Effect of Manganese Partitioning on Transformation Induced Plasticity Characteristics in Microalloyed Dual Phase Steels

N. R. BANDYOPADHYAY and S. DATTA

Dr. M. N. Dastur School of Materials Science & Engineering, B. E. College (a Deemed University), Howrah 711 103, India.

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The manganese contents of the dual phase steels with transformation induced plasticity characteristics are reasonably high. Efforts have been made to study the role of manganese in making stable austenite. The effect of the varying holding time at different intercritical annealing temperatures on the formation of manganese enriched austenite by a competitive process have been studied. The effect of manganese partitioned austenite so produced on the TRIP behaviour of the steel has also been studied through processing structure property correlation. It is seen that manganese enrichment in retained austenite depends on the time and temperature of intercritical annealing.

KEY WORDS: dual phase steel; TRIP; microalloying; manganese partitioning.

1. Introduction

To induce additional formability the concept of transformation induced plasticity (TRIP) was introduced by Zackey et al.1 The concept could not propagate much due to requirement of high amount of alloying elements in low carbon steels (–0.14 wt%). Incidentally retained austenite was found to be present as a microconstituent in dual phase steel,2,3 which was used to effect martensitic transformation during straining. Later the role of retained austenite in enhancing the toughness properties of steel has been greatly emphasised.4 An attempt was made by the present investigators to impart TRIP in a reasonably low carbon (–0.06 wt%) dual phase steel with around 50% of the silicon content used by the previous workers for improving the formability of the steel.5 The loss in strength due to decrease in carbon content was compensated through microalloying as well as thermomechanical controlled processing. It was found that adequate volume fraction of retained austenite to impart TRIP can be achieved in this steel.

Silicon was stated to be indispensable in TRIP aided ferrite bainite steel due to its role of inhibiting the formation of carbide and hence carbon enriched stable retained austenite amenable for transformation induced plasticity (TRIP) was found in the microstructure. Low silicon (~0.45 wt%) boron bearing steel was studied by the present workers and it was found that adequate amount of retained austenite amenable for TRIP was formed in those steels.6

The manganese contents of those steels were also reasonably high but its role in making stable austenite has not been systematically studied or documented. Hence, the objective of the present investigation has been to vary the holding time at different intercritical annealing temperatures to effect the formation of manganese enriched austenite by a competitive process. The effect of manganese partitioned austenite so produced on the TRIP behaviour of the steel has also been studied through processing structure property correlation.

2. Experiments

Steels with two compositions in respect of different alloying elements were produced by air melting in induction furnace of 5 kg capacity. The compositions of experimental alloys are given in Table 1. The cast ingots were then forged and finally hot rolled to 12 mm x 6 mm section in a laboratory rolling mill. The rolled strips were heat treated as per schedules shown in Table 2. The microstructural characterization was carried out using a Versamet Optical Microscope. The mechanical properties were evaluated by Instron 4204 Testing Machine at strain rate of 3.3 x 10^{-4}/s using test specimen according to the ASTM specification.
and with gauge length of 25 mm. Transmission Electron Microscopy with microanalyses of different phases present in the microstructures have been carried out in Jeol-Jem 4000 EX Transmission Electron Microscope fitted with a EDX system. The X-ray diffraction analyses was carried out using a Rigaku-D Max diffractometer with Cu-Kα radiation.

3. Results

3.1. Optical Metallography

Optical microstructures of the samples isothermally reacted at 400°C, in general, show retained ferrite, isothermal decomposition product of austenite and possibly some untransformed divorced pearlite. When alloy 1 is intercritically annealed at 700°C and then isothermally reacted to bainite, fine-grained retained ferrites with large amount of black constituents are seen in the microstructure. It appears that the black phases are mostly the isothermal decomposition product of austenite, though the existences of a small amount of untransformed pearlite are not excluded (Fig. 1(a)). On increasing the time of intercritical annealing the amount of retained ferrite decreases. This means that more austenite is formed with increasing time at the intercritical temperature (Fig. 1(b)). However in some regions, the presence of ferrite stringers indicates that during cooling from 700°C to the bainite reaction temperature 400°C acicular ferrite has formed. Owing to its formation at low temperature during continuous cooling they have assumed the elongated morphology. Degenerated pearlite (marked ‘A’) could also be seen in the microstructures of samples after prolonged holding at the intercritical annealing temperature. When solute rich austenite is cooled to reaction temperature the needle shaped ferrite is formed which is hitherto called the transformed ferrite (Fig. 1(b)). A very long holding time has however led to a decrease in the amount of needle like transformed ferrite (Fig. 1(c)).

