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Theme: Ferrous metallic products

INVESTIGATIONS ON THE ROLE OF COPPER IN CAUSING AND NICKEL IN PREVENTING THE "HOT SHORTNESS" IN STEELS*

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Abstract

An extensive investigation into the role of low copper contents on the hot ductility of C-Mn-Al steels has been carried out in order to better understanding the problem of "hot shortness". Previous work has suggested that this problem results from the build up of Cu that occurs at the surface of the steel as a consequence of the preferential oxidation of iron. This causes the formation of a Cu-rich film of low melting point. A nickel addition has been reported as a solution to the problem, since it increases the solubility of copper in the austenite. After hot tensile testing to failure, samples of Cu-containing steels have been examined using optical, scanning and transmission electron microscopes. Recently published results indicate that copper, in addition to precipitating out as CuS, also segregates to MnS inclusions forming a shell around them. This does not seem to impair the hot ductility under an inert atmosphere, but may have serious consequences under an oxidising environment and lead to "hot shortness". The influence of nickel in improving the hot ductility seems to be due to it forming a higher melting point alloy with the segregated copper. Data from this incomplete work also suggests that Ni reduces the precipitation of CuS particles. Current investigation carried out using confocal microscopy still to be completed will improve the understanding of the role of copper and nickel on the problem of "hot shortness".

Keywords: Hot shortness; Weathering steels; Nickel; Copper; Cracks.

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1 INTRODUCTION

The phenomenon of hot shortness has been reported [1] as being due the enrichment of copper in iron under oxidising conditions due to the preferential oxidation of Fe. Under oxidising conditions, that enrichment causes the solubility limit to be exceeded and Cu precipitates out in the austenite grain boundaries. The low melting point Cu rich phase can melt in the normal temperature range for hot processing [2] of the steels and cracks can then form.
More recently [3], it has been found that higher residual copper levels in steel can under certain conditions result in poor surface quality, and an increase in the likelihood of transverse cracking occurring in continuous casting. In this case the problem is not conventional "hot shortness" but it has been found to be due to the fine precipitation of CuS particles reducing the hot ductility of the steel. It is therefore important to establish the maximum amount of Cu that can safely be added to steel and the cooling conditions required to avoid the problem of low ductility. These fine precipitates also reduce the hot ductility and encourage the transverse surface cracking of slabs during continuous casting [4].
Grain boundary precipitate particles, their size and volume fraction, are fundamental in controlling the hot ductility of steels [5]. Fine precipitates with high volume fractions have been reported as being the worst scenario for obtaining good hot ductility. Cooling rate can affect the size and the volume fraction of precipitation [6]. Slow cooling rates coarsen the precipitated particles and thereby improve the hot ductility
The tonnage of steel produced via the electric arc furnace, which uses scrap, has increased considerably as consequence of the environmental pressure for recycling. This means that steel can now have higher levels of residuals such as Sn, As, Sb and Cu. All these elements have been found to have a detrimental influence on "hot shortness" and of these copper is the most notorious and responsible for “hot shortness” that occurs during hot rolling of steels and possibly the higher incidence of cracking during continuous casting .
In addition to the environmental pressure for recycling, copper has been beneficial in improving the toughness behaviour in Thermo-mechanical Precipitation Control Process (TPCP steels) [7] and also the corrosion resistance of unpainted welded structures.
The present work is part of major investigation carried out to understand the influence of Cu in decreasing ductility and the role of nickel additions in it’s restoration. Results [3] from scanning electron microscopy (SEM) and transmission electron microscopy (TEM) examinations have shown that Cu is not homogeneously distributed in the austenite matrix. Cu can precipitate as fine CuS particles in the matrix but it has been also found that it segregates around the sulphide inclusions present in the austenite grain boundaries. This segregation is to be investigated for both inert and oxidising atmospheres.
The addition of nickel has been suggested [8] to be the solution to the cracking problem because of its effect in increasing the solubility of Cu in the austenite. However, in this work the addition of nickel in samples tested under oxidizing conditions has shown that Ni produces an alloy of higher melting point with copper, delaying the formation of the liquid film of copper.

