Microstructure and Properties of High Silicon Duplex Stainless Steels*

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Synopsis
High silicon duplex (γ plus 30~70 % δ) stainless steels were studied on the changes in mechanical and corrosive properties and microstructure with heat treatment. The roles of silicon as an alloying element in the steels were analyzed in terms of the chromium equivalent and the partition in each phase.

Precipitation of M23C6 and a phase proceeds at a temperature in the range of 550 and 1000 °C. Formation of M23C6 is responsible for grain boundary corrosion after tempering at 450 °C and heat treatment at above 1150 °C. Hardening progresses in two stages during tempering at 450 °C; the first stage has the characteristics similar to the strain aging in that the process is suppressed by alloying of vanadium and tungsten and the second similar to the 475 °C embrittlement.

Resistance to corrosion in non-oxidizing type acid is weakened after tempering at the temperature range of 550 to 1000 °C by decomposition of a phase. Silicon enriched in a phase with a ratio of 1.1 to γ and the value is lower than chromium and molybdenum.

A good combination of mechanical and corrosive properties can be obtained in the high silicon duplex stainless steels by tempering at 450 °C for less than 4 hr after solution treatment at 1050 °C.

I. Introduction
In these twenty years little study has been made on the duplex stainless steels containing silicon more than 4%, because silicon was believed to deteriorate the toughness by promoting grain growth and precipitation of a phase in the steels. However, silicon is an effective element to increase the hardness and the resistance to oxidation and corrosion. Recently an austenitic stainless steel containing silicon was specified as SUS XM15J1 in Japanese Industrial Standards.

Duplex stainless steels can be improved by addition of silicon both in the mechanical properties and the corrosion resistance, as has been shown by Mott1) and Ota.2) Formation of a phase and precipitation of M23C6 were reported in the high silicon duplex stainless steels,3,4) but no further metallurgical work has been made. Addition of molybdenum in the duplex stainless steels was known to lead to 475 °C embrittlement.5)

In this paper the effects of silicon on the mechanical and corrosive properties were presented on the basis of the microstructural changes and the nature of phases. The roles of silicon as an alloying element in the duplex stainless steels were studied in terms of the chromium equivalent and partition in the phases.

II. Experimental Procedure and Results

1. Materials
Table 1 shows the chemical composition of steels used in the present experiment. The basic compositions were 16%Cr-6%Ni-4%Si alloy for Steels A to D, 18%Cr-8%Ni-4%Si alloy for Steel E, and 20%Cr-10%Ni-4%Si alloy for Steels F to H.

Steels A, C, D, F to H were prepared by melting bundles of low carbon in 18%Cr-8%Ni stainless steel scrap in a high frequency induction furnace and controlled the chemical composition by proper addition of electrolytic nickel, chromium, manganese, and iron and metallic silicon. Steels B and E were melted in a low frequency induction furnace and decarburized by vacuum degassing.

Steels A, F to H were hot-rolled into round bars with a diameter of 7 or 10 mm. Steels B, D, and E were forged into square bars with a section of 12 × 12 mm². Steel C was used as cast material because it could not be forged successfully owing to its high copper content. All the specimens were homogenized at 1050 °C for 1 hr prior to the further heat treatment.

2. Hardness
Changes in the hardness of δ ferrite phase with tempering were followed by measurement of Knoop hardness with a load of 15 g. Figure 1 shows the spectrum of hardness of 16%Cr-6%Ni-4%Si and 20%Cr-10%Ni-4%Si alloys tempered at various temperatures for 2 hr. Three maxima appear in the spectrum; the first at about 400 °C, the second at about 600 °C in 16%Cr-6%Ni-4%Si alloys and about 800 °C in 20%Cr-10%Ni-4%Si alloys and the third above 1150 °C.

