

Reducing the Nickel Content in Metastable Austenitic Stainless Steel

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The effect of lowering the nickel content, while substituting with nitrogen, on the transformation-induced plasticity (TRIP) behaviour of metastable austenitic stainless steels was investigated. Several experimental alloys, with a range of nickel-to-nitrogen ratios, were compared with an AISI type 301 alloy during tensile deformation between 0 and 120 °C.

Characterization of the tensile-deformation behaviour, as well as an examination of the formation of deformation-induced martensite during elongation, led to the recognition of some similarities between the TRIP behaviour of an alloy containing 5.1 wt per cent nickel and 0.16 wt per cent nitrogen and type 301 alloy. Formation of deformation-induced martensite is optimized at approximately 60 °C for both alloys, giving rise to maximum uniform elongation under these test conditions. However, there are indications that high nitrogen levels can lead to erratic transformation behaviour during deformation conditions, as evidenced by a comparison of work-hardening rate versus strain curves.

Introduction

Considerable work was carried out during the mid 1950's to mid 1960's on the reduction of the nickel content in austenitic stainless steels¹⁻⁴. The primary reason for exploring alternative alloy compositions was, and remains, the relatively high cost of nickel as an alloying element, particularly in types AISI 304 and 316 (which contain 8 to 12 wt per cent). In many instances, a combination of manganese and nitrogen as substitutes has been adopted, and much of this work has led to the development of the AISI 200 series alloys. A comprehensive study by Nijhawan *et al.* has shown that nickel-free Cr–Mn–N steels containing up to 15 wt per cent Mn and 0.6 wt per cent N have properties comparable with AISI 304, and are successful for applications such as household utensils, motor car and railway fittings, hospital ware, and dairy equipment⁴. Manganese, although classed as a very weak delta-ferrite former³, stabilizes the austenite phase. Nitrogen acts both as a potent austenite former (approximately 20 to 30 times the potency of nickel) and as an austenite stabilizer. It can therefore be expected that various combinations of these elements can have an influence on the stability of austenite and on the overall mechanical properties of a steel.

The present study looked more closely at the consequences of modifying the nickel-to-nitrogen ratios on the stability of austenite, with particular emphasis on the transformation-induced plasticity (TRIP) phenomenon. Metastable austenitic stainless steels of the AISI type 301 are used mostly for products that require moderate strengths, and are produced by stretch forming processes, which rely on the attainment of good ductility. Type 301 alloys nominally contain 6 to 8 wt per cent nickel, and the objective of this paper was to investigate the substitution of a limited amount of nickel content with nitrogen and its effect on the microstructure–property relationships.

Evolution of TRIP steels

Initial research, which eventually led to the development of metastable austenitic stainless steels, was aimed at the production of high-strength stainless steels that could be fabricated with relative ease. The work described here was prompted by the fact that the choice of high-strength stainless steels was limited to cold-worked austenitic or ferritic types, or to martensitic types. These steels, however, presented difficulty where fabrication was concerned, and this led to much interest being shown in the development of controlled-transformation (CT) stainless steels, which have, as an essential feature, a martensite range that occurs below room temperature⁵. Consequently, the steel is austenitic initially and can be fabricated quite readily. A subsequent refrigeration treatment at minus 70 °C will produce transformation to martensite or, alternatively, a heat treatment at 700 °C will precipitate alloy carbides and raise the martensite-transformation range above room temperature so that transformation to martensite will occur. With either treatment, the fabricated steel can be strengthened considerably. The main limitation of these simple CT steels is that accurate control of the martensite transformation is difficult owing to the range of compositions obtained in commercial steel making. Thus, it is difficult to control the M_s temperature owing to the sensitivity of this temperature to alloy composition, particularly regarding interstitial elements such as carbon and nitrogen⁶.