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2 MATERIALS & METHODS - EXPERIMENTAL

Scanning electron microscopy (SEM) examinations have been carried out on five Cu-containing steels. The compositions of the steels are given in Table 1. Samples were machined from the ingot (as cast) and tested in an argon atmosphere either as reheated at 1330°C or cast *in situ* and cooled at the cooling rates of 200°C/min, 100°C/min and 25°C/min and held for 3 min before being strained to failure at a strain rate of $3x10^{-3}$ s^{-1} over a temperature range of 750°C to 950°C. Specimens for SEM examinations were taken from the fracture surfaces as well as longitudinal sections. Some limited work was also carried out to examine the influence of oxidising conditions on the composition of the inclusions and precipitates.

Table 1 - Compositions of the steels investigated (wt%)

	C	Si	Mn	P	S	Al	Cu	Ni	Ti	N
DA0387	0.11	0.23	0.5	0.020	0.0018	0.043	0.48	-	0.005	0.006
DL0096	0.095	0.23	0.5	0.019	0.0016	0.045	0.1	-	0.006	0.006
IL0088	0.12	0.24	1.18	0.021	0.0061	0.033	0.49	-	-	0.0046
IL0089	0.12	0.24	1.18	0.023	0.0059	0.038	0.49	0.33	-	0.0044
IL0090	0.12	0.24	1.18	0.021	0.0062	0.038	0.49	0.49	-	0.0044

3 RESULTS

3.1 Copper Causing "Hot Shortness"

The addition of copper in steels has been found either to produce segregation of copper around inclusions or precipitate out as relatively coarse precipitates of CuS.

3.1.1 Copper segregation around inclusions

The SEM examination and EDS analyses of the fracture showed dimples whose interior contained particles of MnS inclusions surrounded by a thin layer of Cu segregation, Figure 1. Similar examinations in the longitudinal sections near the fracture showed copper segregation in two 0.5% Cu containing steels, at both low and fast cooling rates, as can be seen in the Figures 1 to 5.

3.1.2 CuS precipitation

TEM investigation of carbon replicas taken from close to the point of fracture in the tensile specimens revealed relatively coarse CuS particles, in spite of the steels having a low sulphur content (0.0018%S), Figures 6. The particles, although a few in number, were always relatively coarse. As the precipitates of CuS and the occasional AlN are so coarse, they would not be expected to have any influence on the hot ductility [9].

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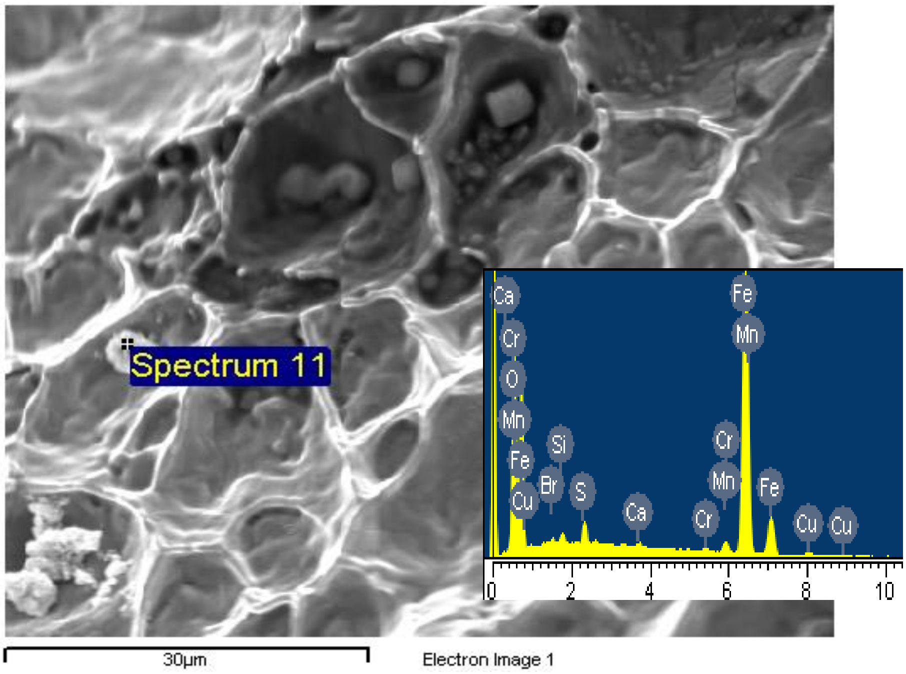

Figure 1 - Cu segregation around Ca/MnS inclusion and respective X ray analysis, 0.5%Cu steel, IL0088, as cast, tested at 25°C/min, 800°C – Reduction of Area 16%.