The third maximum is associated with increasing amount of δ phase particles containing silicon. The hardening rate is higher in the materials with a lower A₄ transformation temperature and a larger fraction of γ phase at 1050 °C. It is evident in Fig. 2 that the third stage hardening is most remarkable in Steel C which has the highest content of austenite among Steels C, D, and H. Hardness of δ and γ phases in Steels A and H was selectively measured by a micro-Vickers tester with a load of 25 g after quenching the specimens from 1050 °C. The average hardness value is about 350 for δ and about 230 for γ phase.
The second maximum occurs with formation of $\sigma$ in $\delta$ phase, as evidenced by X-ray diffraction and magnetic measurement. Figure 3 shows the changes in hardness of Steels D and H during isothermal treatment at 700 and 800 °C. Slight softening proceeds in Steel D. Steel H hardens in two stages. The second hardening occurs after an incubation of about 16 hr and simultaneously with appearance of $\sigma$ in $\gamma$ phase, as shown in an optical micrograph of Photo. 2(d). The hardness of $\sigma$ phase was estimated to be about $H_V = 650$.

Figure 4 shows the hardening curves of 16%Cr–6%Ni–4%Si and 20%Cr–10%Ni–4%Si alloys during tempering at 450 °C. Steels D and H, containing a small amount of tungsten and/or vanadium, harden after 2 and 10 hr without occurrence of the first stage hardening. From the tempering characteristics of each phase shown in Fig. 5, the hardening process is determined by that of $\delta$ ferrite phase.

### Impact Properties

Impact properties were measured at room temperature using the U-notch Charpy specimens of JIS type No. 3.

Solution treatment at 1 050 °C gives twice higher impact values than quenching from a temperature above $A_4$. Figure 6 shows decreases in the impact values of Steels B and E with tempering at 450 °C. Embrittlement progresses faster in Steel E than Steel B, particularly in the stage of second hardening of the steels. The decreasing rate of the impact value is reduced in Steel B by reheating at 900 °C.

### Tensile Properties

Tensile test was performed with a bar specimen of 7 mm diameter by an Instron type machine. Figure 7 shows the tensile properties of Steel A at the temperature range from room temperature to 550 °C. The proof stress and the tensile strength decrease with increasing temperature up to 200 °C, and

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**Table 1.** Chemical composition of steels used in the present experiment and the volume fraction of ferrite and austenite after solution treatment at 1 050 °C.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>N</th>
<th>W</th>
<th>V</th>
<th>Volume fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.03</td>
<td>4.38</td>
<td>1.86</td>
<td>5.62</td>
<td>15.96</td>
<td>1.11</td>
<td>0.98</td>
<td>0.04</td>
<td>---</td>
<td>---</td>
<td>70</td>
</tr>
<tr>
<td>B</td>
<td>0.02</td>
<td>3.62</td>
<td>1.91</td>
<td>5.97</td>
<td>15.37</td>
<td>1.04</td>
<td>2.13</td>
<td>0.05</td>
<td>---</td>
<td>---</td>
<td>40</td>
</tr>
<tr>
<td>C</td>
<td>0.02</td>
<td>4.33</td>
<td>1.01</td>
<td>8.30</td>
<td>15.59</td>
<td>0.95</td>
<td>4.05</td>
<td>0.03</td>
<td>0.50</td>
<td>0.26</td>
<td>20</td>
</tr>
<tr>
<td>D</td>
<td>0.02</td>
<td>4.09</td>
<td>2.38</td>
<td>7.19</td>
<td>15.70</td>
<td>1.47</td>
<td>---</td>
<td>0.03</td>
<td>0.89</td>
<td>0.61</td>
<td>75</td>
</tr>
<tr>
<td>E</td>
<td>0.03</td>
<td>4.06</td>
<td>1.76</td>
<td>7.90</td>
<td>17.98</td>
<td>1.34</td>
<td>1.97</td>
<td>0.06</td>
<td>---</td>
<td>---</td>
<td>40</td>
</tr>
<tr>
<td>F</td>
<td>0.06</td>
<td>3.86</td>
<td>1.78</td>
<td>9.25</td>
<td>22.11</td>
<td>0.92</td>
<td>1.14</td>
<td>0.04</td>
<td>---</td>
<td>---</td>
<td>50</td>
</tr>
<tr>
<td>G</td>
<td>0.04</td>
<td>4.36</td>
<td>1.13</td>
<td>9.62</td>
<td>19.10</td>
<td>1.53</td>
<td>0.74</td>
<td>0.05</td>
<td>---</td>
<td>---</td>
<td>40</td>
</tr>
<tr>
<td>H</td>
<td>0.04</td>
<td>4.19</td>
<td>2.29</td>
<td>9.20</td>
<td>18.97</td>
<td>1.01</td>
<td>---</td>
<td>0.03</td>
<td>0.69</td>
<td>---</td>
<td>60</td>
</tr>
</tbody>
</table>
remain constant in the range of 200 and 450 °C, where an extensive serration appears on the load-elongation curve.

