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Influence of Cu and Ni on the Hot Ductility of Low C Steels with Respect to the Straightening Operation When Continuous Casting

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Abstract: Cu-containing steels can suffer from hot shortness unless Ni is added to protect them but whether this problem also influences the straightening operation is not clear. Previous work on hot ductility has found that only when the tensile samples from Cu-containing steels are oxidised can any deleterious influence of copper be found. However, this paper shows that oxidation is not essential. It is more complex than that and, as Cu has been suggested for TRIP steels at levels up to 2.5% Cu to increase their strength and ductility, a greater understanding is required, both of hot shortness and cracking during straightening. The present paper explores the hot ductility behaviour of steels alloyed with Cu and Ni in the straightening temperature range, 700–1000 °C, when tested in air and in an argon atmosphere. Segregation of Cu to the sulphides and grain boundaries occurred allowing the formation of fine Cu_2S particles at the austenite grain boundaries favouring intergranular failure and this was more pronounced under oxidising conditions and required strain. It was concluded that a Cu addition, as well as causing hot shortness at higher temperatures will also cause cracking problems in the straightening temperature range in the more sensitive to cracking grades of steel and although the problems are different they are nevertheless interrelated and provided there is sufficient Ni, both may be avoided.

Keywords: Cu; Ni; HSLA; steel; hot ductility; straightening; hot shortness

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1. Introduction

Copper is a particularly troublesome contaminant since it is not possible to remove it from the molten steel and, hence, all the copper entering the furnace will be present in the final alloy [1]. As copper is more noble than iron, it is not oxidised in the hot processing route and, while iron is removed with the scale, molten copper concentrates in the external surface and penetrates into the steel's austenite grain boundaries, producing cracks [2]. Consequently, the copper content of scrap needs to be strictly controlled, thereby limiting the extent to which copper contaminated scrap can be recycled. However, environmental pressures are forcing an increased use of steel scrap in both electric-arc furnace and oxygen processing routes. Therefore, there is a need to assess how detrimental residual levels of Cu and actual additions are to the hot ductility and what can be done to ameliorate the problems of hot shortness on rolling and when the strand is straightened, cracking during continuous casting. Most Cu containing steels such as weathering steels are low in Cu (0.3–0.5% Cu) [3], (all the element percentages given in this paper are weight per cent.) and generally, this problem of hot shortness is solved by adding Ni in the ratio of 1 Ni = 2 Cu so that the solubility of Cu in austenite is increased preventing its precipitation [4]. Si additions, by limiting oxidation through scale protection, can also be of help in preventing surface cracking and reducing the amount of Ni required [5]. In TRIP (transformation induced plasticity) steels, higher Cu additions have been suggested and since Ni is an expensive addition to make, such additions [6–9] have to be treated with caution. Cu and Ni are both austenite stabilisers [7–9] and also increase hardenability, so are of great interest for TRIP steels, which rely on the presence of austenite at room temperature, so that the austenite/martensite transformation can take place on deformation. Cu has also been considered for adding to TWIP (twinning induced plasticity) steels, which are austenitic for similar reasons [6,10]. With TWIP steels, as with TRIP, if transformation takes place too early at room temperature under deformation, either to martensite or twins, the work hardening rate becomes too high to maintain a uniform elongation and failure occurs. Cu additions give a more gradual decrease in the work hardening rate so that greater elongations can be obtained. The higher stacking fault energy on adding Cu promotes cross slip, thus reducing the strain hardening rate. There is therefore a need to assess the influence of higher Cu and Ni additions on hot ductility for the straightening operation when continuous casting and for hot shortness when hot rolling [6,10].

The susceptibility of steel to crack initiation and growth during the continuous casting of steel is often assessed by measuring hot ductility in a tensile test conducted at the temperatures the steel experiences during continuous casting or hot rolling. Hot ductility of steel is usually presented as a curve of reduction in area (*RA*) plotted against the testing temperature. For low C steels, including the TRIP steels, the curves show a ductility trough in the temperature range between the Ae_3 and Ar_3 temperatures and this range, unfortunately, normally covers the straightening temperature range, 700–1000 °C. This loss of ductility is attributed to the formation of a thin film of deformation induced ferrite on pre-existing austenite grain boundaries and often is formed over the entire transformation range between Ae_3 and Ar_3. This range can span over 200 °C [11]. On deformation, the strain concentrates in this softer ferrite film surrounding the austenite grain surfaces, leading to crack initiation at the MnS inclusions and carbo-nitride precipitates and subsequent propagation along the grain boundaries and eventually to inter-granular ductile fracture. It is often taken that provided the *RA* value is ≥35–40%, cracking will not occur on straightening [12].

Fortunately, the hot tensile test is very simple to carry out and even though it has many faults in representing the straightening operation, it generally provides a reasonable simulation of the high temperature behaviour of steel and the likelihood of cracking occurring during the straightening operation when continuous casting.

In the case of Advanced High Strength steels (AHSS) such as TRIP and TWIP, these are often difficult to cast and corner cracking on straightening is a common problem [13,14]. This makes information from the hot ductility test very useful in choosing the most suitable compositions and controlling the straightening temperature so it takes place when ductility is most favorable.