In the late 1960's, TRIP steels were developed that differ from CT steels in that essentially no martensite is formed in the latter during straining while, in the former, considerable amounts of austenite can transform to martensite^{6,7}. Thus, the TRIP steels achieved in one process what required at least two stages in CT steels. In addition, TRIP steels pro-

duced high strengths coupled with good ductility. It is now well accepted that resistance to local necking during deformation is achieved by the onset of martensite formation during deformation⁸⁻¹⁰. Once a local contraction occurs during deformation, martensite is gradually induced and the increment in strength caused by this martensite is responsible for the increment in applied stress at the necked portion. Thus, the necked region is hardened more by deformation-induced martensite than is the rest of a specimen, so that the incipient necking no longer grows, and further deformation is partitioned to the adjacent region. In addition to the delayed onset of macro-necking, the suppression of the initiation and propagation of microcracks by the formation of deformation-induced martensite has also been considered a major contribution to increased ductility in metastable austenitic steels⁹. A local stress concentration can be relaxed by the formation of martensite, and the initiation of microcracks may be prevented. Furthermore, even if microcracks are initiated, martensite formed at the tips of micro-cracks will relax the stress concentration and suppress their propagation.

In view of the fact that transformation-induced plasticity may be caused by the suppression of necking, and by the suppression of the initiation and propagation of microcracks, the controlled nature of this transformation is important during deformation. The main prerequisite for maximum elongation is that the martensite is constantly formed little by little during deformation. Elongation is much reduced when martensite is formed rapidly during the early stages of deformation or when the total amount of martensite formed during the late stages is small. The former situation arises when the material is deformed just above the M_s temperature, whereas the latter occurs when the material is deformed just below the M_d temperature. Consequently, it has been found that the elongation shows a peak at a certain temperature between the M_s and M_d ^{9,10}.

Experimental Procedure

Six experimental alloys, prepared by Middelburg Steel & Alloys' research laboratory, were selected to provide an alloy composition based on AISI 301 but with a range in the nickel-to-nitrogen ratios. The compositions of the alloys are presented in Table I, along with the composition of a type 301 alloy for comparative purposes. Each experimental alloy was cast into a 5 kg ingot (50 mm thick and hot-rolled to plate of 10 mm gauge). A portion of this plate for each alloy was further hot-rolled to a sheet thickness of 4 mm. Flat tensile specimens (gauge length 30 mm, gauge width 7.5 mm, thickness 2 mm) were machined from the 4 mm sheet and were used for X-ray-diffraction (XRD) measurements after various levels of tensile deformation. Hounsfield-type tensile specimens (gauge length 20 mm, diameter 4 mm) were machined from the 10 mm plate for evaluation of their general tensile properties over a range in temperature.

Prior to testing, all the test specimens were ceramic-coated and heat-treated in air at 1050 °C for 30 minutes, followed by oil quenching. The tests were performed using a computer-interfaced Zwick tensile tester, which allowed the data to be captured on computer file. The test set-up incorporated a temperature bath regulated by a Eurotherm controller to within 2 °C. Tensile-fracture tests were performed at 20, 60, and 120 °C, while tests to 0.3 true strain were per-

TABLE I
CHEMICAL COMPOSITION OF THE EXPERIMENTAL ALLOYS
AND AISI 301 IN PERCENTAGES BY WEIGHT

Element	A1	A3	A5	A6	D1	D2	301
C	0,084	0,087	0,075	0,071	0,078	0,070	0,029
Mn	1,62	1,61	1,55	1,48	1,51	1,53	1,52
Si	0,65	0,65	0,48	0,44	0,43	0,43	0,44
V	0,08	0,08	0,06	0,06	0,07	0,06	0,05
Cu	0,08	0,08	0,08	0,08	0,06	0,06	0,10
Co	0,02	0,02	0,02	0,02	0,02	0,02	0,03
Mo	0,03	0,03	0,05	0,05	0,05	0,05	0,20
Cr	17,2	17,5	17,9	17,9	17,9	17,9	17,7
Ni	5,12	5,09	5,17	5,03	3,41	3,36	7,48
N	0,087	0,129	0,163	0,276	0,185	0,275	0,074

formed at the same temperatures and also at 0 °C. All the experiments were carried out at an initial strain rate equivalent to 10⁻³ per second.