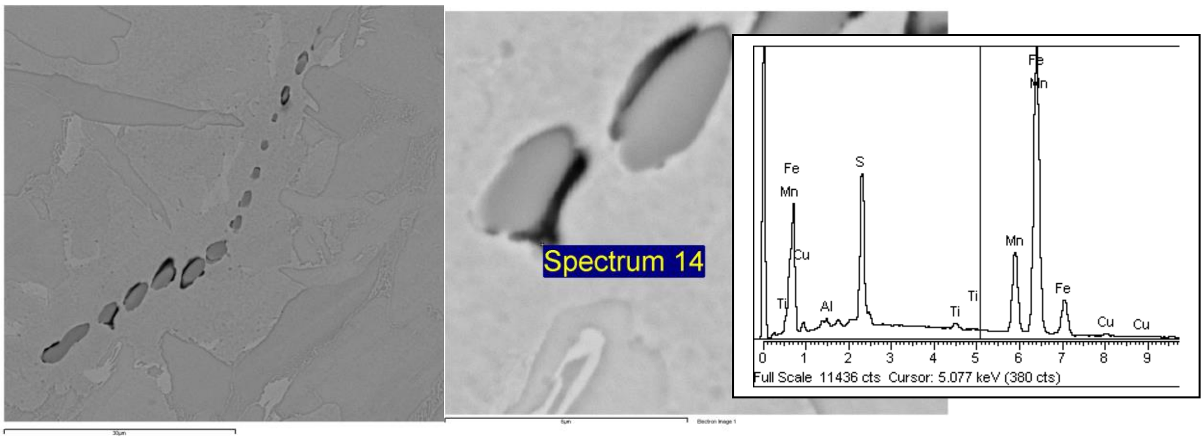

Figure 2 - SEM of same steel (IL0088) and temperature of Fig. 1, but faster cooling rate of 200°C/min. – on left - line of MnS inclusions; on centre - detail showing Cu segregation (~3%Cu) on border of MnS inclusion and - on right - respective spectrum – Reduction of Area 25%

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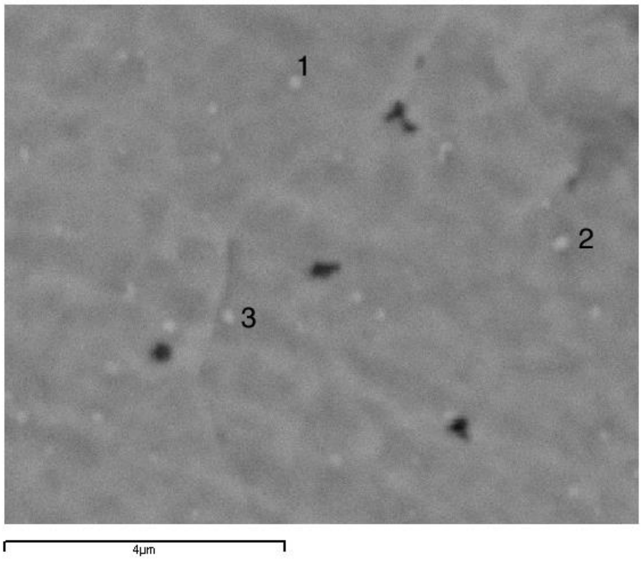

Figure 3 - Cu segregation around inclusions in the same steel (IL0088) as shown in Fig. 1 (~15%Cu average in particles 1, 2 and 3) surrounding CaS/MnS particles in the matrix of 0.5%Cu C-Mn-Al steel, tested at 800°C, Particle size 180 nm; cooling rate 25°C/min (SEM-BEI).