At a lower intercritical holding temperature the amount of second phase is significantly reduced and untransformed pearlite is formed (Fig. 2(a)). Increasing annealing time has increased the amount of second phase and also good amounts of needle shaped transformed ferrites are formed. This is to mean that more austenite is formed after holding at intercritical temperature for higher time (Fig. 2(b)). However a very high annealing time of 4 hrs produced austenite both at the ferrite/ferrite boundary and at the fer-

![Fig. 1. Optical micrographs of alloy 1 intercritically annealed at 700°C for (a) 1 h, (b) 1.5 h and (c) 4 h. All the samples are then isothermally annealed at 400°C for 900 s.](image)

![Fig. 2. Optical micrographs of alloy 1 intercritically annealed at 650°C for (a) 1 h, (b) 1.5 h and (c) 2 h. All the samples are then isothermally reacted at 400°C for 900 s.](image)
rite grain interiors (Fig. 2(c)).

In case of alloy 2 intercritical annealing at 700°C followed by isothermal reaction at 350°C has produced needle shaped transformed ferrite with large volume fraction of second phase. It is to be noted that the microconstituents are coarser in alloy 2 as compared to those in alloy 1 (Fig. 3(a)), though the difference in the amount of second phase is marginally higher in alloy 2. Increasing time of intercritical holding appears to have decreased the amount of needle shaped ferrite to a significant extent (Fig. 3(b)). No significant change in microstructure is noticed by changing the isothermal reaction temperature. Lower intercritical holding temperature has retained a high amount of degenerated pearlite (marked ‘P’ in Fig. 3(c)). The second phase isothermal reaction product is seen to be present at the ferrite/pearlite boundary. A large number of black points like features are seen within the untransformed ferrite. Seemingly these are the second phase particles containing some retained austenite.

3.2. Transmission Electron Microstructure and Energy Dispersive X-ray (EDX) Analyses

Transmission electron micrograph of alloy 1 intercritically annealed at 700°C for 0.5 h followed by isothermal bainitic reaction at 400°C for 900 s have shown black granular constituents at the boundaries of ferrite (Fig. 4(a)). Very fine precipitates are also seen to be present in the matrices of the above microstructures. On increasing the time of holding to 1 h at the intercritical annealing temperature of 700°C, a good amount of retained austenite is seen to be surrounded by the bainitic ferrite (Fig. 4(b)). The black granular constituents seen at the boundaries of ferrite in Fig. 4(a) are identified as retained austenite in its SADP analysis in Fig. 4(c) which shows (011)_{BCC} // (112)_{FCC}. It seems from the micrograph that the austenite is kept retained after the bainitic transformation has ceased, probably due to the solute enrichment in austenite.

When the intercritical annealing temperature is reduced to 650°C and isothermal bainitic reaction is effected at 400°C for 900 s the bainite is found to be much more dislocated (Fig. 5) than when the alloy is intercritically annealed at 700°C and retained austenite is seen to be present at the
The EDX analysis of retained austenite of Fig. 4(a) shows a moderate silicon and manganese content in matrix when the intercritical annealing time is 0.5 h in commensuration with the alloy composition (Fig. 6(a)). As compared to that manganese enrichment in retained austenite is seemed to have occurred with increase in holding time at 700°C (Fig. 6(b)). This implies that manganese has significantly partitioned to austenite. However the silicon content is comparable to that of the matrix. The black cuboidal precipitate in Fig. 4(a) (marked as ‘A’) is found to be very rich in titanium with low manganese and silicon content (Fig. 7). The retained austenite in Fig. 5 is also rich in manganese (Fig. 8). This means that if sufficient time is allowed even at 650°C, manganese enriched austenite can be formed. Compared to this, the manganese content in the matrix is rather low to corroborate with the high manganese content in retained austenite.

### 3.3. XRD Studies

The results of X-ray diffraction analyses, furnished in the Table 3, are indicative of a low volume percent of retained austenite. Comparison of the intensities of (220), and (400), with the 100% intensity peak for α-iron at (110),

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**Table 3.** Results of X-ray diffraction study for Alloy 1.

<table>
<thead>
<tr>
<th>Intercritical annealing</th>
<th>Computed percentage of retained austenite</th>
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<tbody>
<tr>
<td>650°C for 1 br.</td>
<td>5.2</td>
</tr>
<tr>
<td>700°C for 1 br.</td>
<td>8.5</td>
</tr>
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has given information about the retained austenite content in the experimental alloys. The calculation of the amount of retained austenite was done by following the methods used earlier.\(^7\) It is seen from the XRD results that increasing the intercritical annealing temperature increases the amount of retained austenite in the steel.