Cu is considered to be a good addition to make to TRIP and DP (dual-phase) steels because, in addition to stabilising the austenite so that higher elongations and strength can be attained [15], it also has a moderate solid solution hardening effect and can grain refine by solute drag so retarding recrystallisation. This is combined with a unique effect of precipitating out as ductile copper particles which can give considerable strengthening and improve the fracture toughness when age hardened at 400–500 °C [16,17]. For example, an addition of 2.5% Cu to a 0.2% C, 1.75% Mn, 1.5% Al, 0.5% Si TRIP steel, hot rolled and inter-critically annealed at 800 °C, can increase the yield strength by ~250 MPa and the tensile strength by ~300 MPa [6] with only a small decrease in elongation [6]. However, with these higher additions of up to 2.5% Cu, as have been suggested, more Ni is generally required to prevent hot shortness.

The present paper has been designed to explore the hot ductility of steels alloyed with Cu and Ni when tested in an argon atmosphere and compared with previous work [18] in which samples were tested in air but concentrates mainly on the straightening operation rather than hot shortness. Moreover, although the paper is devoted to plain C-Mn and HSLA steels (high strength low alloy) which have very different room temperature properties to the AHSS steels, because TRIP steels are low C they also have a hot ductility trough caused by the thin film of ferrite. This means most of the hot ductility behaviour from these lower strength steels can also be applied to TRIP steels.

2. Experimental

For the compositions of the steels examined, wt.% are given in Table 1.

Table 1. Compositions of the steels examined, wt. %.

Steel	C	Si	Mn	P	S	Al	Cu	Ni	Ti	N
1	0.11	0.2	1.18	0.020	0.007	0.031	-	-	-	0.005
2	0.12	0.2	1.18	0.021	0.006	0.033	0.49	-	-	0.005
3	0.12	0.2	1.18	0.023	0.006	0.038	0.49	0.33	-	0.004
4	0.12	0.2	1.18	0.021	0.006	0.038	0.49	0.49	-	0.004
5	0.10	0.23	0.5	0.020	0.002	0.045	0.10	-	0.006	0.006
6	0.11	0.23	0.5	0.020	0.002	0.043	0.48	-	0.006	0.006

Steels, 1–6 were laboratory air melts. Steels 1–4, were plain C-Mn steels. Steel 1 had no nickel or copper and was used for comparison purposes. Steels 2–4 had a standard Cu addition of 0.5% Cu with varying Ni additions from 0 to 0.5%. Steels 5 and 6 were very low Ti containing steels having 0.1 and 0.5% Cu, respectively. After casting they were forged into plates and tensile samples were machined from the short direction. All testing was carried out protected from oxidation with an argon atmosphere. A Gleeble 1500 thermo-mechanical simulator was employed to determine the hot ductility, defined as the reduction of area (*RA*) in the tensile test. The tensile specimens were rods of 120 mm length and 10 mm diameter. In the case of steels 1–4, the specimens were heated at 25 °C/s up to the melting temperature, a length of 15 mm in the middle part of the specimen being supported by a close-fitting silica tube 60 mm in length. Subsequently, the specimens were directly cooled to the test temperature at cooling rates of 25 °C/min and 200 °C/min held for 15 s and finally strained to failure at a strain rate of 5×10^{-4} s^{-1}.

For steels 5 and 6 the samples were only heated to 1330 °C held for 1 min, cooled to the test temperature and held for 3 min before being strained to failure at the same strain rate of 5×10^{-4} s^{-1}. The cooling rates used for steels 5 and 6 were 25 °C/min and 100 °C/min so as to vary the size of carbo-nitrides and sulphide inclusions. Tests were repeated for two or three times at temperatures between 800–1000 °C and the mean values of RA at each temperature were used when plotting the data.

Selected areas were submitted for electron microscopy (scanning and transmission) and Electron Probe Microscopy Analysis (EPMA). Carbon replicas were taken close to the fracture etched by a 2% nital alcohol solution. The replicas were examined by an electron energy filtered, scanning transmission electron microscope (Carl Zeiss LEO 912, Oberkochen, Germany) and the composition of precipitates were analysed by the EDS (electron dispersiveX-ray spectroscopy) device attached. For some specimens, the size distributions of the numerous precipitates were analyzed by using the "Soft Imaging System" software of EFSTEM.

3. Results

The hot ductility curves for the in-situ cast tensile specimens, steels 1–4 in Table 1 are given in Figure 1 and show that, under slow cooling conditions, 25 K/min, the Cu-containing steel 2, has the worst ductility but adding Ni, steels 3 and 4, 0.3% Ni and 0.5% Ni, respectively restores the hot ductility. Adding 0.5% Cu (steel 2) leads to a 10% lower *RA* throughout the hot ductility curve.

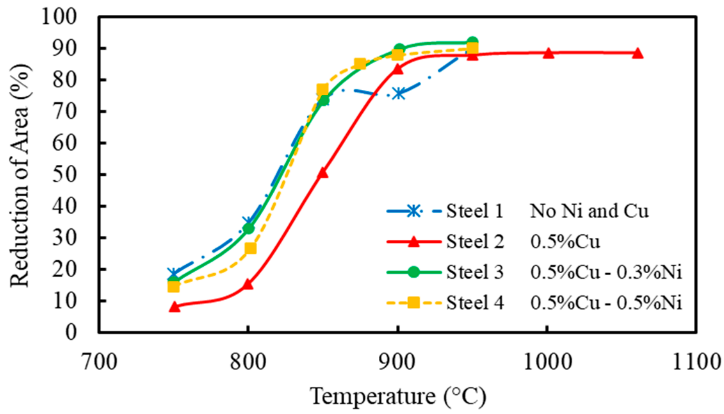

Figure 1. Hot ductility for steels tested under an argon atmosphere at the slow cooling rate of 25 K/min showing that a Cu addition impairs ductility while adding Ni restores ductility.