For XRD phase analysis after deformation, the centre portions of the flat tensile specimens were mounted in resin, mechanically polished to a finish using 1 µm diamond paste, and finally electropolished in a solution containing chromic and glacial acetic acids. Electropolishing was necessary to remove any deformation-induced martensite that may have formed during the mechanical polishing. XRD analysis was performed using Cu Kα-radiation passed through a nickel filter. A step of 0,05° and a counting time of 10 seconds were employed during the direct acquisition of data onto computer file. The martensite-austenite volume fraction was calculated from the integrated area under the (200)α, (211)α, (220)γ, and (311)γ diffraction peaks. The volume fraction was calculated by Dickson's method¹¹ in order to correct for the error introduced as a result of texture development in either phase.

Experimental Results

After solution heat treatment, the microstructures of the experimental alloys and AISI 301 were examined by light microscopy (Nomarski interference), in order to investigate the presence of delta-ferrite. Ferrite was noted as absent in all instances, and it can therefore be inferred that a single-phase austenitic structure existed at the solution temperature (1050 °C). The XRD analysis of the phase composition of all the alloys after solution heat treatment is presented in Table II, and indicates the stability of the austenite during rapid quenching to ambient. As expected, the percentage retained austenite decreased with decreasing nitrogen content for a particular nickel level, and the overall retained austenite was lower for the low-nickel alloy set (D1, D2).

The true stress at maximum uniform elongation (σ_u) and the true uniform strain are plotted in Figures 1 and 2 respectively as a function of test temperature for alloys A1, A3, A5, A6, and type 301. As found by previous workers^{8,10}, a

TABLE II
RETAINED AUSTENITE CONTENT AT AMBIENT TEMPERATURE (AFTER
SOLUTION TREATMENT) FOR THE EXPERIMENTAL ALLOYS AND AISI 301

Alloy	A1	A3	A5	A6	D1	D2	301
Retained austenite, %	70	83	89	91	43	67	98

peak in uniform elongation was detected for type 301 in the vicinity of 60 °C. Alloy A5 also displayed a maximum at 60 °C, whereas the lowest-nitrogen alloy (A1) and the highest-nitrogen alloy (A6) both indicated an increase in uniform elongation up to 120 °C. Alloy A3 had similar elongation at 60 and 120 °C. The tensile strengths of the nitrogen-substituted alloys were consistently higher than that for type 301 at 20 and 60 °C. The strengths generally decreased with increasing temperature (with the exception of A1 and type 301, which have similar strengths at 20 and 60 °C), and the differences in strengths between the set A alloys and type 301 was much reduced at 120 °C.

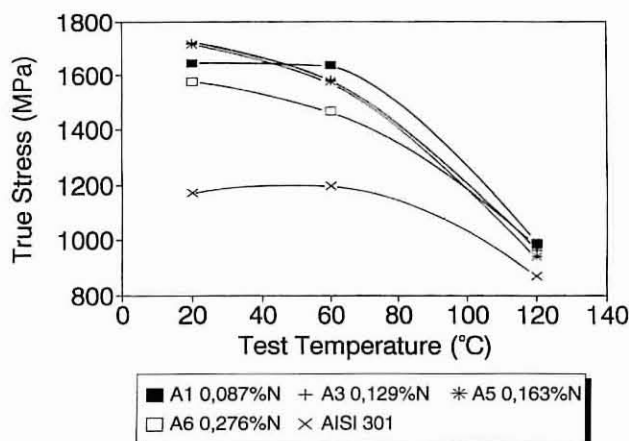


FIGURE 1. True stress at uniform strain (σ_{μ}) as a function of temperature (set A alloys and type 301)