### 3.4. Mechanical Properties

Alloy 1, which contains titanium, is seen to possess high strength at a high ductility level. The effect of intercritical annealing time is shown in Fig. 9(a) and it is seen from the figure that UTS increases with increasing annealing time, initially at a fast rate and later at a slower rate beyond 2 hours of annealing time. At all times of annealing, the higher temperature of annealing has resulted in higher strength, though the difference is greatly lessened for high intercritical annealing time. Figure 9(b) shows that the total elongation decreases with increasing annealing time and then beyond a particular annealing time it rises again. The elongation minimum shifts to longer time for lower intercritical annealing temperature and the total elongation is lower at higher annealing times for the low annealing temperature, whereas the reverse is true at shorter annealing times. For alloy 2 (Table 4) however it is noticed that increasing time of annealing increases both UTS and total elongation at both bainitic reaction temperatures. However for 400°C, the maximum ductility is ensured at the highest achievable tensile strength. It is to be further noted that the tensile strength of alloy 2 is lower than alloy 1 but the achievable elongation is considerably larger in amount for the identical heat treatment schedule. On the contrary, in case the alloy 2 is intercritically annealed at 650°C, the strength is very low. However by increasing annealing time at 650°C, the total elongation increases. The increment in elongation is less for isothermal reaction at 350°C than for that at 400°C. Still, the variation in strength is rather insignificant. It is further observed that both strength and total elongation are reduced a little bit for a very high bainite reaction time where attempt was made to transform all the austenite to bainite.

### 3.5. Computation for Studying the Strain Induced Plasticity

The instantaneous ‘n’ values against true strain for alloy 1 shows a monotonous increase right from the low strain values and continues up to uniform elongation (Fig. 10(a)). This is indicative of the fact that strain hardening rate starts increasing right from the beginning of straining in either alloys during tensile testing. This increase is due to strain induced transformation and accompanying work...
hardening of the steels. The plot of $\frac{d\sigma}{d\varepsilon}$ against true strain is drawn along with true stress vs. true strain curves and the points of intersection are indicative of the values of strain ($\varepsilon_c$) at which necking starts. From Fig. 11 it is noted that the change in time of intercritical annealing time has brought about an insignificant change in the onset strain. In Figs. 12(a) and 12(b) it is noticed that the change in annealing temperature is quite sensitive to work hardening rate and the tensile strength. Decrease of intercritical annealing temperature is seen to decreases the value of the work hardening rate as well as the strength of the steel. This trend is same for both the alloys. Comparing alloy 2 with alloy 1 it appears that for annealing at 700°C, the alloy 2 has considerably higher $\varepsilon_c$ value than alloy 1 whereas it has slightly lower $\varepsilon_c$ value than alloy 1 when they are annealed at 650°C and then bainite reacted at 400°C. However the comparison may be unwise on ground that bainite reaction time is different in the above two cases.

4. Discussion

Alloy 1 contains carbide former like titanium whereas alloy 2 contains boron, which is known to promote bainite formation.8) After rolling, carbides are precipitated in alloy 1 and post-rolling air-cooling produces ferrite pearlite microstructure. In alloy 2 however, a good amount of bainite may have formed during continuous cooling after forging and rolling showing less amount of pearlite. The existence of a good amount of granular bainite in the microstructure can be explained from the concept of diffusional ledge mechanism during slow cooling.9) After reheating to intercritical annealing temperature, several important phenomena take place. On holding at 700°C, equilibrium austenite tends to form at the ferrite pearlite boundaries and grow within pearlite. Cementite dissolves in austenite rather slowly. At shorter holding time austenite, characterized by the equilibrium diagram, forms with low substitutional solute content. When the austenite is cooled from the intercritical temperature to the isothermal bainite reaction temperature, some ferrite is essentially lean in carbon and the remaining austenite gets enriched with carbon. So some austenite is stabilized and remains untransformed during isothermal holding. This may or may not transform to martensite when the alloy is cooled from bainite reaction temperature to room temperature. But increasing the time at intercritical temperature beyond that needed for carbon equilibration, has the implication equivalent to increasing the intercritical annealing temperature. An increase in intercritical holding leads to the formation of high manganese austenite. At any temperature close to $A_1$, conventional austenite with low manganese content may attempt to nucleate along with high manganese austenite as manganese lowers the $A_1$ temperature. The high manganese austenite i.e. manganese-partitioned austenite has higher driving force for formation. So there is a competitive process of austenite formation where it is found that austenite of high manganese can form in preference to low manganese austenite when diffusion of manganese is favourable. A low manganese high carbon austenite is preferred kinetically at a higher temperature and shorter holding time. At lower annealing temperature high manganese austenite requires a higher annealing time, during which regions rich in man-

Fig. 11. Variation of critical strain of (a) alloy 1 at intercritical annealing temperature and 700°C for 1 and 2 h. and (b) alloy 2 at intercritical annealing temperature and 650°C for 1 and 2 h.