Figure 8 indicates the changes in tensile properties by tempering at 450 and 550 °C. The increase of tensile strength in two steps is well correlated with the hardening characteristics of the steel. Loss of ductility is slight in the first stage and marked in the second stage. Increasing tempering temperature changes the mode of fracture from transgranular to intergranular type as shown in the scanning electron micrographs of Photos. 1 (a) and (b).

5. Microstructure

Quenching from a temperature above $A_4$ resulted in a single phase microstructure of $\delta$ ferrite with a fine dispersion of precipitates (Photo. 2 (a)). The precipitates remained insoluble when the specimen was dissolved in aqua regia. The extracted residue was identified as $M_{23}C_6$ by X-ray diffraction (Fig. 11 (c)).

Heat treatment at a temperature between 1 050 °C and 1 100 °C produced a duplex structure of $\delta$ and $\gamma$ phases without precipitation of $M_{23}C_6$ (Photo. 2 (b)). Mixed structures of $\gamma + \alpha$ (Photos. 2 (c) and 2 (d)) or $\delta + \gamma + \alpha$ (Photo. 2 (e)) phases were observed in the specimens heated in the temperature range of 550 and 1 000 °C. Particles of $M_{23}C_6$, identifiable by etching Murakami's reagent, was found in grain interior and/or boundary of $\delta$ phase.
6. Corrosive Properties

Corrosive properties were evaluated in terms of the rate of corrosion for duration of 6 hr in boiling sulfuric acid of 5% concentration (5% H$_2$SO$_4$) and in boiling chloric acid of 1.5% (1.5% HCl). Figure 9 shows the changes in corrosion loss of the specimens tempered at various temperature for Steels A and F. The amount of corrosion loss in H$_2$SO$_4$ solution increases in the temperature range where the steels harden by tempering and that in HCl solution has two maxima at about 600 and 1 000 °C. Preferential attack precedes in δ phase in HCl solution. The nature of preferential corrosion sites in H$_2$SO$_4$ solution depends upon the prior heat treatment; one type of ferrite grain boundary, as reported by Streicher, in the materials quenched from a temperature above 1 150 °C or tempered at 450 °C (Photos. 3 (a) and 4 (c)) and the other type of selective attack to γ and grain boundary of δ phase (Photo. 4 (c)), as reported by Tsukamoto et al. as a result of increase in corrosion resistance with progress of the 475 °C embrittlement. Changes in corrosivity with tempering at 450 °C are shown in Fig. 10 for Steel F. Resistance to corrosion decreases with progress of the second stage hardening.

7. Chemical Analysis of Phases

In the present study chemical analysis of the constituent phases in steels was made for the extracted residue obtained from selective dissolution of matrix,
as reported by Shirley. After separation of the corrosion products in 30% HNO₃ solution, extraction was made by a series of filtration, rinsing, drying, and sieving. Chemical analysis was performed in accordance with JIS procedure.