The influence of cooling rate on the hot ductility of Cu free and Cu-containing steels, 1 and 2, respectively is shown in Figure 2. Increasing the cooling rate from 25 K/min to 200 K/min causes the hot ductility curves for steel 1 and 2 to move to higher temperatures, indicating worse ductility, as is normally found [11] due to a refinement of the inclusions at the austenite grain boundaries. However, at the slower cooling rate, (dashed curves in Figure 2) increasing the Cu content from 0 to 0.5% decreases the hot ductility, whereas at the higher cooling rate (solid curves in Figure 2), there is no significant difference between the hot ductility curves of the two steels. Thus, increasing the cooling rate (solid curves) removes the influence of Cu so that it is no longer detrimental to the hot ductility. A similar behaviour with regards to cooling rate is noted in Figure 3 with the low Ti containing steels 5 and 6. Again at the slower cooling rate 25 K/min, (dashed curves in Figure 3) the higher Cu addition (0.5% Cu) can be seen to have a detrimental influence on ductility in the trough, reducing the *RA* values by ~10% in the temperature range 750–875 °C. Behaviour at the high temperature end of the trough where dynamic recrystallisation (DRX) takes place is not as yet understood but this region is not of consequence for the straightening operation [12]. DRX is not possible on straightening because the strains are too low (1–3%) and the as-cast grain size too coarse [12]. However, increasing the cooling rate (solid curves in Figure 3), this time to 100 K/min, results, as before, in Cu having no influence on the hot ductility curves (solid lined curves in Figure 3).

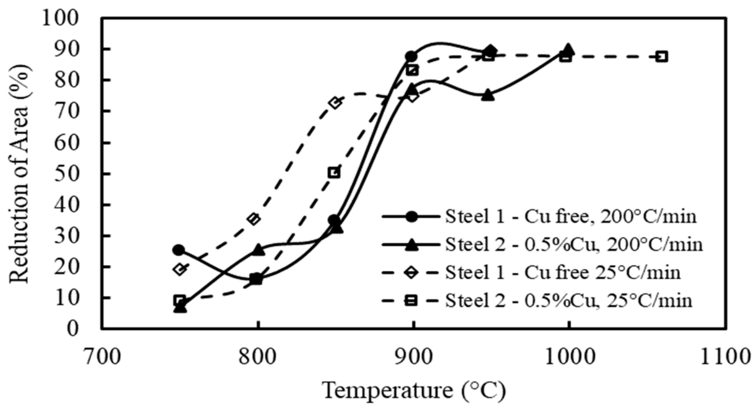

Figure 2. Hot ductility curves for a Cu free steel, steel 1 and a Cu-containing steel, steel 2, tested using two different cooling rates, 25 K/min and 200 K/min in an argon atmosphere,. The tensile specimens were cast in-situ. It can be seen that Cu only causes impairment of ductility at the slower cooling rate.

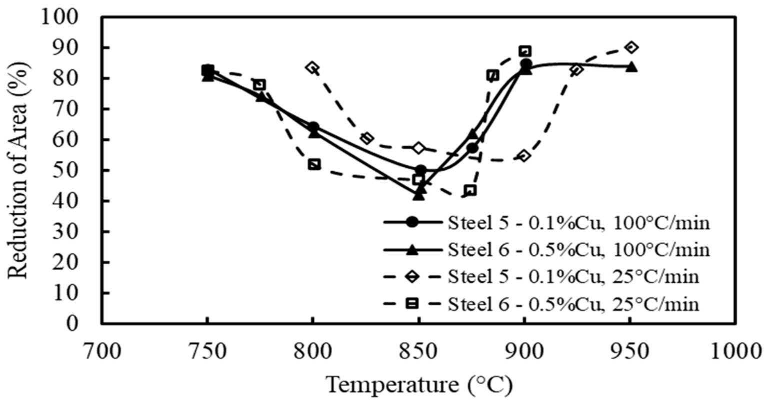

Figure 3. Hot ductility curves for low Ti (0.006%) "microalloyed" steels, steels 5 and 6 having residual Cu and ~0.5% Cu, respectively, tested at two different cooling rates, 25 K/min and 100 K/min.

Examination of the replicas taken from 0.5% Cu containing steels, steels 2 and 6, which had been tested in an argon atmosphere found fine Cu_2S precipitates at the austenite grain boundaries, Figure 4, as well as high Cu-containing rims around the MnS inclusions, Figure 5. The fine copper sulphides found in Figure 4a–c are very similar to the Cu_2S precipitates at pre-existing austenite grain boundaries found in the previous work [18] for a similar steel tested in air (in which no Cu_2S precipitation occurred when the testing was carried out in an argon atmosphere), Figure 4c, indicating that oxidation during testing is not essential for Cu_2S to form. The precipitates in Figure 4a–c were all copper sulphides and they were either rod or globular shaped. It is assumed that the precipitates are located at the austenite grain boundaries. The Cu enrichment in the rim in Figure 5 was analysed to be 3–5%.