Fig. 12. Variation of critical strain with intercritical annealing temperature 650°C and 700°C for 2 h of (a) alloy 1 with bainitic reaction temperature 350°C and (b) alloy 2 with bainitic reaction temperature 400°C.
ganese is formed by diffusion. In the steels under observation increasing time has lessened the amount of ferrite due to the fact that effective $\Delta_t$ is low when high manganese austenite is considered to form. Initially higher holding time changes solute concentration of austenite and CCT diagram shifts towards right. When the austenite is cooled to bainite reaction temperature some primary ferrite forms at a lower temperature and hence appear acicular. On the other hand, a very high holding time leads to austenite enrichment so much so that the bainite bay becomes fully exposed and the ferrite bay is displaced more towards right. Hence this primary acicular ferrite becomes absent from the microstructures. At a lower intercritical temperature, the amount of second phase formed is low because high manganese austenite can form only at a later time when adequate solute diffusion has taken place. Thus untransformed pearlite (of the initial microstructure) is seen in the micrographs. With increasing holding time more high manganese austenite can form competitively and hence the amount of second phase after isothermal treatment equals to that obtained in case of high temperature intercritical holding. Alloy 2 contains boron and so its starting microstructure contains some granular bainite. When high temperature annealing is done, the second phase content is very high as usual. But the structural coarseness is due to the fact that it does not contain titanium, which has exerted its grain refining effect in alloy 1. A continued holding at a lower temperature has produced a degenerated pearlite. However due to the effect of boron in promoting bainite formation, the amount of second phase is slightly higher in alloy 2.

The transmission electron microscopy with EDX analysis has shown that matrix ferrite of the alloy 1 annealed at 700°C is less dislocated. This is because the retained ferrite is recrystallised during intercritical annealing. When the austenite formed during intercritical annealing is transformed isothermally, bainite laths are formed. When this bainite is formed, the adjacent ferritic area becomes more dislocated so as to accommodate the plastic strain. The chemical analysis of the matrix shows that silicon is mostly partitioned in ferrite. However the austenite formed during intercritical annealing is very high as usual. But the structural coarseness is due to the fact that it does not contain titanium, which has exerted its grain refining effect in alloy 1. A continued holding at a lower temperature has produced a degenerated pearlite. However due to the effect of boron in promoting bainite formation, the amount of second phase is slightly higher in alloy 2.

In case of alloy 2 which contains boron, the carbides are present in form of $(\text{Fe,Mn})_3\text{C}$. Therefore increasing holding time at 700°C has increased the manganese content of the austenite. Otherwise the austenitic manganese is very close to that of steel composition. This means that austenite can be enriched by manganese only when sufficient time is given. When temperature is low, 650°C, a continuous and prolonged holding leads to the degeneration of pearlite existing in the microstructure and the carbides undergo coarsening. At 700°C, most of the pearlite is transformed to austenite and so such carbides are not seen. After sufficient holding, manganese rich austenite is formed. When this austenite is reacted, bainite forms leaving behind highly solute rich austenite, which does not transform further to bainite. The austenite, which is formed at the grain boundaries, is less rich in manganese to mean that their genesis is different.

Since bainite transformation is promoted by boron, the initial microstructure contains a good amount of granular ferrite, which are formed at intermediate transformation temperature and hence more densely dislocated than alloy 1. At 650°C, the globular precipitate like phase is present owing principally to the degeneration of pearlite and coarsening of carbides transform to austenite under paraequilibrium. However this equilibrium austenite will be leaner with respect to carbon. Regarding manganese content competitive austenite formation will be the primary consideration. At higher temperature austenite can form with lower manganese but at lower temperature austenite has to contain higher amount of manganese. During holding at intercritical temperature the equilibrium austenite may also form due to conversion of pearlite to austenite by inverse eutectoid reaction. Therefore austenite so formed is moderately rich in carbon and manganese. The austenite formed through equilibrium is more prone to bainitic transformation and during the course of bainitic transformation the remaining austenite ultimately becomes adequately enriched with carbon and manganese and is retained. Therefore the austenite finally retained in the above microstructures is heterogeneous in composition due to the difference in the genesis of their formation.

