The Effect of Nitrogen on Martensite Formation in a Cr-Mn-Ni Stainless Steel
T. Biggs, R. Knutsen

To cite this version:

T. Biggs, R. Knutsen. The Effect of Nitrogen on Martensite Formation in a Cr-Mn-Ni Stainless Steel. Journal de Physique IV Colloque, 1995, 05 (C8), pp.C8-515-C8-520. <10.1051/jp4:1995879>. <jpa-00254128>

HAL Id: jpa-00254128
https://hal.archives-ouvertes.fr/jpa-00254128
Submitted on 1 Jan 1995

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.
The Effect of Nitrogen on Martensite Formation in a Cr-Mn-Ni Stainless Steel

T. Biggs and R.D. Knutsen*

Mintek, Physical Metallurgy Division, Private Bag X3015, Randburg, 2125, South Africa
* University of Cape Town, Materials Eng. Dept, Private Bag Rondebosch, 7700, South Africa

Abstract. The influence of nitrogen (0 to 0.27 wt%) on martensite formation in an experimental low-nickel stainless-steel alloy (Fe-17Cr-7Mn-4Ni) has been investigated. The alloys containing 0.1 wt% or more nitrogen are fully austenitic at room temperature; those containing less nitrogen consist of a mixture of austenite, martensite and δ-ferrite. The alloys containing less than 0.2 wt% nitrogen are metastable and undergo a transformation from austenite to martensite on deformation. Transmission electron microscopy investigations suggest that, within the nitrogen range considered in this investigation, the addition of nitrogen causes an increase in stacking fault energy which in turn inhibits the nucleation of martensite. As the low-nitrogen alloys (less than 0.2 wt% nitrogen) undergo deformation, ε-martensite (with the [110], and [1210], zone axes parallel) is observed at the intersection of stacking faults. With increasing strain, the presence of α'-martensite is observed in conjunction with the ε-martensite, and only α'-martensite is observed at very high strains. Both the Nishiyama-Wasserman and Kurdjumov-Sachs orientation relationships are observed between austenite and α'-martensite. The transformation to martensite during deformation causes a significant variation in room-temperature mechanical properties, despite the overall narrow range in composition considered.

1. INTRODUCTION

Austenitic steels account for a large proportion of the total production of stainless steel. Metastable austenitic alloys (alloys which undergo a deformation-induced transformation to martensite) are used in the fabrication of an extensive selection of components for architectural, automotive, industrial and domestic applications. They generally fall within the AISI 300 series of alloys, which have an excellent combination of strength, elongation, toughness and corrosion resistance. These steels contain 8% nickel, however, and since the availability and price of nickel is unstable, this is undesirable. Much research has been directed towards the need for partial or total replacement of nickel [1,2]. Since nickel is a strong austenite-forming and -stabilising element, it must be replaced with elements of a similar nature. Nitrogen is a potent austenite-former, and -stabiliser and is an obvious choice for the replacement of nickel [3]. Manganese is often added in conjunction with nitrogen, since, in addition to being an austenite-stabiliser, it also promotes the solubility of nitrogen in the steel [3]. The addition of nitrogen and manganese to replace nickel partially or totally led to the development of the AISI 200 series.

Austenite stability is influenced predominantly by temperature and composition. If insufficient nitrogen is added to replace nickel, the austenite is inadequately stabilised and this can promote the formation of δ-ferrite at higher temperatures. Upon quenching or deforming the alloy, some or all of the remaining austenite can transform to martensite. The formation of these secondary phases modifies the deformation behaviour of the alloy. The effect of nitrogen on martensite formation is thus highly important for understanding the overall mechanical properties of these alloys.
2. COMPOSITIONS AND MICROSTRUCTURES OF ANNEALED ALLOYS

The alloys examined in this investigation (Table 1) consist of Fe-18Cr-4Ni-7Mn base alloys with a range of nitrogen contents from 0 to 0.27 wt%. The ingots were rolled to a thickness of 1mm, annealed at 1050 °C for 45 minutes and quenched in water. The alloys containing 0.1 wt% and higher nitrogen (alloys 3 to 6), have fully austenitic microstructures, an example of which is shown in Figure 1. The 0 wt% and 0.05 wt% nitrogen alloys (alloys 1 and 2) comprise a mixture of austenite, δ-ferrite in a banded morphology, and small amount of martensite (Figure 2). Alloy 1 contained 77 wt% austenite whereas alloy 2 contained 95 wt% austenite.