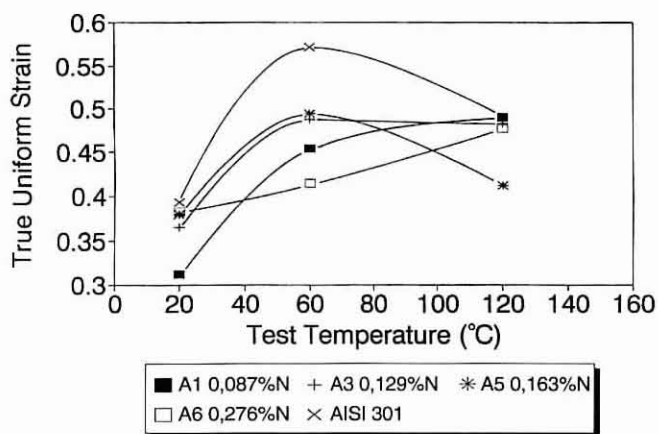


FIGURE 2. True uniform strain as a function of temperature (set A alloys and type 301)

In order to characterize the tensile properties further, the true stress at 0,3 true strain was also plotted as a function of test temperature (including the tests at 0 °C) for the above-mentioned alloys (Figure 3). The difference in stress at 0,3 strain recorded at 20 and 60 °C for set A alloys is much greater than the difference in σ_{μ} for these alloys over the same temperature interval. An interesting observation is the anomaly that seems to occur at 0 °C for A1, A3, and A5. In each case, the stress at 0,3 strain is higher during testing at 20 °C than at 0 °C.

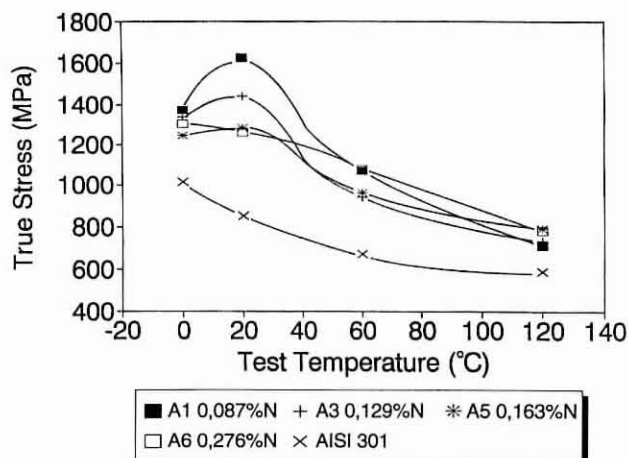


FIGURE 3. True stress at 0,3 strain as a function of temperature for alloys A1, A3, A5, A6, and type 301.

The tensile behaviour of alloys D1 and D2 are characterized by σ_{μ} and true uniform strain plotted as a function of test temperature in Figures 4 and 5 respectively. The σ_{μ} value for D1 and D2 follows a similar trend to that shown by alloy A1 (Figure 1), but the uniform strain values are very low (Figure 5).

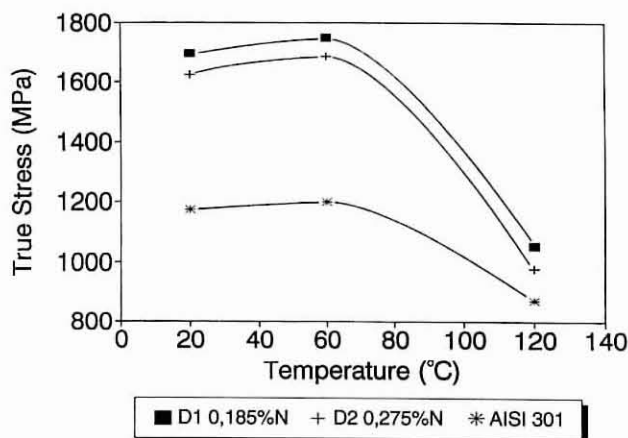


FIGURE 4. True stress at uniform strain (σ_{μ}) as a function of temperature (set D alloys and type 301)

