Effect of Manganese and Nitrogen on the Mechanical Properties of Fe-18%Cr-10%Ni Stainless Steels*

By Masakuni FUJIKURA,** Katsunori TAKADA** and Kiyohito ISHIDA**

Synopsis

A study has been made of the effect of manganese and nitrogen on the mechanical properties of Fe-18%Cr-10%Ni stainless steels. It is observed that manganese addition reduces the yield strength, tensile strength and elongation. Moreover, manganese addition decreases Charpy impact value in single austenite phase, while the formation of martensite causes the pronounced drop in the energy absorbed in Charpy test. On the other hand, nitrogen addition increases the yield strength, tensile strength and Charpy impact value, but decreases the ductility. The relation between the austenite stability and the mechanical properties is discussed in terms of the stacking fault energy and the formation of martensite.

I. Introduction

Mechanical properties of stainless steels have been investigated extensively and it has been well recognized that the stability of austenite is an important factor which affects strength, ductility and toughness. However, the austenite stability is also dependent on many variables such as chemical composition, temperature, stacking fault energy and the amount of deformation.

In the present paper, the effect of manganese and nitrogen on the relation between austenite stability and mechanical properties of Fe-18%Cr-10%Ni alloys has been studied. Since manganese and nitrogen are typical austenite stabilizing elements, the systematic changes of mechanical properties from metastable to stable austenite can be expected. A special interest was taken to clarify the relation between stacking fault energy and mechanical properties by systematically varying the chemical composition, because it has been reported that stacking fault correlates the brittle and ductile behavior at cryogenic temperature.

II. Experimental Procedure

The alloys were prepared by induction melting. The four series of steels of widely differing compositions in Fe-18%Cr-10%Ni base alloys were studied; (a) 0.15N-XMn, (b) 0.30N-XMn, (c) 4Mn-XN and (d) 8Mn-XN. Ingots were forged at 1200°C into 20 mm diameter bar. The specimens were subsequently solution-treated for 30 min at 1100°C and quenched in water, producing an average grain size of about 70 μ.

In order to study the formation of stacking faults in austenite, powder specimens were prepared by filing and measurements were made at room temperature on Rigaku-RU-100PL type diffractometer. The extents of martensite were also evaluated from the integral intensity of X-ray data.

The mechanical properties were examined by Charpy V-notch impact and tension test between 20°C and -196°C.

III. Results and Discussion

Figure 1 shows the section diagram of Fe-18%Cr-10%Ni-Mn-N system strained 20% at -180°C after homogenization at 1100°C. It is evident that nitrogen stabilizes austenite, while manganese is a ferrite former for higher content. This is in good agreement with the recent investigation of the effect of manganese on delta ferrite formations by Hull. A series of steels of varying stability containing manganese and nitrogen in the present investigation is also shown in Fig. 1.

1. Stacking Fault Probability

According to the theory of the effect of stacking faults on the scattering of X-rays, a peak shift occurs by deformation stacking faults. The stacking fault probability α which is inversely proportional to the stacking fault energy can be calculated from the peak displacement by next equation:

\[
\alpha = \frac{a}{b} = \frac{\alpha G_{hk1}}{\sqrt{3} \sum (\pm)(h+k+l)} \quad (1)
\]

\[
G_{hk1} = -4\varepsilon(h^2+k^2+F)(u+b) \quad (2)
\]

where, \(\alpha\) is a lattice parameter, \(b\) is the number of components of the powder pattern which are affected by stacking faults (for which \(h+k+1=3N+1\), where \(N\) is an integer), and \(u\) is the components for which are not affected by stacking faults (i.e., \(h+k+1=3N\)). The

* Received November 22, 1974.
** Central Research Laboratory, Daido Steel Co., Ltd., Minami-ku, Nagoya 457.
values of $a_{lat}$ is evaluated from all specimens which is plotted by Nelson-Riley's function\(^{(15)}\) \[ a_{lat} = a_0 + m/2(\cos^2 \Theta/\theta + \sin^2 \Theta/\sin \Theta) \] where, $a_0$ is the true lattice parameter and $m$ the slope of the straight line. Figure 2 shows the effect of manganese and nitrogen on the lattice parameter in stainless steel, where the influences of chromium and nickel are also plotted to compare with ones. Manganese and nitrogen increase lattice parameter remarkably and these results coincide with the previous data.\(^{(16)}\) Figure 3 shows the effect of manganese, nitrogen, nickel and chromium on the stacking fault probability, where the average value of $a_{lat}$ of [111], [200] and [220] reflections are given.\(^{(17)}\) It can be seen that manganese increases the stacking fault probability (i.e. lowers stacking fault energy) for low contents, while decreases for higher manganese concentration. This trend was previously reported\(^{(18)}\) for the effect of chromium and nickel on the stacking fault energy, but it is first observed in this study that manganese increases stacking fault energy in higher regions. It is interesting to note that the change of stacking fault energy with manganese content is in good correspondence with the effect of manganese on the phase stability between ferrite and austenite as shown in Fig. 1, that is, manganese changes from $\gamma$ to $\alpha$ former with increasing manganese content.