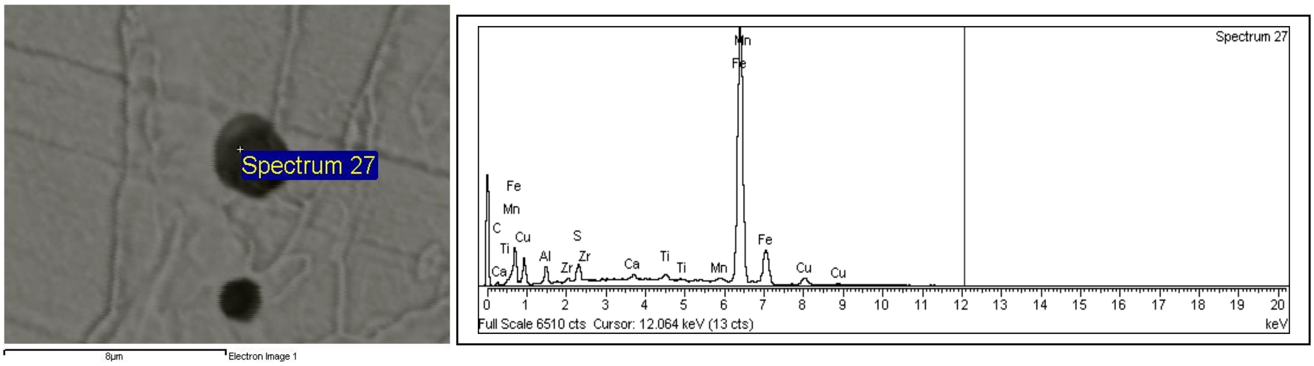

Figure 4 - Cu surrounding a S-containing inclusion (and respective spectrum) (~5%Cu) in the matrix of 0.5%Cu, C-Mn-Al steel (DA0387), tested at 850°C, reheated at 1330°C, cooled at 100°C/min. Reduction of Area 44%.

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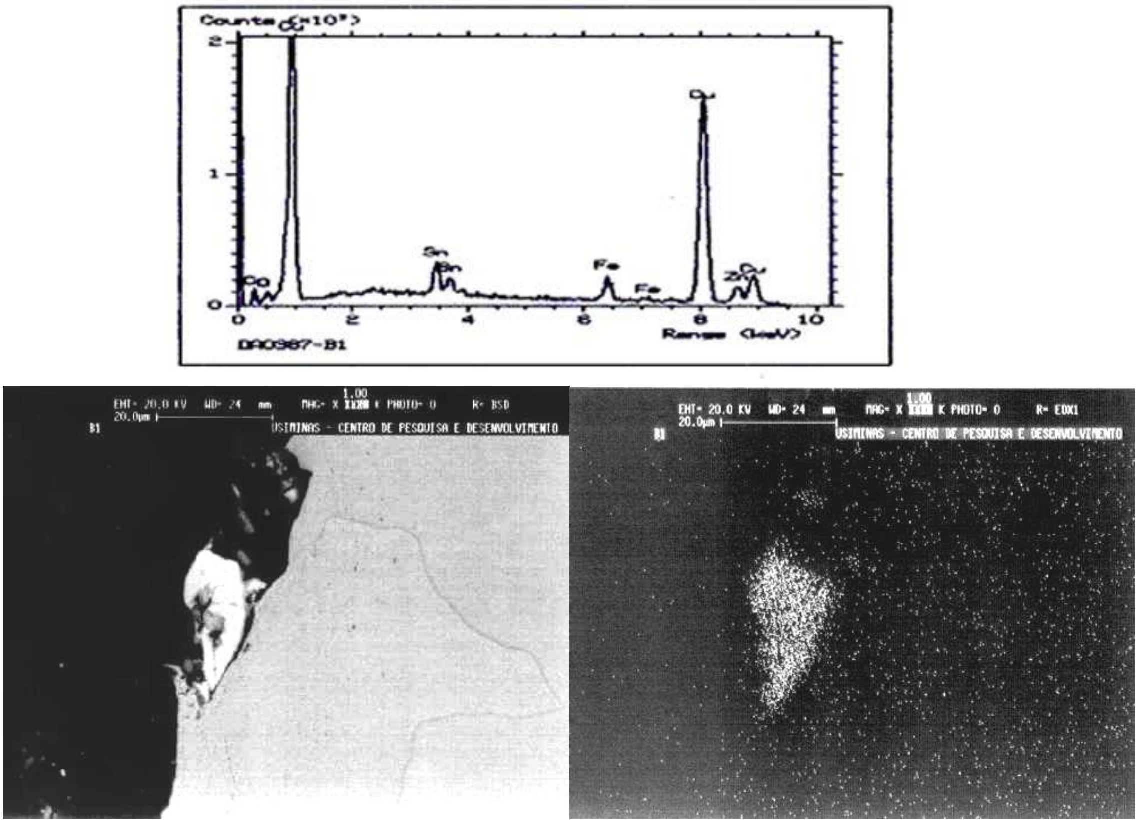