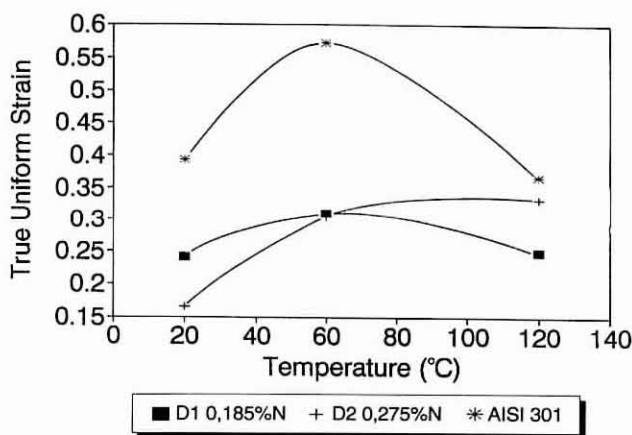


FIGURE 5. True uniform strain as a function of temperature (set D alloys and type 301)

Discussion

Although a fully austenitic microstructure was achieved at the solution treatment temperature (1050 °C) for all the nitrogen-substituted alloys, varying degrees of austenite stability were obtained on rapid cooling to ambient. As far as could be gathered from the literature, TRIP phenomena have been studied mostly on steels whose M_s temperatures were below ambient. Therefore it must be expected that the existence of a two-phase microstructure (austenite and martensite) prior to testing must influence the nature of tensile deformation. Notwithstanding these differences, the TRIP phenomenon should still play a major role in the deformation of the alloys containing low volume fractions of thermally induced martensite (e.g. A3, A5, and A6).

In order to explain the changing tensile behaviour of the set A alloys as a function of temperature, the tendency to form martensite during deformation needs to be investigated. To this end, the total martensite content was measured at 0,3 strain for each test temperature using XRD, and the total deformation-induced martensite (total martensite at 0,3 strain minus martensite prior to testing) was plotted as a function of test temperature (Figure 6). The results for the experimental alloys at 60 and 120 °C appear somewhat spurious in that they have negative values. This can be explained only by the difficulty in measuring the phase ratio in a deformed material due to an increasing amount of noise arising from the strained volume. Nevertheless, it can be stated with a certain degree of confidence that very little, if any, martensite formed during straining of the alloys up to a strain of 0,3 at these temperatures. The values for the type 301 alloy under the same conditions are also included.

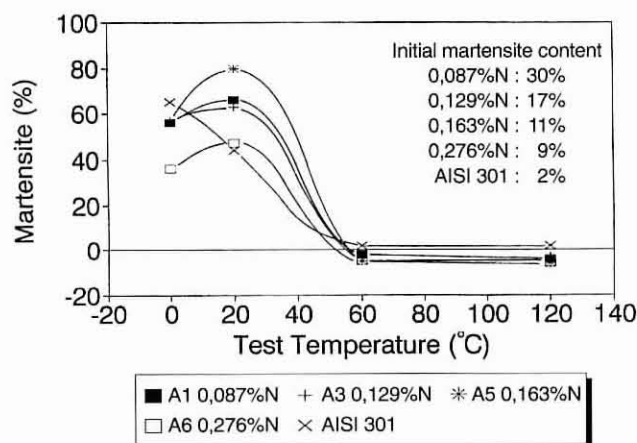


FIGURE 6. Total deformation-induced martensite at 0,3 strain as a function of temperature (set A alloys and type 301)

In addition to these observations, the work-hardening rate (WHR) as a function of true strain is shown for A5 and type 301 at 20 and 60 °C in Figures 7 and 8 respectively. This information will be used in the following paragraphs to explain the tensile behaviour.