After prolonged corrosion of δ+γ duplex steels, a considerable amount of non-magnetic particles of γ phase remained insoluble in the solution as a consequence of selective dissolution of δ phase. Chemical analysis of the γ particles extracted from five types of steels is shown in Table 2. Concentration of C, N, Ni, Mn, and Cu and depletion of Si, Mo, and Cr in γ phase are confirmed.

Tempering at 450 °C induces selective attack to γ phase and grain boundary of δ phase, so that the particles of δ phase can be extracted for chemical analysis. Composition of δ and γ phases in Steel H is shown in Table 3.

8. X-ray Diffraction

Identification and quantitative analysis of the constituent phases in steels were made by X-ray diffraction with Fe Kα and Cu Kα radiation.

In the insoluble substance obtained by dissolving Steel H, tempered at 550 °C for 64 hr, in aqua regia (10% aqueous solution), it was found besides γ phase particles to contain a material similar to that detected and identified as M₄Si (M=Ni) by Brown and Allsop in 12%Cr-4%Ni alloy (Fig. 11 (a)).

Table 2. Chemical analysis of γ particles extracted from five types of steels in 1.5% HCl solution.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.09</td>
<td>4.02</td>
<td>2.25</td>
<td>6.78</td>
<td>14.37</td>
<td>0.89</td>
<td>0.84</td>
<td>0.06</td>
</tr>
<tr>
<td>B</td>
<td>0.04</td>
<td>3.58</td>
<td>2.07</td>
<td>6.63</td>
<td>14.93</td>
<td>0.63</td>
<td>2.18</td>
<td>0.06</td>
</tr>
<tr>
<td>E</td>
<td>0.05</td>
<td>3.67</td>
<td>1.78</td>
<td>9.57</td>
<td>17.03</td>
<td>1.15</td>
<td>2.17</td>
<td>0.09</td>
</tr>
<tr>
<td>F</td>
<td>0.10</td>
<td>3.90</td>
<td>1.68</td>
<td>10.68</td>
<td>18.52</td>
<td>0.72</td>
<td>1.28</td>
<td>0.06</td>
</tr>
<tr>
<td>G</td>
<td>0.08</td>
<td>4.10</td>
<td>1.19</td>
<td>11.24</td>
<td>17.62</td>
<td>1.32</td>
<td>0.81</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 3. Chemical composition of phases in Steel H extracted in 5% H₂SO₄ for δ and 1.5% HCl for γ phase.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Chemical composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrite</td>
<td>Si</td>
</tr>
<tr>
<td></td>
<td>4.8</td>
</tr>
<tr>
<td>Austenite</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Relative amount of ferrite and austenite was determined by referring mixtures of SUS 430 and SUS 304 powders as standards. Presence of σ phase was confirmed by X-ray diffraction in combination with the hardness and the magnetic measurement. In particular, σ phase amounts as much as 20% in
III. Discussion

Embrittlement due to σ formation is known to be intensified by alloying of silicon in the steel.10-12 It is shown in the phase diagram of stainless steels containing silicon that the γ/γ+δ boundary is shifted to a lower content of chromium and the region of γ phase is reduced (Fig. 12). Also σ phase is stabilized by holding at about 800 °C.

Tempering at 800 °C diminishes the ferromagnetic property in 18%Cr–8%Ni–4%Si alloy and preserves it in 16%Cr–6%Ni–4%Si alloy. This suggests a critical condition for σ phase formation at 800 °C to be a composition of 17%Cr–7%Ni–4%Si. This critical composition is lower in the chromium content than that reported by Cook and Brown14 for steels free of silicon. Therefore silicon is thought to be effective three or four times in terms of the chromium equivalent in promoting the decomposition of σ phase. Time-temperature diagram of σ phase decomposition shows a G-type curve as indicated in Fig. 13. Decomposition progresses fastest at 850 °C, so as to be reduced below 0.5% within 1 hr in 20%Cr–10%Ni–4%Si alloy.