Figure 5 - SEM Cu rich region on the border of the sample of solution treated steel, DA0387, containing 0.5%Cu, CR 100°C/min – Test temperature 800°C – Reduction of Area 62% - 1,000X.

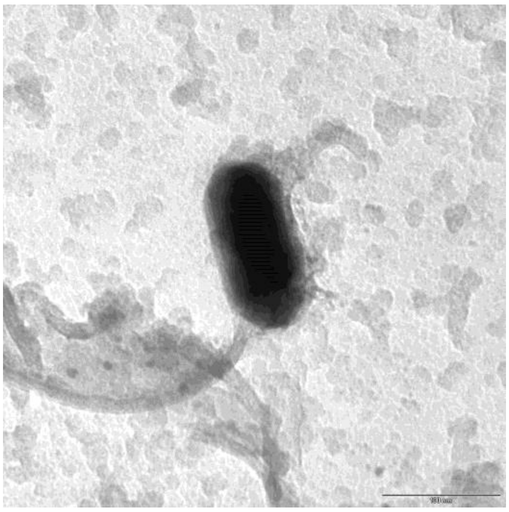

Figure 6 - Coarse CuS particle found in 0.5%Cu steel tested at 100°C/min, 850°C - CuS - PS 100nm; Reduction of Area 44%, 200,000X.

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3.2 Nickel Preventing “Hot Shortness”

3.2.1 Copper-containing steels with a nickel addition (steels IL0089 and IL0090)

The addition of 0.3-0.5 % Ni in similar (0.5% Cu) copper-containing steels, (steels IL0089 and IL0090) also showed copper segregation around the inclusions, Figs. 7 and 8. However, the inclusions seemed to be somehow modified regarding their shape and composition by the addition of nickel, changing from typical MnS to more complex Si containing inclusions, Figs. 7 and 8. Furthermore, the presence of copper around inclusions seemed to be less common in this steel. This may help to explain the role of nickel in counterbalancing the harmful effect of copper.

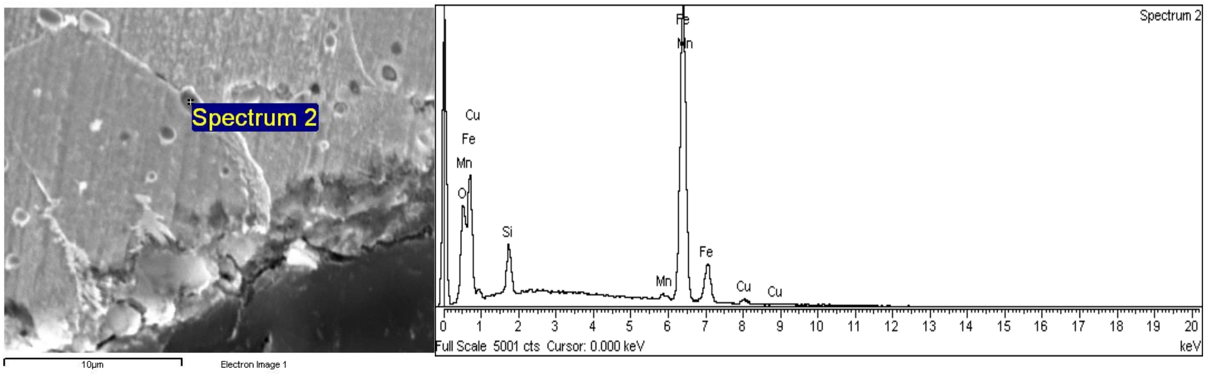

Figure 7 - Copper segregation (~2.5%Cu) surrounding inclusions in the 0.5% Cu-0.3% Ni steel IL0089, as cast, cooled at 25°C/min, tested at 850°C – Reduction of Area 74%.