As reviewed in the section dealing with the evolution of TRIP steels, maximum elongation is obtained when martensite forms during the latter part of deformation and, in addition, it must form at a controlled rate. The fact that the type 301 alloy has a maximum uniform elongation at approximately 65 °C is consistent with this belief in that negligible

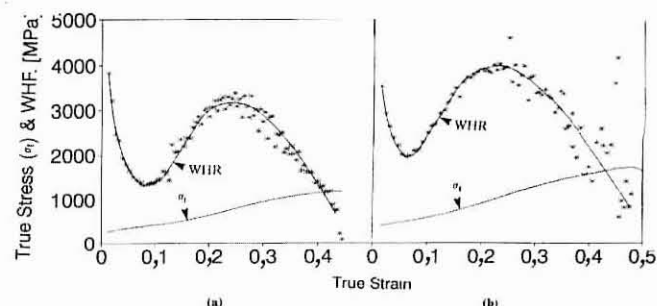


FIGURE 7. (a) Work-hardening rate (WHR) of type 301 as a function of true strain at 20 °C

(b) Work-hardening rate (WHR) of alloy A5 as a function of true strain at 20 °C

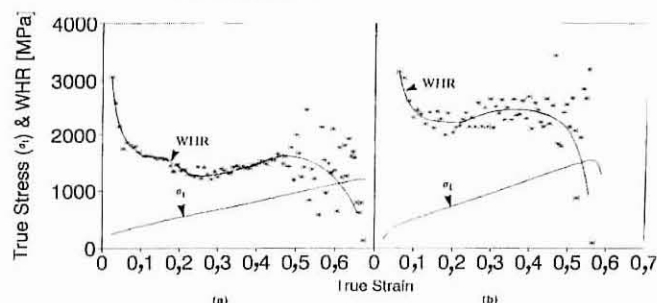


FIGURE 8. (a) Work-hardening rate (WHR) of type 301 as a function of true strain at 60 °C

(b) Work-hardening rate (WHR) of alloy A5 as a function of true strain at 60 °C

amounts of martensite are formed in the initial stages of deformation (Figure 6). At temperatures below the peak value, the martensite forms too rapidly in the early stage of deformation whereas, at the higher temperatures, insufficient martensite forms to enable a considerable contribution to enhanced plasticity and, instead, elongation is provided mostly by deformation of the austenite phase. Alloy A5 follows the same trend in uniform elongation, except that the amount of elongation at the peak temperature is considerably lower. Despite these differences in elongation, the trend observed indicates that the TRIP phenomenon must play a role in alloy A5. This is examined more closely before the remaining set A alloys are dealt with.

Examination of the WHR versus strain curves in Figure 7 indicates similar trends in work-hardening behaviour for the two alloys when tested at 20 °C. In each case, the rise in WHR can be attributed to the gradual formation of martensite during straining, whereas the drop in WHR after the peak value is reached is associated with the more rapid formation of martensite. It has been shown by Tomota *et al.*¹² that, when martensite forms rapidly, the stress relief accompanying the transformation strain can lead to a lowering of overall applied stress. (Martensitic transformation accompanies shear and dilatation, and therefore a certain value of positive transformation strain occurs along the direction of applied stress.) This suggests that the drop in WHR after the peak is reached is at least partly due to dilatation associated with transformation strain. The peak WHR is reached at a strain of approximately 0,22 in the case of alloy A5, and the suggestion that martensite forms rapidly after this point is consistent with the high value of deformation-induced martensite recorded after 0,3 strain (approximately 80 per cent). In the case of type 301, the peak WHR occurs at a similar strain value to that of alloy A5. However, it is

apparent that the rate of martensite formation is not quite as high when compared with the latter alloy, since only 43 per cent martensite has been measured at a strain of 0.3. Nevertheless, it is clear that, for both alloys, martensite forms at a high rate relatively early during straining, and the total uniform elongation attained by each alloy is similar. It can be suggested that the TRIP phenomenon is not prominent in either material during the latter stages of deformation, since the martensite does not form slowly enough to prevent incipient necking.