Taking account of the diagram of compositional limit shown in Fig. 12, it is predicted that the steel type SUS XM15J1 has a microstructure similar to the steel type SUS 309 and has to be reduced its chromium content to 15% for formation of the structure equivalent to that of the typical duplex stainless steel of type SUS 329J1.

The phenomenon of 475 °C embrittlement, which is known to develop in chromium rich ferrite, is reported in duplex stainless steels.5,15,16 In the present study hardening during tempering at 450 °C was found to proceed in two steps. The second stage hardening was thought to be caused by the 475 °C embrittlement. The alternative possibility is the hardening due to formation of martensite and retained austenite.17 The Ms temperatures were estimated to be –140 °C for 16%Cr–6%Ni–4%Si alloy and –200 °C for 20%Cr–10%Ni–4%Si alloy by using the empirical formula by Eichelman and Hull,18 Irvine et al.19 and Hull.20 Supporting evidences for the 475 °C embrittlement in connection with the second stage hardening in tempering at 450 °C are listed in the following.

1) Fast hardening in chromium rich alloys
2) Decrease in the corrosion rate of σ phase in 5% H2SO4
3) Increase in the rate of corrosion of σ in 1.5% HCl
4) Exclusive hardening in δ phase
5) Occurrence of transgranular fracture in the hardened material
6) Removal of embrittlement by reheating at a higher temperature
7) Exothermic process in the differential thermal analysis

Among these evidences changes in hardness during the history of heat cycles were shown in Fig. 14. Hardened specimen by holding at 450 °C softens by reheating at 500 °C, which suggests the existence of a critical temperature between 450 °C and 500 °C for the hardening process. Bandel and Tofaute have reported that the 475 °C embrittlement enhances the rate of corrosion in boiling 50 % HCl solution.

Hoshino et al.16) have reported that susceptibility to the 475 °C embrittlement is reduced by reheating to induce ferrite to austenite transformation. Reheating at 900 °C has an effect to suppress progress of the embrittlement in tempering of 16%Cr–6%Ni–4%Si alloy. However, the effect is masked by formation of σ in the alloys of higher chromium contents. Reheating at 900 °C is thought to promote precipitation of M23C6 and thus to prevent loss of toughness by minimizing formation of the grain boundary precipitates during subsequent holding at 450 °C. On the other hand, Floreen and Hayden22) have suggested another possibility that increase in austenite fraction by the reheating recovers embrittlement of ferrite. However, this is considered to be not so important in the steels with a low fraction of austenite.

The first stage hardening in tempering at 450 °C has been found in 25%Cr–4%Ni15) and 20%Cr–10%Ni–2%Mo alloys.23) The hardening is not accompanied by reduction in corrosion resistance and toughness and is suppressed by addition of the carbide forming elements such as tungsten and vanadium. These characteristics, together with appearance of serration on the load–elongation curve of tensile test in the temperature range, suggests operation of a mechanism similar to the strain aging phenomenon. Kanao et al.24) have reported contribution of C and N to the embrittlement of 25 % Cr-6 %Ni alloy by tempering below 450 °C.

Corrosion resistance of δ phase is remarkably deteriorated after an incubation time by holding at a temperature between 500 °C and 600 °C. This is considered to be associated with formation of M23Si, which has been confirmed for its presence in Steel H by X-ray diffraction. Bond et al.25) has reported a large contribution of nickel to corrosion resistance of 25 % Cr alloys in H2SO4 aqueous solution. Precipitation of M23Si containing nickel may decrease the resistance to corrosion.

In a number of studies on partition of elements into phases, it has been shown C, N, Ni, Mn, and Cu are enriched in austenite and Si, Mo, and Cr in ferrite phase.26–34) On the basis of the chemical analysis shown in Table 3 and the volume fraction of δ and γ phases, the distribution coefficients of alloying elements between δ and γ were estimated and are tabulated in Table 4.