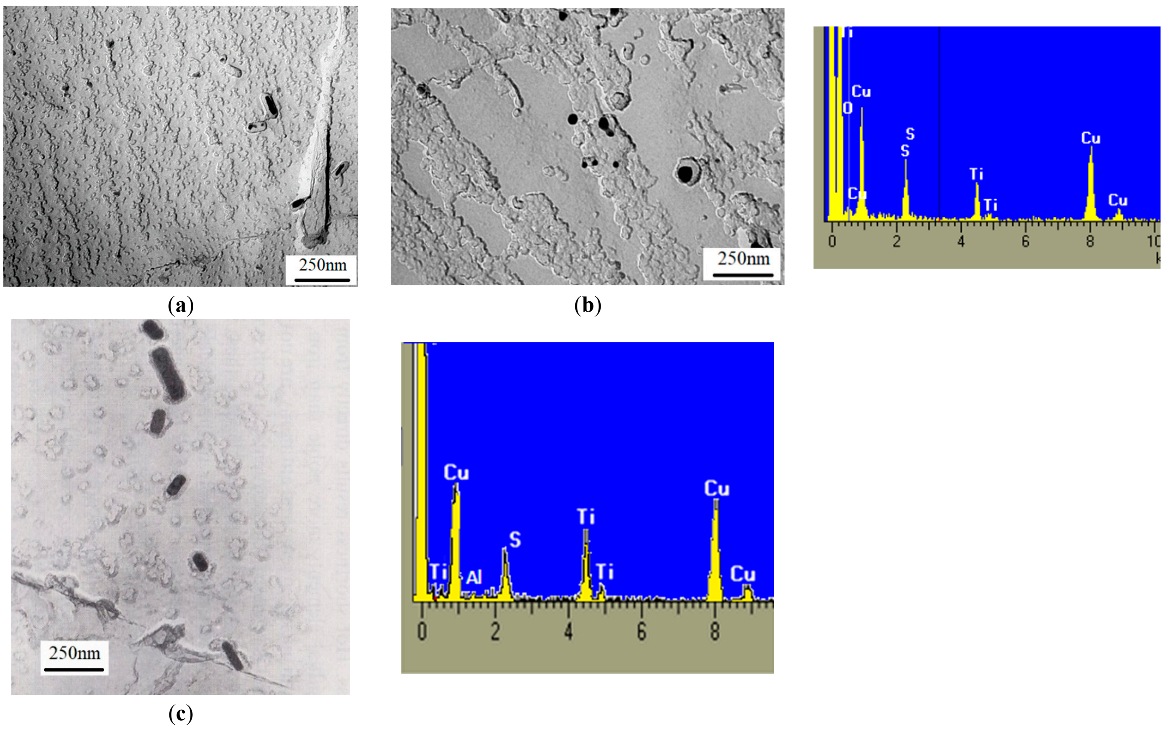

Figure 4. (**a**,**b**) Examples of Copper sulphide inclusions found along pre-existing austenite grain boundaries in Steel 2, hot tensile tested at 800 °C in an inert atmosphere and cooled at 25 K/min with EDAX analysis. (Ti grid), (**c**) Similar steel with 0.5% Cu taken from previous work [18] tested in air but at a faster cooling rate 60 K/min showing the same precipitation, this being absent when tested in an inert atmosphere.

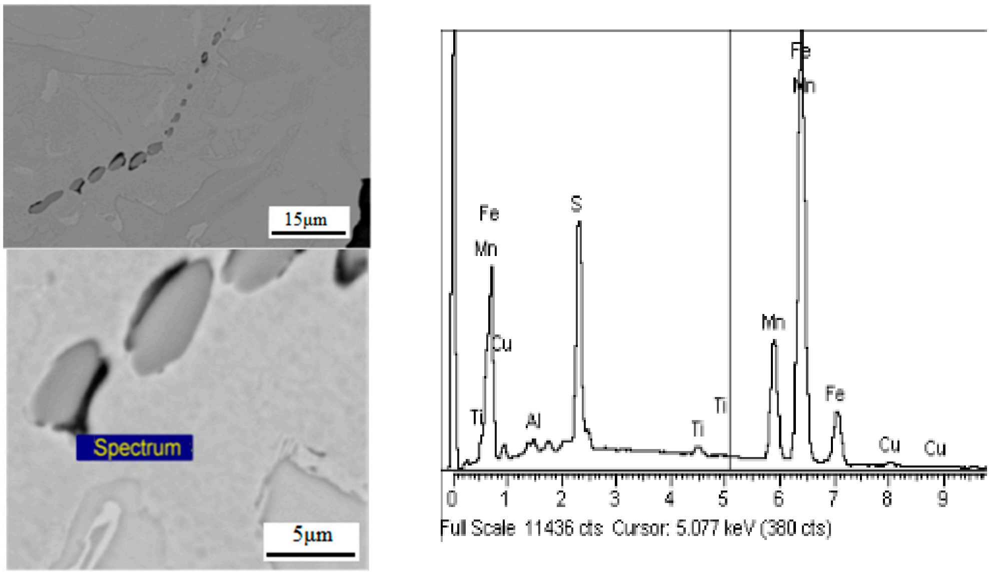

Figure 5. Line of MnS inclusions situated at pre-existing austenite grain boundaries, which have a high Cu rich rim (black areas) round the periphery of the manganese sulphide inclusions, Steel 2 (0.5% Cu) tested at 800 °C.

4. Discussion

Few experiments have been carried out to explore the influence of Cu on the hot ductility of Cu-containing steels in the straightening temperature range. Hannerz [19] has probably examined the influence of Cu on hot ductility most comprehensibly by relating his laboratory tensile testing results with Works data on cracking. He examined additions of Cu up to 1% in a 0.07% C, 1.5% Mn, plain C-Mn steel and showed there was no significant influence of Cu on hot ductility in the straightening temperature range 600–1000 °C when the tensile samples were tested in an inert atmosphere. In his work, the tensile specimens were solution treated at 1330 °C and cooled at 60 K/min to the test temperature. This behaviour contrasted very much with the Works data which clearly showed that residual Cu could cause poor surface quality and cracking, indicating that the testing procedure needed modifying to include an oxidising atmosphere, as is present commercially [19].