The influence of nitrogen as shown in Fig. 3 (b) is very interesting because stacking fault probability is inclined to decrease for low content while increase for higher contents. It has been observed\(^{(18,19)}\) that nitrogen does not change the fault energy and promotes planar glide dislocations. Considering the fact, however, that the hcp $\gamma$ phase is formed in Fe-N system,\(^{(20)}\) it has a great possibility to lower the stacking fault energy.

Nickel increases the fault energy and chromium has little effect as shown in Figs. 3(c) and (d), respectively. Table 1 summarizes the effect of alloying elements on stacking fault energy including the previous data.\(^{(17-22)}\) The effect of chromium on the stacking fault energy differs extremely according to the investigators, but it is convinced that nickel increases fault energy.

The present results can be also compared with the thermodynamic data because stacking fault energy is related with the free energy difference $\Delta G_{fe-hcp}$ between fcc and hcp forms.\(^{(23)}\) The change of $\Delta G_{fe-hcp}$ due to alloy addition in Fe–18%Cr–10%Ni alloy is approximately given by\(^{(23)}\)

\[
\Delta G_{fe-hcp} = \Delta G_0 + m/2(2\cos^2 \Theta/\theta + \sin^2 \Theta/\sin \Theta) \]

Figure 2. Effect of Mn, N, Cr and Ni on the lattice parameter

Figure 3. Effect of Mn, N, Cr and Ni on stacking fault probability
Table 1. Summary of the effect of Mn, N, Cr and Ni on stacking fault energy

<table>
<thead>
<tr>
<th>Element</th>
<th>Base composition</th>
<th>Stacking fault energy</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>Fe-18Cr-10Ni-0.3N Mn &lt; 10</td>
<td>Present Work</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe-18Cr-10Ni     Mn &gt; 10</td>
<td>↑</td>
<td></td>
</tr>
<tr>
<td>Fe-18Cr-10Ni-8Mn N &lt; 0.14</td>
<td>↑</td>
<td>Present Work</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>Fe-18Cr-10Ni     N &gt; 0.14</td>
<td>↓</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>Fe-10Ni-4Mn      ↓</td>
<td>Present Work</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe-10Ni          ↓</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe-20Ni          ↓</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe-18Cr-4Mn      ↓</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>Fe-16-20Cr       ↓</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe-20Cr          ↓</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe-20Cr          ↓</td>
<td>22</td>
<td></td>
</tr>
</tbody>
</table>

↓: decrease      ↑: increase    -: no change

\[
JG_{	ext{Fe-Cr-Ni}}^{(\text{face})} = JG_{	ext{Fe-Cr-Ni}}^{(\text{face})} - \left( JG_{\text{Fe-Cr-Ni}}^{(\text{face})} - JG_{\text{Fe-Cr-Ni}}^{(\text{hcp})} \right) \approx X_f \left( JG_{\text{Fe-Cr-Ni}}^{(\text{face})} - JG_{\text{Fe-Cr-Ni}}^{(\text{hcp})} \right) + JG_{\text{Fe-Cr-Ni}}^{(\text{hcp})} X_f \]

where, \( JG_{\text{Fe-Cr-Ni}}^{(\text{face})} \) and \( JG_{\text{Fe-Cr-Ni}}^{(\text{hcp})} \) are the free energy difference of iron and alloying element \( X \) between fcc and hcp structures respectively, and \( JG_{\text{Fe-Cr-Ni}}^{(\text{hcp})} \) is the difference in interaction parameter. The computed \( JG_{\text{Fe-Cr-Ni}}^{(\text{face})} \) at 300°C by using the values of thermodynamic function is shown in Fig. 3, where the effect of nitrogen is not presented because of the lacking of the thermodynamic information. It will be seen that the stacking fault probability is in good accordance with \( JG_{\text{Fe-Cr-Ni}}^{(\text{face})} \). Thus, it is reasonably recognized that manganese decreases stacking fault energy in lower content and then increases it for higher regions.