Otoguro et al.28) have reported the efficiency of formation of austenite for the austenite stabilizing elements; the distribution coefficient is higher in the order of Ni, Mn, and Cu in accordance with increasing efficiency. No such relation, however, is found between the distribution coefficient and the efficiency of ferrite formation for ferrite stabilizing elements as Mo, Ti, and Al.

Commonly, the efficiency of formation of austenite and ferrite is estimated with chromium and nickel equivalents of constituent elements36,37) which are written in the following way:

\[
Cr_{eq} = \%Cr + a\%Si + b\%Mo \quad (1)
\]

\[
Ni_{eq} = \%Ni + c\%Mn + d\%Cu + e\%(C+N) \quad (2)
\]

where, \(a, b, c, d, e\): the equivalent factors of Si, Mo, Mn, Cu, and C+N, respectively.

The chromium equivalent of silicon for δ/δ+γ and γ/γ+δ boundaries relates in terms of the distribution coefficients of silicon and chromium and is given by

\[
\frac{a_{(\delta)}}{a_{(\gamma)}} = \frac{k_{Cr}}{k_{Si}} = 1.08
\]

where, \(a_{(\delta)}, a_{(\gamma)}\): the chromium equivalent factors of silicon for the δ/δ+γ and γ/γ+δ boundaries, respectively.

\(k_{Cr}, k_{Si}\): the distribution coefficients shown in Table 4.

Inoue and Tsuchiya38) have reported that the chromium equivalent of silicon is higher than the value of 1.5 shown by Schaeffler’s diagram36) for austenitic and ferritic cast stainless steels containing silicon.

The nickel equivalent of C+N at δ/δ+γ boundary is three times higher than that of γ/γ+δ boundary.

<table>
<thead>
<tr>
<th>C+N</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.22</td>
<td>1.11</td>
<td>0.90</td>
<td>0.70</td>
<td>1.20</td>
<td>1.62</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Fig. 14. Changes in hardness with heating cycles in Steel F.
so that an amount of C+N lower as possible should be strictly controlled at the lowest for making duplex stainless steels containing silicon.

**IV. Conclusion**

16%Cr-6%Ni-4%Si and 20%Cr-10%Ni-4%Si alloys containing copper and those containing a small amount tungsten and/or vanadium with duplex structures were studied on the changes in mechanical and corrosive properties and microstructure with heat treatments. The results obtained are;

1. Precipitation of $M_2\text{Cr}_7\text{C}_6$ proceeded at a temperature in the range of 550 and 1 000 °C, and it was responsible for grain boundary corrosion after tempering at 450 °C and heat treatment at above 1 150 °C.
2. Precipitation of $\text{M}_2\text{Si}$ was confirmed by X-ray diffraction in 20%Cr-10%Ni-4%Si alloy containing a small amount of tungsten after tempering at 550 °C for 64 hr.
3. Heat treatment at the temperature range between 1 050 °C and 1 100 °C produced a duplex structure of $\delta$ and $\gamma$ phases without precipitation of $\text{M}_2\text{C}_6$ and $\sigma$ phases.
4. Hardening progressed in two stages during tempering at 450 °C; the first stage had the characteristics of the strain aging accompanied by a slight loss of ductility and corrosion resistance and the second similar to 475 °C embrittlement.
5. A good combination of mechanical and corrosive properties could be obtained in the high silicon duplex stainless steels by tempering at 450 °C for less 4 hr after solution treatment at 1 050 °C.
6. Si, Cr, and Mo were enriched in ferrite with a ratio of 1.11, 1.20, and 1.62 to austenite phase, respectively, and C, N, Ni, Mn, and Cu were depleted in ferrite with a ratio of 0.22 (C+N), 0.70 (Ni), 0.90 (Mn), and 0.94 (Cu) to austenite phase at 1 050 °C, respectively.
7. Chromium and nickel equivalents of constituent elements for $\delta|\delta+\gamma$ and $\gamma|\gamma+\delta$ boundaries at 1 050 °C were estimated from the distribution coefficient of the elements.