### Table 1: Chemical Composition of the Alloys

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>% Cr</th>
<th>% Mn</th>
<th>% Ni</th>
<th>% Cu</th>
<th>% C</th>
<th>% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.0</td>
<td>7.1</td>
<td>4.2</td>
<td>0.5</td>
<td>0.036</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>17.1</td>
<td>7.2</td>
<td>4.1</td>
<td>0.5</td>
<td>0.035</td>
<td>0.05</td>
</tr>
<tr>
<td>3</td>
<td>17.5</td>
<td>7.2</td>
<td>4.2</td>
<td>0.5</td>
<td>0.035</td>
<td>0.10</td>
</tr>
<tr>
<td>4</td>
<td>17.5</td>
<td>7.1</td>
<td>4.1</td>
<td>0.5</td>
<td>0.033</td>
<td>0.13</td>
</tr>
<tr>
<td>5</td>
<td>17.3</td>
<td>7.3</td>
<td>4.0</td>
<td>0.5</td>
<td>0.038</td>
<td>0.19</td>
</tr>
<tr>
<td>6</td>
<td>17.5</td>
<td>7.1</td>
<td>4.1</td>
<td>0.5</td>
<td>0.034</td>
<td>0.27</td>
</tr>
</tbody>
</table>

![Figure 1: Fully austenitic microstructure of alloy 3 (0.10 wt% N) (etched with a mixture of chromic acid, acetic acid and distilled water).](image1.png)

![Figure 2: Microstructure of alloy 1 (0 wt% N) consisting of austenite matrix containing δ-ferrite and martensite (etched with oxalic acid).](image2.png)

3. DEFORMATION-INDUCED MARTENSITE AND ITS EFFECT ON THE WORK HARDENING RATE

The alloys in this investigation were generally metastable, undergoing a room-temperature deformation-induced transformation to martensite. As the nitrogen content increased, the
transformation became more inhibited, and as a result alloy 6 (0.27 wt% N) was not observed to undergo this deformation-induced transformation. The amount of retained austenite as a function of deformation for all the alloys is given in Figure 3.

The steels containing at least 0.13 wt% nitrogen exhibited true stress-true strain curves that were essentially parabolic in shape, as shown in Figure 4 for alloy 6 (0.27 wt% N). The lower nitrogen-containing steels (alloys 1 to 3) displayed true stress-true strain curves that were more sigmoidal in shape (Figure 5 for alloy 1), which is a consequence of the formation of strain-induced martensite. As the nitrogen content increased, the degree of sigmoidal nature of the true stress-true strain curve diminished.

Figure 3: The amount of retained austenite as a function of nitrogen content and true strain.

Figure 4: Room-temperature true stress-true strain curve for alloy 6 (0.27 wt% N).

Figure 5: Room-temperature true stress-true strain curve for alloy 1 (0 wt% N).

The work-hardening rate (WHR) of alloy 6 (0.27 wt% N) as a function of strain (Figure 6) shows a parabolic decline, subsequently decreasing in an almost linear fashion with continuing strain. Alloy 1
(0 % N) however, starts with a similar initial parabolic decline (Figure 7), in which the WHR actually dropped to a lower value than the higher nitrogen-containing steel. At larger strains, the WHR of this alloy rises rapidly to a peak, which is associated with the formation of martensite [4], and then subsequently diminishes with continuing strain. A gradual transition occurs between these two extreme behaviours as the nitrogen content is altered, the peak diminishing and appearing at greater strains with increasing nitrogen content. The ultimate tensile strength showed no consistent behaviour as a function of increasing nitrogen content.