Later work by Mintz et al. [18] repeated Hannerz's work establishing the effects of Cu and Ni on hot ductility of plain C-Mn steels using both air and argon atmospheres for the testing media.

Using the same solution temperature ~1300 °C and cooling rate that Hannerz used of 60 K/min, again, no influence of Cu on hot ductility could be found. Only when oxidation was introduced and the tensile specimens were cast directly and tensile tested in air, so that the conditions were more in keeping with the continuous casting operation, did the ductility deteriorate. Under these conditions, a Cu addition of 0.5% decreased the hot ductility in the straightening temperature range in both plain C-Mn and C-Mn-Nb-Al steels but was restored with a similar Ni addition (0.25% Ni, 0.25% Cu), Figure 6. No evidence for Cu rich films penetrating along the austenite boundaries could be found, ruling out the conventional hot shortness as an explanation. The deterioration, however, could be explained by the observation of fine copper sulphides (or oxysulphides) at the austenite grain boundaries, 50–70 nm in size, as found in the present work, as shown in Figure 4. In the previous paper [18] it was suggested that the Cu_2S precipitates in Figure 4a–c formed by the MnS inclusions reacting with Cu in the presence of oxygen to form Cu_2S on cooling, probably according to the reaction in Equation (1) [2]:

$$2MnS + O_2 + 4Cu = 2Cu_2S + 2MnO \quad (1)$$

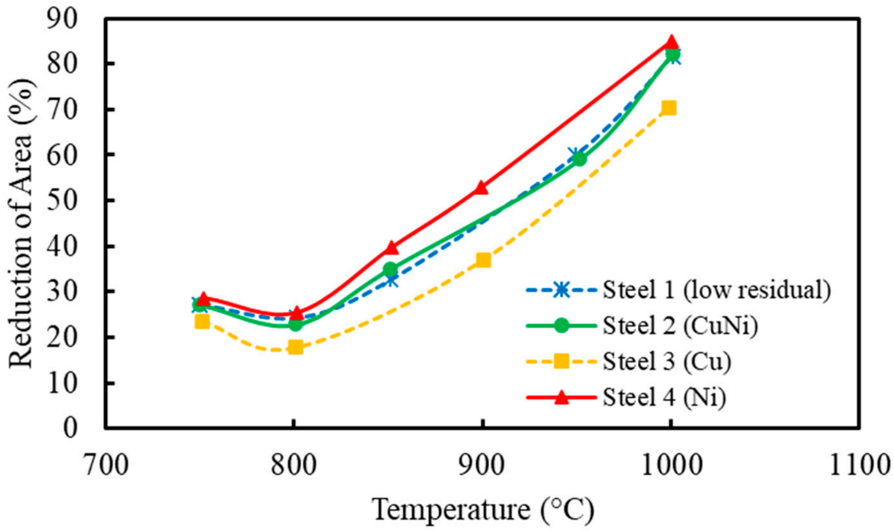

Figure 6. Hot ductility curves for as-cast tensile specimens of C-Mn-Al-Nb steels tested in "air" (argon flow discontinued). Steel 1 has the base composition, having a residual Cu content with no Ni. Steel 2 has additions of 0.25% Cu and 0.25% Ni. Steel 3 has additions of 0.5% Cu and no Ni, Steel 4, additions of 0.5% Ni and no Cu [18].

However, although such a reaction is possible it is unlikely that this reaction could create the pure copper sulphide precipitates shown in Figure 4a-c. The fine precipitates in Figure 4a-c are most likely caused by Cu and S atoms segregating to the boundaries where they combine.

The reaction shown in Equation (1) more likely takes place on the periphery of the MnS inclusions as shown in Figure 5.

Ishiguro et al. [20] have also found a thin coating (300–500 nm thick) of Cu–S complex precipitates on the surface of MnS inclusions even on fast cooling when water quenched at over 500 °C/s. Cu apparently has such a strong affinity for sulphur that it can make Cu–S complex precipitates, even in the short time available during quenching [20].

Thus, although Cu could deteriorate the hot ductility on straightening this was not the conventional hot shortness involving the melting of Cu rich phases. This occurs only on hot rolling rather than straightening, the melting point of Cu_2S being 1130 °C and that of copper, 1085 °C [21]. However, Ni by increasing the solubility of Cu in iron and so reducing the driving force for Cu precipitation, restored the hot ductility for both straightening and hot rolling.

It can be seen from the latest work, Figure 1, that Cu additions to steel can cause the ductility to deteriorate even when tested in an argon atmosphere and is restored with the addition of a similar amount of Ni, provided the cooling rate is slow. The rapid rise in ductility that occurs at the high temperature end of the trough is always due to DRX and Figure 1 indicates that for the 0.5% Cu containing steel, DRX occurs at a higher temperature than for the other steels. This is likely caused either by this fine precipitation of copper sulphide at the austenite grain boundaries preventing DRX or Cu in solution exerting a solute drag on the boundaries, Figure 4a,b [6,18]. This deleterious effect of Cu on hot ductility is different to that found in previous work, where this effect only occurs when the test is carried out under oxidising conditions [18] but the one cooling rate used in the present work which led to Cu deteriorating the ductility was slower, (25 K/min compared to 60 K/min) and this may increase the Cu segregation without the need for marked oxidation. In this previous work [18], no effect of Cu on the hot ductility was noticeable when testing was carried out in an argon atmosphere, either after solution treating or when cast in-situ. This suggests that the oxygen content in the steel in the previous work was too low to allow the Cu content to increase sufficiently for Cu and S to combine.