2. Strain-induced Martensite

The formation of martensite was observed in several alloys. The extents of \( \alpha \) and \( \epsilon \) martensites were determined from the relative integral intensity of X-ray profile using the reflections \( \{200\}_0, \{200\}_1, \) and \( \{101\}_1 \). The effect of manganese and nitrogen on the amount of martensite at 20% strain at -180°C are shown in Fig. 4, where the only \( \alpha \) martensite is plotted. The extents of \( \epsilon \) martensite are about one-fourth of \( \alpha \) martensite. As the deformation-induced martensite are analyzed and will be reported elsewhere, the brief outline is discussed here. The theoretical evaluation of the effect of alloying content on the extent of martensite at constant strain and temperature predicts that transformation curve is. alloying content can be expressed as \( f = k(x_o - x)^3 \), where \( k \) is constant and \( x_o \) is the concentration at which martensite are no longer formed. This equation explains the present transformation curves in Fig. 4, quantitatively.

Figure 5 shows the amount of martensite on the fracture surface of Charpy impact test at -196°C. It should be noted that the only \( \alpha \) martensite is formed and no evidence of \( \epsilon \) martensite. This phenomenon was also observed in SUS 304 stainless steels. Although the mechanism of martensitic transformation in Charpy test is known scarcely, the present results suggest that \( \alpha \) martensite is very stable and the transformation proceeds \( \gamma \rightarrow \alpha \rightarrow \epsilon \) or \( \gamma \rightarrow \alpha \) at high speed deformation. Furthermore, it is expected that the martensite fraction must be dependent on the strain rate.

3. Mechanical Properties

The tensile properties were examined by an Instron testing machine at a crosshead speed of 3 mm/min (strain rate is 1.80 × 10^{-9}) sec. Figure 6 shows the effect of manganese on the tensile properties of 0.15%N and 0.30%N steels at 20°C and -180°C. It is observed that manganese reduces tensile strength, yield strength and elongation slightly both 0.15%N and 0.30%N steels, which is in good agreement with the previous data. Although it is expected that manganese has a great effect of solid solution hardening of austenite because it increases the lattice parameter as shown in Fig. 2, there is some doubt concerning the exact functional relationship between the properties and the concentrations. In high solute contents, the mechanical properties are affected by other factors rather than the lattice distortion of the austenite. These
1. Stability of Austenite

Irvin et al.\(^\text{29}\) have shown that the ferrite forming elements have a great effect on the flow strength of austenite rather than the austenite stabilizing elements. Although there is no satisfactory explanation for this effect, it suggests that lower the stability of austenite, higher the strength of austenite. In other words, the increase of the chromium equivalent increases the strength of austenite.

2. Stacking Fault Energy

It is known that the stacking fault energy is one of the most important factor which affects the strength of fcc alloys. The low stacking fault energy would give a large number of dissociated dislocation and difficulty of cross-slip, resulting in high strength.

3. Martensite

Deformation-induced martensite has a significant effect on the strength of stainless steels. Mangonon and Thomas\(^\text{3}\) showed that the yield strength of 304 stainless steel is linearly proportional to the amount of a martensite. Furthermore, the hexagonal \(\epsilon\) martensite is generally observed in stainless steels and is expected to increase the strength.

4. Size and Shear Modulus Misfits

According to Fleisher's theory,\(^\text{28,29}\) solid solution hardening is due to the size and shear modulus misfits. The large variations of these misfit parameters with solute content give rise to an increment of the strength.

5. Cottrell Interaction\(^\text{30}\)

This factor is only significant for the alloys containing interstitial atoms. The interaction between a dislocation and an interstitial atom leads to the resistance of moving dislocation. Although other factors must be taken into consideration, the effect of manganese on these factors is now considered. As shown in Fig. 1, manganese changes the stability from austenite to ferrite with increasing the content, which corresponds to the change of stacking fault energy. However, the effect of austenite stability and stacking fault energy of manganese on the contribution of flow strength is in contrast, and so the apparent change of the strength with manganese content might not appear. On the other hand, the strain-induced martensite in 0.15\(\%\)N steels is formed during testing in low manganese content but inhibited in high region, while there is no formation of martensite in 0.30\(\%\)N steels as shown in Fig. 4. This structural difference between 0.15\(\%\)N and 0.30\(\%\)N alloys affects tensile strength slightly as shown in Fig. 6 but not considerable effect. From these features, austenite stability and stacking fault energy has a great effect on the strength rather than the extent of martensite and the size and shear modulus misfits.

Figure 7 shows the effect of nitrogen on the mechanical properties. It is evident that nitrogen increases the yield strength and tensile strength remarkably, but decreases the ductility. The increments of the yield and tensile strength per 1wt\(\%\)N in the present investigation are 50 kg/mm\(^2\) and 75 kg/mm\(^2\) respectively, which are in close agreement with the values of 51 kg/mm\(^2\) and 87 kg/mm\(^2\) by Irvin et al.\(^\text{29}\) As shown in Fig. 7, however, the elongation of Fe-18\(\%\)Cr-10\(\%\)Ni-4\(\%\)Mn alloys at -180°C shows the maximum about 0.2\(\%\). This phenomenon can be understood as TRIP effect because martensite is formed below 0.3\(\%\)N as shown in Fig. 4. Figure 8 shows the effect of nitrogen on the 0.2\(\%\) proof stress between 20°C and -180°C, where the square root of the concentration is plotted as suggested by Fleisher. With lowering temperature, the considerable increase of the strength is observed. The largest strengthening effect, even though nitrogen is austenite stabilizer, may be due to the Cottrell interaction between a dislocation and nitrogen.

