shift to the lower pressure side in Fig. 5. It, therefore, is predicted that the oxide film on SUS 347 is difficult to be reduced compared to the film on SUS 304; in fact, the results in Fig. 3 supports this prediction. In addition, a comparison between the results below 1000°C in Fig. 2 and in Fig. 4 shows that no matter how SUS 347 is heated at 1.33 Pa which is lower than 5.33 Pa for SUS 304, the brightness of SUS 347 decreases with increasing heating time contrary to its increase in SUS 304. On the basis of this result, there is no doubt that the conditions 950–1000°C–1.33 Pa are in the oxidation region for SUS 347 in spite of being in the reduction region for SUS 304.

(4) Brightness of several varieties of stainless steels

It is evident from the results listed in Table 2 that an increase in C content and/or a decrease in Cr content in stainless steels give rise to the more satisfactory brightness. In other words the reduction proceeds easily with higher C content and lower Cr content. Equation (12) shows that $P_{CO}$ is a product of activities $a_C$ and $a_{Cr}$ which can represent not only the effects of C and Cr but also the effects of other elements. Therefore, $P_{CO}$ must be very useful for evaluating the effects of alloying elements on the difficulty in reduction of the oxide film. The activities $a_C$ and $a_{Cr}$ were calculated in the same way as described above. Against the values of $P_{CO}$ obtained the brightness listed in Table 2 are plotted in Fig. 8. The brightness of the steels heated at 1050°C for 30 min is thought to be in equilibrium, since all its values are near 100%. On the other hand, as seen in Table 2, in all cases the brightness of the steels heated at 970°C increases with increasing time from 30 to 150 min. This result proves that the steels whose brightness is less than 100% after heating at 970°C–150 min are in progress of reduction. The reduction proceeds presumably through the following steps: (1) diffusion of solute carbon from the bulk to the oxide/steel interface; (2) direct reduction of oxide by the solute carbon taking place at the interface; (3) effusion of gaseous products of the reduction, CO, from the interface. The above result may be explained by the assumption that at least at 970°C the effusion of CO governs the total rate of chemical reaction in the direct reduction. Then, it is reasonable to anticipate that when steels are heated under a constant pressure, $P$, the greater difference in pressure, ($P_{CO}-P$), results in enhancement of the rate of CO effusion. The higher effusion rate may accelerate the reduction and consequently may give a higher brightness. While the results in

![Fig. 8 Relationship between brightness and Log $P_{CO}$ for various stainless steels. Numerical numbers indicate specimen numbers shown in Table 2.](image-url)
Fig. 8 shows an undesirably large scatter, there is a clear indication that the brightness increases as $P_{CO}$ increases.

V. Conclusion

Brightness of stainless steels heated in a vacuum is governed to a large extent by the surface conditions, i.e., formation of an oxide film and surface roughening. The oxide film once formed on heating through a lower temperature range again disappeared gradually with increasing temperature and/or heating time. The disappearance of the film results in a remarkable increase in brightness. An excess increase in temperature brings about a decrease in brightness due to surface roughening. The disappearance of the oxide film is able to be interpreted in terms of reduction by solute carbon in the steels, that is, $Cr_2O_3 + 3C = 2Cr + 3CO$. The oxide films are more easily reduced for the steels whose equilibrium CO pressure is higher. In general, the types of stainless steels may be classified in order of the difficulty in the reduction of the oxide films; heat resisting cast steels—austenitic stainless steels—martensitic and ferritic stainless steels.

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