At 60 °C, the WHR curves for alloy A5 and type 301 demonstrate a behaviour that is more typical of the TRIP phenomenon (Figure 8). In both cases, the peak WHR is delayed to much larger strain values, with this strain value being consistently greater for type 301. The gradual drop in WHR up to a strain of 0.3 is consistent with the deformation of austenite. This is supported by negligible formation of deformation-induced martensite up to this strain value. Above a strain of 0.3, the increase in WHR is due to the favourable formation of martensite, which resists incipient necking. At strains greater than 0.5, Fukase *et al.*⁸ have shown that the rate of formation of martensite increases in type 301 at 50 °C. Since their alloy composition was virtually identical to the 301 alloy in the present investigation, it is expected that very much the same behaviour must be occurring at 60 °C, and hence the drop in WHR after a strain of 0.5 can once again be partly explained by the occurrence of transformation strain. It would seem that much the same behaviour is demonstrated by alloy A5, except for the indications that the onset of rapid martensite formation occurs earlier in this alloy. This would explain the lower uniform strain recorded for alloy A5 compared with type 301 during deformation at 60 °C. In addition, the curve for type 301 in Figure 8(a) is relatively smooth up to about 0.45 strain, whereas the corresponding curve for alloy A5 in Figure 8(b) shows a greater amount of scatter. These observations have been produced from several stress-strain curves and would seem to demonstrate a more erratic transformation behaviour in alloy A5, which must be related to some function of the high nitrogen content. Serrations have been identified in the stress-strain curves, and this possibly indicates that martensite forms in bursts over certain strain intervals.

It makes sense that, for reasons similar to those described above, the elongation occurring at 60 °C for alloys A1, A3, and A6 is also improved owing to the favourable formation of martensite during deformation. However, the uniform strain for both A1 and A6 increases further at 120 °C. This can be rationalized more easily for A1 in that, because it has the highest M_s temperature (largest amount of thermally induced martensite at ambient), the peak elongation temperature is expected to be higher. On the other hand, alloy A6, owing to its much greater austenite stability, should not behave like this, and no explanation can be offered for this performance at the moment. The low stability of the austenite in the lower nickel-containing alloys, D1 and D2, is responsible for the low uniform elongation recorded for these alloys. It is expected that the TRIP phenomenon is not significant in these alloys.

The overall strength differences between the nitrogen-substituted alloys and type 301 at room temperature can be attributed to two factors. Firstly, the nitrogen alloys are all being deformed below the M_s temperature (to varying degrees), and it can therefore be expected that a much

greater total volume fraction of martensite is present at fracture. The flow stress over any particular strain interval can be related to the amount of martensite present (compare Figures 3 and 6). Secondly, it is well known that nitrogen strengthens both austenite and martensite to a much greater extent than nickel does. The observation of a lower stress and lower martensite fraction at 0 °C than at 20 °C for the set A alloys needs further investigation. It is possible that there is some effect on incubation time due to the refrigeration of a microstructure already containing appreciable amounts of martensite.

Summary

This investigation into the effects of substituting nickel with nitrogen in type 301 alloys on the occurrence of transformation-induced plasticity has given rise to the following conclusions.

- (1) There is clearly a careful balance between nickel and nitrogen content that needs to be maintained in order to produce a sufficiently stable microstructure during cooling to ambient. Alloys with poor austenite stability give rise to limited elongation during tensile testing.
- (2) An alloy containing 5.1 wt per cent nickel and 0.16 wt per cent nitrogen (A5) compares favourably with the TRIP behaviour shown by the type 301 alloy when tested at 60 °C. The more erratic work-hardening behaviour displayed by the high-nitrogen alloy at this temperature, however, indicates that the formation of martensite during straining is less gradual when compared with type 301.

An exact explanation for the effect of nitrogen on the transformation behaviour during deformation is still not available. Generally, nitrogen-rich alloys follow the same rules in terms of the requirements for optimum enhanced plasticity. However, there are certain anomalies that require further examination.

Acknowledgments

The authors would like to thank Middelburg Steel & Alloys, Transvaal, and the Foundation for Research and Development (FRD), Pretoria, for supporting this work, with special thanks to Mr J Hewitt of Middelburg Steel & Alloys for his interest and encouragement.

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