Figures 9 (a) and (b) show the effect of manganese
on Charpy V-notch impact value of 0.15%N and 0.30%N steels, respectively. It is found that the impact value reaches the maximum at about 12% Mn in 0.15%N steels, which is correspondent with the change of stacking fault energy as shown in Fig. 3. However, this fact is in contrary with the observation by Defilippi et al.20 that the increase of stacking fault energy raises the toughness. The result of 0.30%N steels in Fig. 9 (b) is different with that of 0.15%N steels, i.e. the impact values decrease continuously with increasing manganese content in 0.30%N steels. This may be due to the structural difference because the small amounts of martensite are formed in 0.15%N steels, while no evidence of martensite in 0.30%N steels as already shown in Fig. 4. Consequently, the effect of manganese on the toughness is dependent on the formation of martensite. Manganese decreases the impact value in single austenite phase, while the formation of martensite causes the pronounced drop in the toughness. Therefore, the apparent increase of the impact value below 12% Mn in Fig. 9 (a) is due to the increase of the fraction of austenite and so the impact value takes the maximum. Thus, it is concluded that the formation of martensite is the embrittling agent in Fe-18%Cr-10%Ni steels.

Figure 10 shows the effect of nitrogen on the Charpy impact value at various temperatures. It is demonstrated that the energy absorbed is increased by the addition of nitrogen above -100°C, while decreased only at -196°C. The cause of this anomaly is not clear but it is probable that it is associated by the short range ordering at low temperature. Comparing with the case of manganese, nitrogen increases the impact value in spite of the martensite formation as shown in Fig. 4. In other words, the formation of martensite of the alloys with varying the nitrogen content little affects on the energy absorbed in Charpy test. The cause of this difference of the effect of martensite formation on Charpy impact value in Figs. 9 and 10 is not known. Considering the fact, however, that the transformation enthalpy of $\gamma \rightarrow \alpha$ reaction by alloying the interstitial element is larger than that of substitutional element,21 the pronounced local increase of the specimen temperature in Charpy test by the addition
of nitrogen would be produced. Therefore, the drop of the impact value due to the formation of martensite was offset by the outward increase of the test temperature.

IV. Conclusion

The effect of manganese and nitrogen on the mechanical properties of Fe-18%Cr-10%Ni stainless steels has been studied. The relation between the austenite stability and the mechanical properties is discussed. The results obtained are as follows:

1) Manganese decreases stacking fault energy for low content level, while increases it for higher concentrations. On the other hand, nitrogen raises and then lowers it with increasing content. The observed change in stacking fault energy by alloy addition is in good accordance with the free energy difference between fcc and hcp structures.

2) The additions of manganese and nitrogen inhibit the martensite formation and the effect of alloy content on the transformation fraction is shown as a form of \(-k(x_0-x)\).

3) The deformation-induced martensite on the fracture surface of Charpy impact test is only \(\alpha\) martensite and no evidence of \(\epsilon\) phase is observed. This result suggests that \(\alpha\) martensite is very stable and the transformation proceeds \(\gamma \rightarrow \epsilon \rightarrow \alpha\) or \(\gamma \rightarrow \alpha\) and not \(\gamma \rightarrow \alpha \rightarrow \epsilon\) on the fracture surface of Charpy impact test.

4) Addition of manganese reduces the yield, tensile strength and elongation slightly. While, addition of nitrogen increases the yield and tensile strength remarkably but decreases the ductility.

5) Addition of manganese decreases the Charpy impact value in single stable austenite phase, while the formation of martensite causes the pronounced drop in the energy absorbed in Charpy test. On the other hand, the impact value is increased with increasing nitrogen concentration above \(-100^\circ C\), while decreased at \(-196^\circ C\).

6) There is no obvious correlation between stacking fault energy and the Charpy impact value.

Acknowledgements

The authors would like to express their hearty appreciation to Dr. C. Asada, Managing Director, and Dr. T. Fujiwara, Director of Daido Steel Co., Ltd. for permission to publish this paper. They are also indebted to Dr. K. Nakajima at Toyota Research Center for his valuable discussion on stacking fault energy.

REFERENCES

24) K. Ishida: to be published.