Deformation at an elevated temperature (120 °C) resulted in true stress-true strain curves and work hardening rate curves of similar shapes for alloys 1 to 6, and of the same shape as that observed in alloy 6 at room temperature, as no deformation-induced transformation to martensite was observed. The effect of increasing nitrogen was observed to cause an increase in the ultimate tensile strengths of the alloys at 120 °C.

4. THE INFLUENCE OF NITROGEN ON THE CHANGES IN MICROSTRUCTURE WITH STRAIN

The alloys (1-6) were subjected to uniaxial tensile strain, and were examined at varying strains using a transmission electron microscope (TEM) under bright field and dark field conditions. TEM examinations of the unstrained alloys in the annealed condition showed an essentially strain-free microstructure containing numerous stacking faults, annealing twins and discrete dislocations. Both \( \alpha' \)-martensite and \( \varepsilon \)-martensite were observed in alloy 1 (0 wt% N). The strained samples also contained dislocations and stacking faults, and the density of these increased with increasing strain. During straining, plastic deformation of the steels was observed to occur by a combination of planar glide and mechanical twinning. Deformation twins became more noticeable with increasing deformation and decreasing nitrogen content. As the samples were strained, a transformation from austenite to martensite was observed. As the nitrogen content increased, this transformation became less evident. Electron diffraction patterns confirmed the presence of \( \varepsilon \)-martensite at low degrees of deformation in the low nitrogen steels. \( \varepsilon \)-martensite was generally observed at the intersection of
stacking faults, and had an orientation relationship where the [1210] zone axis was parallel with the [110] austenite zone axis.

Figure 8: The selected area diffraction pattern associated with ε-martensite in an austenite matrix showing the [110], [1210], [100], and [111] zone axes.

Figure 9: Bright field TEM micrograph of alloy 1 (0 wt% N), annealed showing ε- and α'-martensites in an austenite lattice. Areas denoted by E and A correspond to ε- and α'-martensites, respectively.
As the degree of deformation increased further, $\alpha'$-martensite was observed in conjunction with the $\varepsilon$-martensite, suggesting that it was perhaps nucleating from the $\varepsilon$-martensite. At high strains $\varepsilon$-martensite was also observed to nucleate at the intersection of shear bands. Two $\alpha'$-martensite orientation relationships (Kurdjumov-Sachs and Nishiyama-Wasserman) as well as the presence of $\varepsilon$-martensite, were sometimes observed within the same selected area (Figure 8). The selected area for this observation is shown in Figure 9. At higher degrees of deformation, no $\varepsilon$-martensite was observed, and the amount of $\alpha'$-martensite rapidly increased. In addition to its influence on the degree of martensitic transformation at varying strains, nitrogen was also observed to influence the stacking fault energy and degree of planarity of glide.

5. CONCLUSIONS

The addition of nitrogen has a profound effect on the formation of martensite in a Fe-17Cr-7Mn-4Ni based alloy. The base alloy (1) contains $\delta$-ferrite and martensite in addition to austenite after annealing. The addition of nitrogen stabilises the austenite phase so that, for nitrogen contents of at least 0.1 wt% or more, fully austenitic microstructures are obtained after annealing. The transformation of austenite to martensite as a result of deformation becomes more inhibited with the addition of nitrogen, and is not observed in alloy 6 which contains 0.27 wt% nitrogen. Both $\varepsilon$- and $\alpha'$-martensite are observed in the lower nitrogen alloys, the $\varepsilon$-martensite predominantly at lower degrees of deformation and the $\alpha'$-martensite at higher degrees of deformation. In the absence of martensite formation (120 °C), the tensile strength at this elevated temperature increased with nitrogen content. However, at room temperature there was no correlation between nitrogen content and tensile strength. This is a result of several factors [5], including the formation of martensite. The addition of nitrogen to replace nickel has been successfully achieved (in terms of austenite stabilisation) only for alloys 5 and 6, which contain 0.19 wt% or more nitrogen.

Acknowledgements

This paper is published with the permission of Mintek and the University of Cape Town

References

3] Rowlands, D.P., The Southern Africa Stainless Steel Development Association, P.O. Box 3737, Randburg, 2125, South Africa.