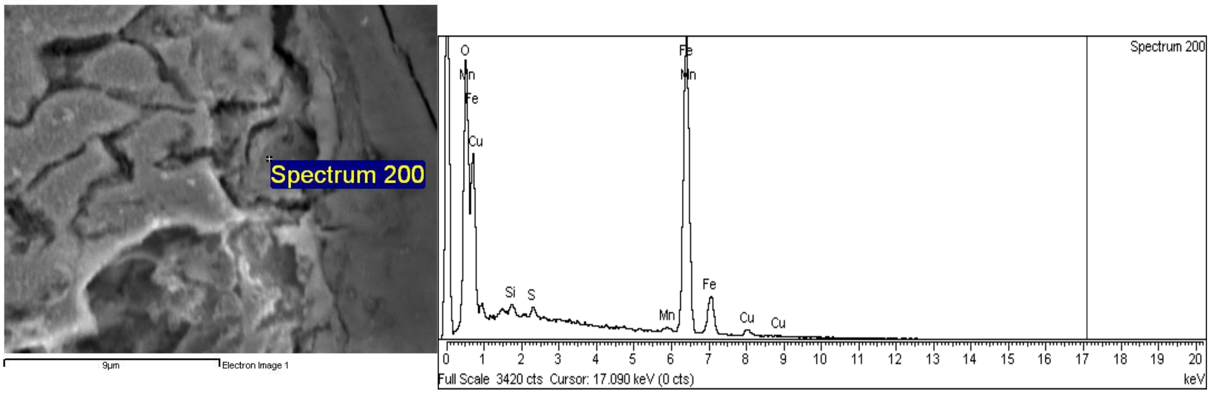

Figure 8 - Copper segregation (~2.5%Cu) in 0.5% Cu-0.5% Ni steel, steel IL0090, as cast, CR 200°C/min, tested at 800°C. Reduction of Area 17%.

However, the most important role of nickel is when the steel is exposed to an oxidizing atmosphere. The preferential oxidization of iron produces segregation of copper and also a nickel rich segregation near the fracture, as can be seen in Figure 9. The higher melting point of the alloy compared to that of pure copper helps to prevent hot shortness.

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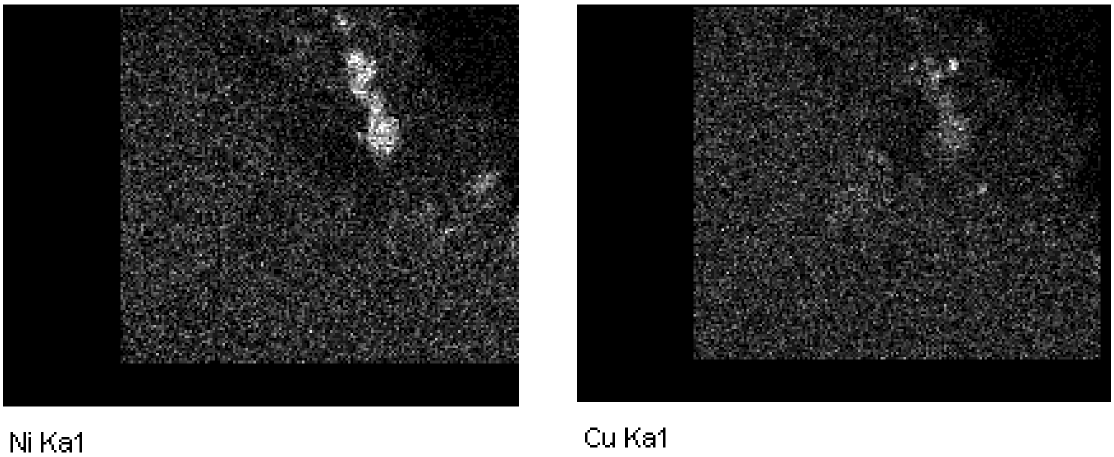

Figure 9 – X ray map show superposition of copper and nickel forming alloy near fractured surface of sample tested in air. - steel IL0090, (bulk composition: 0.5% Cu; 0.5% Ni).

No significant presence of nickel has been found in samples tested in argon but in oxidising conditions its concentration increases as one moves from the interior of the sample, Figure 10-left, to the heavily oxidized external zone, Figure 10-right.

