Understanding the role of aluminium in low level nitrogen steels via microstructural characterisation

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Abstract. The mechanical and microstructural properties of steels can be affected by dopant elements or the presence of impurities. Aluminium has historically been added to steels principally as a de-oxidant but it has also been shown to have a significant effect on the mechanical properties. It is well known that aluminium usually combines with nitrogen to form AlN precipitates at high temperature mostly in austenite (dependent on the relative concentrations of Al and N). Aluminium therefore acts as a grain refining element. A series of low carbon, low nitrogen steels have been prepared with varying additions of aluminium up to 1 wt%. These changes in properties of the steel cannot be attributed to the presence of aluminium nitride and hence it important to understand the specific role and mechanism which the aluminium plays. The location, concentration and chemistry of the aluminium have been investigated using SEM and TEM. The results show clear evidence for segregation of aluminium to the grain boundaries.

1. Introduction
Aluminium traditionally has been used almost exclusively as a grain refining or deoxidising element in steel in amounts rarely exceeding 0.01 to 0.07 wt%, except in specialised steels for nitriding or forging applications. However, recent research has shown that Al additions used as a specific alloying element can improve strength by solid solution strengthening and modify toughness by processes such as solid solution softening (1). There is also great commercial interest in Al additions, of the order of 1-2 wt%, to high strength low carbon strip steels to produce a highly desirable dual phase microstructure containing retained austenite for cold forming applications (2,3) for which a coarse grained structure is desirable. These steels rely on conventional strip mill processing to produce a microstructure of ferrite, austenite and martensite which can then be used to develop a combination of high strength and ductility by transformation-induced plasticity (TRIP), i.e. transformation of austenite to martensite during plastic deformation, for optimum forming response. However, inappropriate processing of such steels is known to produce a ferrite/martensite microstructure with very poor formability behaviour and toughness. A recent review of this type of steel (4) concluded that there is much to learn about the design of such steels particularly in regard to the role of Al on transformation behaviour. The effects of Al on transformation behaviour are not well understood and therefore developing optimum mechanical properties of these TRIP steels has remained entirely empirical. In seeking an understanding of the role, in particular, of Al on the transformation behaviour, analytical FEG-TEM

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and HRTEM studies of the behaviour of Al during transformation to ferrite are being undertaken and this paper reports some preliminary findings on the segregation of Al to interfaces.

2. Experimental Methods
To investigate the influence of aluminium in steel, steels of differing aluminium composition were prepared (50 kg) in a laboratory vacuum melt furnace and hot rolled to 13mm thick plate. The finish rolling temperature was in the range 1000-970 ºC. The level of nitrogen was kept as low as possible to avoid the formation of aluminium nitride precipitates. The chemical compositions of the alloys are shown in Table 1. To understand the role of the aluminium in the steels, the following series of two heat treatments were designed and carried out:

1. Austenitising at 1050 ºC for 20 min and cooling at 0.75 ºC s⁻¹ down to 600 ºC and then oil quenching
2. Reheating to 950 ºC for 20 min and then cooling to 595 ºC and holding for 20 min and oil quenching

Heat treatment 1 was designed to show the effect of aluminium on the transformation behaviour. Heat treatment 2 was carried out to promote aluminium segregation to grain boundaries. Following heat treatment 1, the specimens were polished and then etched using nital and picric acid. Light microscopy and SEM, in secondary electron imaging mode, were used as a first step to reveal the effect of aluminium on the microstructure. TEM techniques were further used to investigate the role of aluminium on microstructure on a finer scale for samples having undergone heat treatment 2. Thin foil specimens were prepared by twin jet electro-polishing using a solution of ethanol, 2-butoxyethanol and (60%) perchloric acid (6:2:1 by volume). The polishing temperature was - 12 ºC at a voltage of 15 V. Prior to electro-polishing, chemical polishing was performed to obtain a smoother surface for the thin foils. A Philips CM20 TEM operated at 200 kV and equipped with an ultra thin window energy dispersive X-ray spectrometer (EDX) system (Oxford Instruments ISIS) was used.