**References**

1. N. S. Mott: *Iron Age*, 183 (1959), April, 118.
5. B. Cina and J. D. Lavender: *JISI*, 173 (1953), 97.

**Appendix**

Mayerhofer and Kohli[27] have expressed $\text{Cr}_{eq}$ and $\text{Ni}_{eq}$ by means of the formula;

$$\text{Cr}_{eq} = k \cdot \text{Ni}_{eq} + 1 \quad \text{.........(A-1)}$$

For $\gamma|\gamma+\delta$ and $\delta|\delta+\gamma$ boundaries, it is written as follows.

$$\text{Cr}_{eq} (\gamma) = k_1 \cdot \text{Ni}_{eq} (\gamma) + 1 (\gamma) \quad \text{.........(A-2)}$$

$$\text{Cr}_{eq} (\delta) = k_2 \cdot \text{Ni}_{eq} (\delta) + 1 (\delta) \quad \text{.........(A-3)}$$

Equations (A-2) and (A-3) by arranging these are given by substitution of Eqs. (1) and (2) as follows.
\[
\% \text{Cr}(r) = -a(\% \text{Si}(r)) - b(\% \text{Mo}(r)) + k(\% \text{Ni}(r)) \\
+ k(\% \text{Mn}(r)) + k(\% \text{Cu}(r)) \\
+ k(\% (\text{C} + \text{N})(r)) + I(r) \quad \text{.........(A-4)}
\]

\[
\% \text{Cr}(a) = -a(\% \text{Si}(a)) - b(\% \text{Mo}(a)) + k(\% \text{Ni}(a)) \\
+ k(\% \text{Mn}(a)) + k(\% \text{Cu}(a)) \\
+ k(\% (\text{C} + \text{N})(a)) + I(a) \quad \text{.........(A-5)}
\]

Equation (A-5) is transformed by means of the distribution coefficients, \( k_i (i = \text{Si}, \text{Mo}, \text{Cr}, \text{Ni}, \text{Mn}, \text{Cu}, \text{and C+N}). \)

\[
\% \text{Cr}(r) = -\frac{k_{\text{Si}}}{k_{\text{Cr}}} a(\% \text{Si}(r)) - \frac{k_{\text{Mo}}}{k_{\text{Cr}}} b(\% \text{Mo}(r)) \\
+ \frac{k_{\text{Ni}}}{k_{\text{Cr}}} \% \text{Ni}(r) + \frac{k_{\text{Mn}}}{k_{\text{Cr}}} \% \text{Mn}(r) \\
+ \frac{k_{\text{Cu}}}{k_{\text{Cr}}} \% \text{Cu}(r) \\
+ \frac{k_{(\text{C} + \text{N})}}{k_{\text{Cr}}} \% (\text{C} + \text{N})(r)) + \frac{1}{k_{\text{Cr}}} I(r) \quad \text{..........(A-6)}
\]

hence

\[
I(r) = \% \text{Cr} + a(\% \text{Si}) + b(\% \text{Mo}) - c(\% \text{Ni}) \\
+ d(\% \text{Mn}) + e(\% (\text{C} + \text{N})) + I(r) \quad \text{.........(A-7)}
\]

since the first term of the above equation is thought to be nearly 1,

\[
I(r)/I(a) = k_{\text{Cr}}
\]

Thus the coefficients of Eqs. (A-4) and (A-6) must be equal. By means of a least squares method, the following relations are obtained.

\[
a(\%) = k_{\text{Cr}} = 1.08 \text{ for Si} \\
b(\%) = k_{\text{Cr}} = 0.74 \text{ for Mo} \\
c(\%) = k_{\text{Cr}} = 0.78 \text{ for Mn} \\
d(\%) = k_{\text{Cr}} = 0.74 \text{ for Cu} \\
e(\%) = k_{\text{Cr}} = 3.18 \text{ for C+N}
\]