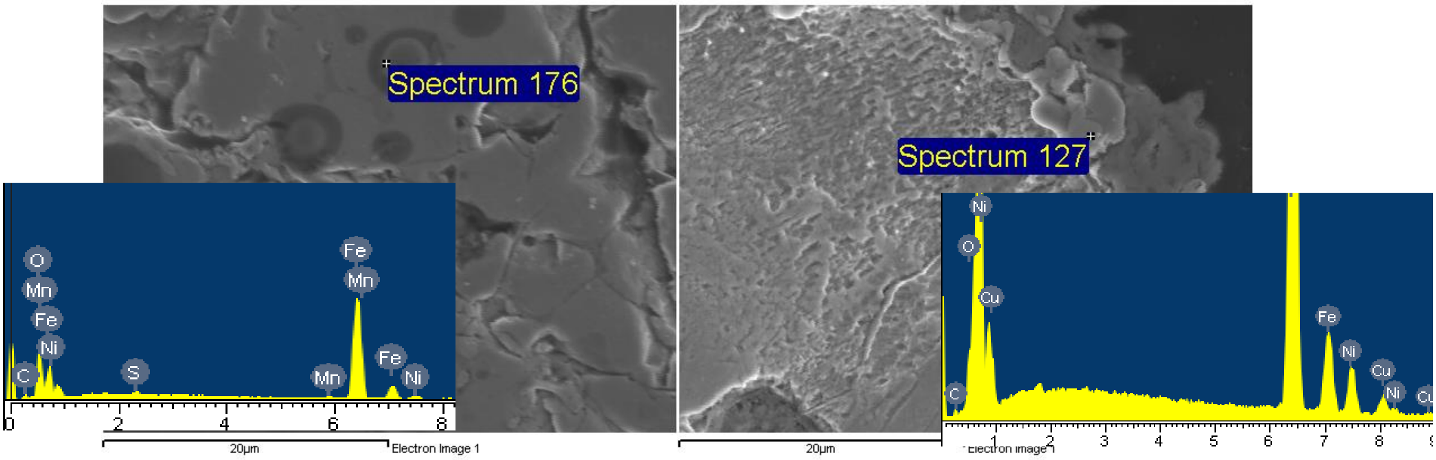

Figure 10 – SEM and x ray spectrums of steels tested under air oxidizing - left – ~4.3% Ni segregation around MnS near fracture - steel IL0089, (0.5% Cu; 0.3% Ni); right - Ni/Cu alloy in the fractured surface contained about 64% Ni and 36% Cu - steel IL0090, (0.5% Cu; 0.5% Ni).

4 DISCUSSION

4.1 Steels Investigated in Current Work

The influence of Cu on steels with microalloying additions has already been previously investigated [3,10,11]. Also, some preliminary work concerning the role of nickel in preventing that problem has been reported [12]. Accordingly, this investigation has been focused on the role of sulphide inclusions in influencing the segregation of Cu and its possible influence regarding the hot shortness and low ductility in carbon steels. As shown in Table 1, the compositions of the present C-Mn-Al steels varied considerably.

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4.2 Hot Shortness – Hot Ductility Behaviour

Over the last few decades several research investigations [5,6,9,12-14] have dealt with the problem of cracking in continuous casting. Basically, the problem is related to the formation of a thin film of ferrite surrounding the austenite grains, on cooling between the Ae_3 and Ar_3 temperatures. In this temperature range, this ferrite film is very weak and as a result the strain concentrates there initiating cracks resulting finally in failure. The presence of precipitates on the grain boundaries encourages the formation of cracks and thereby impairs the hot ductility [6,9]. This is a particular problem in microalloyed steels, where fine precipitates are formed on grain boundaries. In these steels, increasing the cooling rate always impairs the hot ductility, for the faster cooling rate leads to finer precipitation [15].

In copper-containing steels the problem of cracking is more serious as there is always the possibility that hot shortness may occur. Hot shortness is reported to be a consequence of the enrichment of copper on the surface, caused by the preferential oxidation of iron rather than copper, since copper is a nobler element. This Cu rich phase region can be melted during hot rolling causing serious cracking problems and the presence of CuS particles can impair ductility making it more difficult to produce Cu-containing steels by continuous casting.