In the present work the deleterious influence on hot ductility of Cu is again present as shown in Figures 1–3 but the conditions required to show it up in a hot ductility test are very different to those found in the previous work. Whereas oxidation seemed a necessary requirement, the present work shows that an oxidation atmosphere is not always necessary and, secondly, increasing the average cooling rate from 25 K/min to over 60 K/min can prevent Cu from influencing ductility in the straightening operation.

The lack of any effect of Cu on hot ductility when the cooling rate is increased suggests the detrimental influence at the slower cooling rate may be a grain boundary segregation phenomenon and the hot ductility is only influenced when the segregation of copper to the boundaries is high due to the slower cooling rate.

When the changes in *RA* are relatively small, (10% *RA*), as is the case for both Cu and Ni additions, it is generally very difficult to diagnose the cause and past literature then becomes a great help. However, it should be noted that for TRIP steels and steels which have the film of deformation induced ferrite resulting in a ductility trough, these small changes can make all the difference as to whether cracking can occur on straightening [22].

The past work which is most pertinent to the present work is that carried out by Nachtrab and Chou [23]. It is indeed the key paper to giving credence to the foregoing explanations and all the apparently conflicting experimental findings. They examined the grain boundary segregation of the tramp elements, copper, tin and antimony in tensile specimens from commercial casts of plain C-Mn steels after furnace cooling from 1200 °C and straining them at 900 °C. The technique they used for analysing segregation was Auger electron spectroscopy. The copper level in these commercially made casts varied from 0.06% to 0.26% and they found that Cu segregated to the austenite grain boundaries but only when strained. The steel with 0.26% Cu was found to have as much as 4% Cu present at the austenite grain boundaries after straining 10% but no segregation occurred without strain. This finding is very important as the strain at the straightening temperature will favour segregation. It appears that the maximum segregation of Cu can occur when oxidation, strain and slow cooling rates are present together as in the work of Nachtrab and Chou [23] and all of these variables will allow some degree of segregation. Presumably, oxidation is important, as in the same way as in hot shortness it limits the amount of Cu at the surface and is available for segregation.

No difference in hot ductility was found in the present work between the Cu free steel 1 and the 0.5% Cu containing steel 2 for the faster cooling rate of 200 K/min, as shown in Figure 2 in accord with segregation being most likely the important mechanism affecting hot ductility. Cu segregation associated with inclusions was found in SEM analysis of the fractured tensile specimens as shown in Figure 5, this being more enhanced at the slower cooling rate.

Peng et al. [24] have more recently examined the influence on the hot ductility of adding 0.2% Cu and 0.02% Sn to a steel with base composition 0.2% C, 1% Mn, 1% Cr, 0.07% Ti and 0.009% N using an inert atmosphere for the testing media, Figure 7. Sn was found to segregate to the austenite grain boundaries but no segregation of Cu to the boundaries was detected. However, the presence of fine precipitates of copper sulphide was evident and the poor ductility was ascribed to both these particles and the segregation of Sn to grain boundaries reducing the cohesive strength of the boundary favouring intergranular failure. The absence of segregation can be accounted for by the high cooling rate they used, 180 K/min and the relatively small deterioration of 10% *RA*, Figure 7 is probably mostly accounted for by the segregation of Sn to the boundaries.

The other factor that has to be taken into account when interpreting all these contradictory experimental results is that both Cu and Ni additions have been found to coarsen the carbonitrides [25–27].

It is suggested that, in the present work, Cu segregates from the surface to the austenite grain boundaries and precipitates out on MnS inclusions as in Figure 5 or forms Cu_2S precipitates as in Figure 4. Sulphur is also noted for segregating to the boundaries [28,29] so that it is likely that copper and sulphur can combine together forming pure Cu_2S precipitates. In the presence of oxygen, the reaction shown in Equation (1) takes place, which results in coarser sulphides, the MnS inclusions acting as nucleation sites for the precipitation of Cu. In contrast, the Cu_2S precipitation most likely occurs when the segregated Cu and segregated S in solution at the boundaries are high and the two metals can combine without the presence of a MnS as a nucleating site. The enrichment of the periphery of the MnS inclusions by Cu leads to a coarser MnS and with a given volume fraction of MnS inclusions this is equivalent to having the same number of MnS inclusions but effectively coarsening them and this will also favour crack growth.

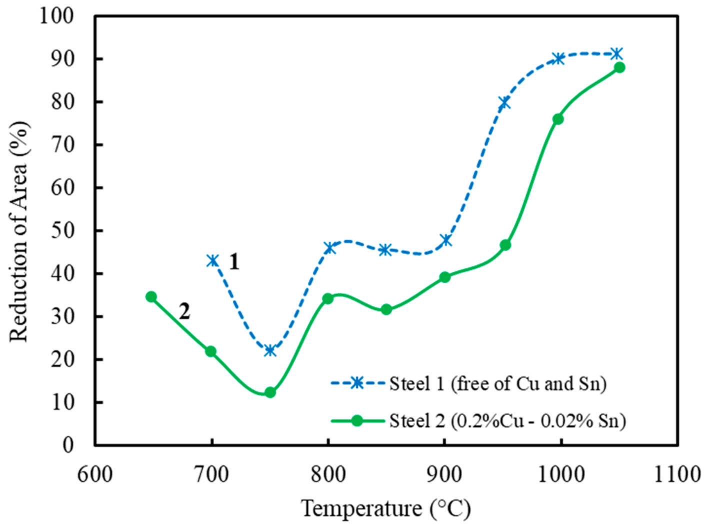

Figure 7. Influence of Cu and Sn on the hot ductility of steels [24].