Table 1. Steel compositions (wt %)

|    | C  | Si  | Mn  | P    | S     | Al   | N   |
|----|----|-----|-----|------|-------|------|-----|
| C1 | 0.11 | 0.28 | 1.4 | 0.001 | 0.0008 | 0.02 | 0.001 |
| C2 | 0.11 | 0.28 | 1.4 | 0.001 | 0.0008 | 0.48 | 0.001 |

3. Results and discussion
Light microscopy and secondary electron images of alloys C1 and C2, held at 1050 ºC and continuously cooled to 600 ºC and oil quenched, are shown in figures 1 and 2, respectively. This heat treatment should in principle result in a fully transformed ferritic microstructure if sufficient time is given. However, it is expected that kinetic limitations will result in a partially transformed structure. Significant differences are observed between the two microstructures from the alloys with different aluminium content. Figure 1 shows a semi transformed microstructure with martensite (M) surrounded by ferrite (F) grains. Aluminium is known to delay the kinetics of the austenite/ferrite transformation (5) and hence it was expected that alloy C2 (0.48% Al) would have a more austenitic structure. Figure 2, which shows the Al added steel microstructure, illustrates a finer and more transformed structure (there is approximately 50% ferrite in C1 and 70% ferrite in C2) and also some elongated grains with acicular ferrite within a martensite matrix leading to more rough interfaces. It is believed that this microstructure is a consequence of the segregation of aluminium to ferrite/austenite grain boundaries. This has been previously shown for steels with lower levels of added aluminium (6).
Figure 1. Alloy C1 held at 1050 °C and continuously cooled to 600 °C and oil quenched (F: ferrite, M: martensite). Light microscopy, left. SEM, right.

Figure 2. Alloy C2 held at 1050 °C and continuous cooled to 600 °C and oil quenched (F: ferrite, M: martensite). Light microscopy, left. SEM, right.

Figure 3. (a) EDX from within the grain, (b) EDX from the grain boundary for alloy C2 (CM20 TEM)

It is well known that AlN precipitates can affect the microstructure when they are located at the grain boundaries where they suppress grain boundary growth and promote grain refinement. This is one of the main reasons for the deliberate addition of Al to steels. Imaging within the TEM showed that the investigated grain boundaries in these steels were ‘clean’ i.e. there was not any second phase or precipitation present. This is to be expected given the very low levels of nitrogen in the steels. However, aluminium nitride can form even at these low nitrogen levels and a limited number of precipitates were observed; these were found to be within the grains rather than at the grain
boundaries. It should be noted that because of the relative levels of Al and N, the difference between the Al and Al free steels’ microstructure can not be a consequence of aluminium nitride.

Figures 3a and 3b show the TEM EDX results, obtained in the steel which had undergone the additional heat treatment, number 2, to promote segregation, from within a ferrite grain and a ferrite-ferrite grain boundary, respectively. Elemental quantification of the spectra using Al K and Fe K from within the grains was consistent with the bulk alloy composition (0.48 wt% Al, 0.96% at%). There is clearly a higher aluminium concentration at the grain boundaries for the higher Al composition alloy (C2); the aluminum to iron atomic ratio at the grain boundary is 0.015 while 0.5 m away from the grain boundary and within the grain it is 0.0082. This is consistent with the expected segregation towards the grain boundaries. It should be noted that the analysis spot size used was large (approximately 50 nm) which greatly limited our ability to detect the segregant elements and hence deduce an accurate model for the grain boundary composition. However, these aluminium levels have been estimated to be consistent with a grain boundary composition of approximately 1.5 monolayers. Having established that segregation of aluminium is taking place, further TEM will be undertaken using a CM200 FEG-TEM offering higher spatial resolution EDX and EELS analysis.

4. Conclusion:
The initial results show the influence of aluminium on the transformation temperature and transformation behaviour. There is some evidence to prove that aluminium can affect the ferrite/austenite interface and this is suspected to be a result of aluminium grain boundary segregation. The results show that in addition to the influence of aluminium on the steels’ microstructure and mechanical properties as a precipitant forming element (e.g. AlN), aluminium is also able to act as solute element. Little attention has been paid to this aspect of the role of aluminium in steels and its potential significant effect on the microstructure. Based on initial results, it was found that aluminium can segregate to the grain boundaries and can affect the type of interface between ferrite and martensite. However, further more detailed nanoscale analytical investigations are required to fully understand the specific role aluminium plays in affecting the mechanical properties.

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