Mintz et al. [16] have pointed out that copper is only effective in decreasing the hot ductility of cast structures under oxidising conditions. No effect has been detected in other conditions. In the same work, no influence on ductility was found in C-Mn-Al-Nb and C-Mn-Al steels, when tested in the argon atmosphere. In that work, the cooling rate was relatively fast (60°C/min). At a lower cooling rate of 25°C/min, copper has been reported [10] as having a beneficial influence on the hot ductility of microalloyed steels containing Nb and Ti, as its addition coarsens the Ti/Nb carbonitrides precipitates that are present. In recent research work [3,11], it has been reported that copper can impair the hot ductility in samples tested in an inert atmosphere because of the precipitation of CuS or by moving the A_3 transformation temperature to match the temperature of fine precipitation of nitrides.

Japanese investigation [17] has confirmed by using electron microscopy that the copper segregation occurs on the atomic scale, forming clusters similar to those found in Guinier-Preston zones. Also, another recent Japanese study [18] dealing with pure materials, reported that the presence of MnS can affect the precipitation of copper in pure iron-copper alloys, containing 5% and 10% of Cu.

Recent investigation [19] has shown that copper segregates around sulphide inclusions both in C-Mn-Al and C-Mn-Al microalloyed steels and this segregation takes place on the fracture surface as well as inside the matrix. Although not shown in the current work, the segregation was evident, even in steels with the copper content as low as 0.1% Cu. Also, increasing the cooling rate up to 200°C/min does not seem to reduce the segregation (Figure 2). However, the influence of sulphide inclusions on the hot ductility is not clear. It can be assumed that since they are coarse, although they may slightly impair the hot ductility this impairment is insufficient to seriously influence the cracking risk in continuous casting.

The problem of the presence of sulphide inclusions in copper-containing steels may become more serious, when the steels are cast under the oxidising atmosphere, which is present during continuous casting. Under this condition, the segregation of copper around the sulphides would make a bigger contribution to the hot shortness.

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4.3 Addition of Nickel - Oxidization

Nickel is reported to be a remedy for hot shortness, so that its addition to copper containing steel is one effective solution to the problem. Nickel has also been reported [8,20] to increase the solubility of copper in the austenite.
Current work carried out under oxidizing conditions in air, shows that the principal role of nickel is combining with the pure copper on the fracture surface, forming a Ni-Cu alloy, Figure 7, whose melting point is well above that for pure copper, so that the problem of hot shortness is delayed by the formation of a more ductile phase.
More recent work [4] has shown that nickel also can improve the hot ductility by coarsening Ti/Nb precipitates in steels tested at a slow cooling rate and in an inert atmosphere. A study still incomplete [21] suggests that the addition of nickel affects the CuS precipitation and the amount of copper segregated. Further, although the conclusion is still provisional, the addition of nickel seems to somehow modify the sulphide inclusions. Also, the segregation of nickel seems to be dependant on the presence of oxidising atmosphere. A deeper investigation into this effect may be very important when it comes to understanding the beneficial role of nickel in relation to the problem of hot shortness.

5 CONCLUSIONS

Some conclusions drawn from this work may have commercial implications and help in avoiding the problem of cracking during continuous casting which are due to the presence of Cu.
1 – Cu precipitates as CuS but it also migrates to the sulphide inclusions forming a shell surrounding the inclusions. It is not clear whether it also segregates around inclusions not containing sulphur.
2 – A Cu addition as low as 0.1% is enough to produce this segregation.
3 - This Cu segregation has not been found either to have any effect or only slightly impair the hot ductility in steels tested in an argon atmosphere. However, it may play a more important role in producing hot shortness, when the steel is cast under an oxidising atmosphere.
4 - Addition of nickel seems to modify the segregation, which may be important for the mechanical properties of the steel.
5 – The principal role of nickel may be in producing a higher melting point alloy with the copper that has segregated so that when it is segregated to the fracture surface it is less likely to melt.

5.1 Commercial implications

In order to reduce the problem of hot shortness caused by Cu in C-Mn steels, it is advised to reduce the volume fraction of sulphide inclusions to a minimum level. Otherwise a nickel addition is mandatory.

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