The presence of these particles and copper rich rims is therefore dependent on the degree of oxidation, cooling rate, strain and the Cu and S content of the steel. Clearly more work is required to confirm this theory. This only occurs if the cooling rate is slow, and time is given for the copper and sulphur to segregate to the boundaries. When strain takes place, the diffusion rate of copper is enhanced, and deformation provides dislocations so that fine precipitation of Cu_2S can take place. Adding Ni, (0.3–0.5%) improves ductility in the same way as it does for hot shortness by increasing the solubility of Cu in austenite and preventing oxidation so that there is no copper available to form copper sulphide.

4.1. Influence of Nickel on Hot Ductility

Previous work, Figure 8 [27,30], more relevant to high strength steels, as shown in Table 2, has been carried out on examining the influence of adding nickel to an HSLA steel having just a normal residual level for scrap copper of 0.01%, steels 7, 8 and 9. The composition of the steels examined, wt. percent. is given in Table 2, the steels having a base composition of 0.1% C, 1.5% Mn, 0.35% Si and 0.03% Nb and 0.015% Ti. The three steels 7, 8 and 9 all had the same residual Cu content but had Ni additions of 0.025%, 0.5% and 1%, respectively.

Table 2. Composition of Ni containing HSLA steels, weight % [30].

Steel	C	Si	Mn	P	S	Cu	Ni	Ti	Nb	V	Al	N	Ti/N
7	0.11	0.35	1.47	0.003	0.005	0.01	0.025	0.014	0.029	0.001	0.04	0.005	2.8
8	0.10	0.34	1.44	0.004	0.005	0.01	0.50	0.014	0.033	0.001	0.04	0.005	2.6
9	0.10	0.39	1.51	0.009	0.006	0.01	1.00	0.011	0.030	0.001	0.03	0.005	2.2

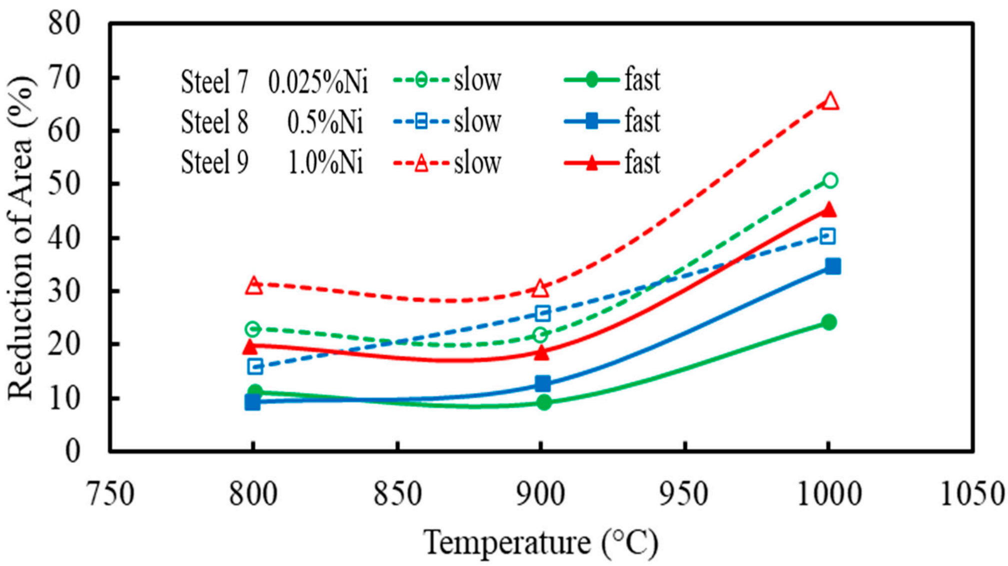

Figure 8. Hot ductility curves for Nb–Ti-containing steels with increasing Ni contents, 0.025%, 0.5% and 1%. Increasing the Ni content and decreasing the cooling rate improve the hot ductility by coarsening the carbo-nitrides [30].

Increasing the nickel content to 0.5%, (steel 8) improved the ductility and a further increase to 1% (Steel 9) gave an even better improvement, Figure 8. Nevertheless, in the temperature range 800–900 °C ductility was still very poor ~30% *RA*, a value below that needed to avoid cracking, normally >40% [21]. However, these results indicate that Ni has a beneficial influence on hot ductility independent of the presence or absence of Cu in HSLA steels. This beneficial effect was ascribed to Ni causing the TiCN precipitates to coarsen, as shown in Table 3, which gives the average size of the Ti(CN) precipitates together with the *RA* value at 900 °C (in brackets). Both, slower cooling and increasing the Ni content result in coarser precipitation.

Table 3. Average particle size, nm of Ti(C,N) precipitates at 900 °C [30].

Steel	Ni %	Slow Cooled	Fast Cooled
7	0.045	15 nm (26% *RA*)	10 nm (13% *RA*)
8	0.5	No Value	12 nm (10% *RA*)
9	1.0	No Value	20 nm (19% *RA*)

Other instances of nickel additions improving hot ductility can be found in Cr containing creep resistant steels [31–33] where its ability to speed up the growth of carbides so coarsening them leads to the ductility improving. The work in Table 3 also shows the same behaviour occurs in HSLA steels.