This austenite does not transform to ferrite and hence more austenite is available for bainite reaction. So more stable austenite can form. Hence ductility increases. The lower ductility of alloy annealed at 700°C is due to the fact that at low times, the ferrite formation is more. This ferrite forms at low temperature, and is highly dislocated. Contrary to this, the alloy at 650°C cannot produce austenite to any greater extent only paraequilibrium austenite is formed. During holding, pearlite is degenerated and isolated carbide forms in ferrite matrix, which is soft. This microstructure gives higher ductility as compared to the microstructure for 700°C. However the annealing at low temperature takes more time for effective manganese partitioning, and hence for the formation of stable austenite. This is the reason why ductility increase starts at a later time. The total elongation of the sample annealed at 650°C is lower at higher times because of the fact that the amount of manganese-partitioned austenite always lags behind that for 700°C. Hence stable austenite amount is less in case of 650°C.

In case of alloy 2 which contains boron, the carbides are present in form of $(\text{Fe,Mn})_3\text{C}$. Therefore increasing holding time increases the amount of austenite formed, which is essentially rich in carbon. This is true for both equilibrium and paraequilibrium austenite.

Equilibrium austenite enriches with carbon taken from pearlite and paraequilibrium austenite forms at a later time when isolated carbides are formed. Moreover boron increases the hardenability and assists in bainite formation. Hence both strength and ductility increase with increasing...
annealing time. The lower strength level of alloy 2 is due to the absence of microalloys which tends to precipitation harden the matrix. Since paraequilibrium austenite formation envisages the conversions of TiC in alloy 1, its kinetics is slow owing to slower diffusion of titanium. Therefore amount of paraequilibrium austenite is more in alloy 2 under identical heat treatment and this is responsible for higher ductility in alloy 2. The very low strength level in boron treated alloy intercritically annealed at 650°C is due to the fact that the austenite formed here is only of high manganese and high carbon containing. In both cases the elongation is maximized at 400°C rather than when austenite is reacted at 350°C. This is due to the fact that when austenite is reacted at 350°C, carbide precipitation takes place along with bainite formation. The bainite formed at this low temperature is also more densely dislocated. These are why the total ductility is less than when the alloy is intercritically annealed at 650°C. At a very high reaction time both strength and ductility is reduced because, for a very high holding time, the amount of retained austenite is reduced. This leads to a decrease in total elongation and the dislocation recovery in already formed bainite during isothermal holding, lowers the strength properties. This dual decrease cannot be explained unless it is accepted that a considerable portion of total ductility is contributed by strain induced \( \gamma \rightarrow M \) transformation. But for this, strength decrease would have been accompanied by an increase in total ductility. It has been discussed earlier that austenite formed in alloy 2 is essentially richer in manganese content because either the high manganese austenite forms by a competitive process or the paraequilibrium austenite, very rich in manganese and carbon is formed in this case. The effect of manganese is giving rise to discontinuous yielding is noticed earlier and was attributed to the formation of Mn–C complex at dislocations. Also in alloy 2, due to presence of boron, the microstructure is dominated by granular bainite and acicular bainite of high dislocation density. The absence of microalloy has always envisaged a higher availability of carbon to enrich austenite whereas some un-dissolved titanium carbides or titanium carbosulphides always reduce the available carbon content of steel for subsequent metallurgical reactions. This means that during the course of isothermal reaction a good amount of precipitates are formed onto the dislocations in bainitic ferrite. Notwithstanding the composition of precipitates, TEM study makes it very obvious that fine precipitates are present in the bainitic ferrite thereby pinning the dislocations. Boron has the similar effect of getting segregated at grain and sub-grain boundaries and likewise impedes dislocation motion by pinning them. The shape of instantaneous ‘n’ vs. true strain curve indicates a continuous rise in work hardening rate. Though it is advocated that retained austenite is needed to be moderately stable to give rise to \( \gamma \rightarrow M \) strain induced transformation at or near uniform elongation the present results show that it is more important that transformable retained austenite is available over a wider range of strain. This means that plastic stability of retained austenite should be spread over a larger range of true strain values so as to ensure a good ductility enhancement.

5. Conclusions

Higher annealing temperature or higher annealing time at low annealing temperature gives rise to formation of higher amount of second phase. In these cases retained austenite has more manganese content, hence more manganese partitioning has occurred. For shorter annealing time, the manganese partitioning is less and needle shaped transformed ferrite is formed. Titanium forms titanium carbosulphides. The enrichment of manganese in retained austenite is dependent on intercritical annealing time and temperature and it is less influenced by bainitic reaction temperature. Retained austenite formed at low annealing temperature and higher holding time is more stable due to manganese partitioning and hence TRIP will be better induced in duplex ferritic bainitic steel in such cases.

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