Here, in Figure 8, the normal influence of cooling rate is seen, decreasing the cooling rate and increasing the Ni content both improving ductility as both coarsen the carbides, Table 3 [11].

4.2. Use of Cu and Ni Additions in AHSS Steel

For AHSS steels, the copper and nickel levels suggested for TRIP steels are and have been based on their ability to improve the properties and are not normally more than 2%.

Work by Allain and Lung [15] has shown that very good room temperature properties can be developed commercially in a hot rolled copper/nickel alloyed, carbon free bainitic TRIP steel. The steel had the following composition; 0.19% C, 1.49% Mn, 1.39% Si, 0.29% Mo, 1.21% Cu, 0.04% Al and 0.95% Ni was added to prevent hot shortness. The design philosophy of this carbide-free bainitic TRIP steel was to have a low C level to assist welding. Si was added to delay carbide precipitation and Mo to ensure that bainite would be produced. This produced a steel, when the coiling temperature was 400 °C, with a tensile strength of ~1050 MPa and total elongation of 16% compared to a similar Cu/Ni free steel with a tensile strength ~900MPa and total elongation of 20%. However, the yield strengths of these steels were relatively low: 500−600 MPa. More recent work [6] has also shown the beneficial influence of Cu in the development of TRIP steels but no Ni was added as part of the composition to combat conventional hot shortness.

However, in the high C, high Mn TWIP steels, Ni additions can give poor hot ductility as Ni causes the solubility of P in austenite to decrease encouraging the low melting point iron phosphide eutectic to form [34,35]. This work again emphasises the need to have a low P content < 0.01 in these high C steels if Ni is added.

Summarising, the evidence is that adding Cu to produce a TRIP steel will cause the hot ductility to deteriorate on straightening but, as with hot rolling, provided sufficient Ni is present there should be no problems. It seems most likely that Cu deteriorates the ductility by segregating to the austenite grain boundaries and the MnS inclusions situated at the boundaries. Provided sufficient Cu is present and enough oxygen, fine Cu_2S particles can form under strain, as well as the growth of original MnS by forming a Cu rich rim. Segregation is favoured with increasing Cu content in the steel and slower cooling rates but to produce these fine precipitates strain is always required. Ni can improve hot ductility in the same way as it does for hot shortness but in addition, by an entirely different mechanism, coarsening the carbides.

Finally, in the high C TWIP steels as well as high carbon levels encouraging the low melting point iron phosphide to form, Ni increases the solubility of P in austenite making it even more susceptible to iron phosphide forming [34,35] so it is important in these steels to always have as low a *P* level as is possible (<0.01% *P*).

5. Conclusions

- Increasing the copper content reduces the hot ductility on straightening probably by copper segregating to the austenite grain boundaries as well as to the MnS inclusions situated at the austenite grain boundaries and this segregation is enhanced by deformation. An oxidising atmosphere adds additional enhancement of the segregation enabling Cu to transfer from the surface to the interior. This segregation, in the presence of an oxidising atmosphere enlarges the MnS inclusions by the Cu nucleating on the MnS inclusions but it can also cause the copper and sulphur to combine directly forming fine copper sulphides precipitates at the austenite grain boundaries. Low S levels are therefore recommended to avoid the detrimental precipitation of Cu_2S.
- The work has shown that segregation of Cu to the boundaries is often needed to cause a cracking problem when straightening and this segregation can be avoided by increasing the cooling rate in the continuous casting operation. However, increasing the cooling rate refines the inclusions and precipitates making any benefit to ductility questionable.
- The fine precipitation of Cu_2S is most likely dynamically induced on deformation at the austenite grain boundaries and will encourage ductile failure in the films of deformation induced ferrite at the boundaries causing ductile intergranular failure. Similarly, a coarsening of the MnS inclusions by the formation of a Cu rich rim on the inclusions will also encourage "ductile" crack propagation.
- It is likely that, if there is enough Cu and S present in solution, fine precipitation of copper sulphide can occur without oxidation and segregation, leading to poor ductility on straightening, whereas oxidation is always needed for hot shortness to occur.
- Nickel additions raise the solubility of copper in the austenite reducing the driving force for precipitation of Cu. It also prevents oxidation so preventing Cu precipitating out in the surface layers which becomes important for both preventing hot shortness and cracking in the straightening operation, but it also in its own right improves the hot ductility in HSLA steels by coarsening the carbides.

- It is believed that conventional hot shortness occurs when the rolling temperature is in excess of 1100 °C by the copper sulphides or Cu rich areas melting at the austenite grain boundaries.
- Cu additions in the more sensitive to cracking grades of steel (steels which have fine dynamically precipitated carbo-nitrides formed on straightening) always need to have a similar amount of nickel present to restore the ductility to what it was before the presence of Cu. The same applies to TRIP steels and provided there is sufficient nickel present should give no problems on straightening or rolling.
- More work is required to establish the influence Cu has on the hot ductility of TWIP steels but the evidence from the literature is that it does cause the hot ductility to deteriorate and again Ni might be beneficial by preventing oxidation and coarsening carbides. However, Ni lowers the solubility of P in austenite encouraging the formation of the low melting point iron phosphide phase and this, combined with the often high C contents of these steels, means it is essential to have very low P level in the steels.

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