THE INFLUENCE OF INCLUSIONS ON THE “HOT SHORTNESS” OF Cu CONTAINING STEELS[1]

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Abstract
An investigation into the influence of low copper contents on the hot ductility of C-Mn-Al steels has been carried out in order better the understanding on the problem of “hot shortness”. Previous work has suggested that this problem results from the segregation 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. Nickel addition has been reported as a solution for the problem, since it increases the solubility of copper in the austenite. Samples of Cu-containing steels have been investigated using scanning electron microscopes after hot tensile testing to failure. Results indicate that copper, in addition to precipitating out as CuS, also heavily segregates to MnS inclusions forming a shell around them. This does not seem to be very deleterious to hot ductility under inert atmosphere, but it may be responsible for “hot shortness” in oxidising environment. The influence of Ni in improving the ductility is not very clear yet, but Ni may reduce the hot shortness by increasing the melting point of the segregated Cu phase. Data from this incomplete work also suggests that Ni reduces the precipitation of CuS particles.
Key words: Copper; Steels; Hot shortness; Inclusions; Precipitation; CuS.

INFLUÊNCIA DAS INCLUSÕES NA “FRAGILIDADAE À QUENTE” DOS AÇOS CONTENDO Cu

Resumo
Foi realizada uma pesquisa sobre a influência de baixos teores de Cu na ductilidade à quente dos aços C-Mn-Al, como forma de melhor entender o problema da “fragilidade à quente”. Trabalhos anteriores indicam que o problema é causado pela segregação de Cu na superfície do aço lingotado, por causa da oxidação preferencial do ferro. Isto causa a formação de um filme rico em Cu, com baixo ponto de fusão. Adição de Ni é reportada como a solução para o problema, pois o mesmo aumenta a solubilidade do cobre na austenita. Amostras de aços contendo Cu, depois de rompidos à quente, foram investigadas usando microscopia eletrônica de varredura. Os resultados indicam que o cobre, além de precipitar como CuS, também segrega intensamente ao redor das inclusões de MnS, formando um invólucro em torno delas. Isto não aparenta ser muito prejudicial para a ductilidade à quente em atmosfera inerte, mas pode ser responsável pela “fragilidade à quente” em atmosfera oxidante. A influência do Ni em recuperar a ductilidade à quente não é muito clara ainda, porém o Ni pode reduzir a fragilidade pelo aumento da temperatura da fusão da fase de cobre segregada. Dados ainda incompletos também sugerem que o Ni reduz a precipitação de CuS.
Palavras-chave: Cobre; Aços; Fragilidade à quente; Inclusões; Precipitação; CuS.

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INTRODUCTION

The tonnage of steel produced via the electric arc furnace, which uses scrap, has increased considerably as a 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 ductility and of these copper is the most notorious and responsible for the problem of "hot shortness" that occurs in the course of continuous casting and hot rolling of steels.

More recently,[1] 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 Cu affecting precipitation of AlN and also due to fine precipitation of CuS particles, both 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.

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)[2] and also the corrosion resistance of unpainted welded structures.

The phenomenon of hot shortness has been reported[3] by enrichment of copper due to its limited solubility in the austenite. Under oxidising conditions, that enrichment causes the solubility exceed the limit and precipitate out in the austenite grain boundaries, forming cracks, once copper can be melted in the normal temperatures of hot processing[4] of the steels.

However, it is also known that copper precipitates in the steels as CuS. These fine precipitates also reduce the hot ductility and encourage the transverse surface cracking of slabs during continuous casting.[5]

Grain boundary precipitate particles, their size and volume fraction, are fundamental for the hot ductility of steels.[6] Fine precipitates and high volume fraction have been reported as the worse condition for the hot ductility. Cooling rate can affect the size and the volume fraction of precipitation.[7] Slow cooling rate coarsens the precipitated particles and thereby improves the hot ductility.

Recent works[8,9] have reported that the combination of slow cooling rate and addition of copper or nickel also encourage the coarsening the precipitates in microalloyed steels.

The hot ductility measured as the reduction of area in the hot tensile test is one of the various simulations possible for investigating the problem of cracking at high temperatures. Many investigations[10,11] have been carried out in order to understand the problem of the hot shortness and some solutions have been suggested for the industrial practice. Among them, the addition of nickel has been reported as the most important, because it increases the solubility of copper in the austenite.[11] However, the useful level of nickel addition is not clear.

The mechanism of the building up of copper enrichment and causing the hot shortness is also somewhat still unclear, so that improved understanding is essential to be able to deal with the problem.

The present work is a part of major investigation carried on to study different variables affecting Cu as a factor for hot shortness and the role of nickel addition to prevent it. Previous results[1] 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. Here, the investigation has been carried out on the influence of inclusions in the segregation of Cu in steels tested under inert atmosphere. The influence of Cu segregation on the hot ductility results is not clear yet, but the present findings are very important, for such occurrence can be fatal for the ductility under the actual condition of steel processing in oxidizing atmosphere.

If the problem of hot shortness and low ductility behaviour is solved, copper-containing scraps can be much more easily recycled, since Cu can improve corrosion performance and mechanical properties of steels, if finely precipitated as CuS.

EXPERIMENTAL

Scanning electron microscopy (SEM) examinations have been carried out on five Cu-containing steels. Compositions of the steels are given in Table 1. Samples were machined from the ingot (as cast) and tested in 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 strained to failure at a strain rate of $3 \times 10^{-3}\ s^{-1}$ 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.

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

RESULTS

Scanning Electron Microscopy

Segregations of copper were found in all copper steels investigated. SEM examinations showed extensive copper segregation in the longitudinal section near the cracked zone. Similarly, copper segregation was found around MnS and CaS inclusions both on the longitudinal sections nearby the cracks and on the fracture surface, as shown in Figure 1. However, it seems that the segregation does not affect the ductility of the steel, as tested under inert atmosphere.

In the following, more detailed results are given obtained from inspection of fracture surfaces and longitudinal sections near the fracture:

1. High copper containing steels, without nickel (0.5% Cu – steels IL0088 and DA0387)

The SEM examination and EDS analyses of the fracture, showed dimples containing inside particles of MnS inclusions surrounded by Cu segregation, Fig 1. Similar examinations in the longitudinal sections near the fracture show copper segregations in two 0.5% Cu containing steels, at both low and fast cooling rates, as can be seem in the Figures 1 to 8.

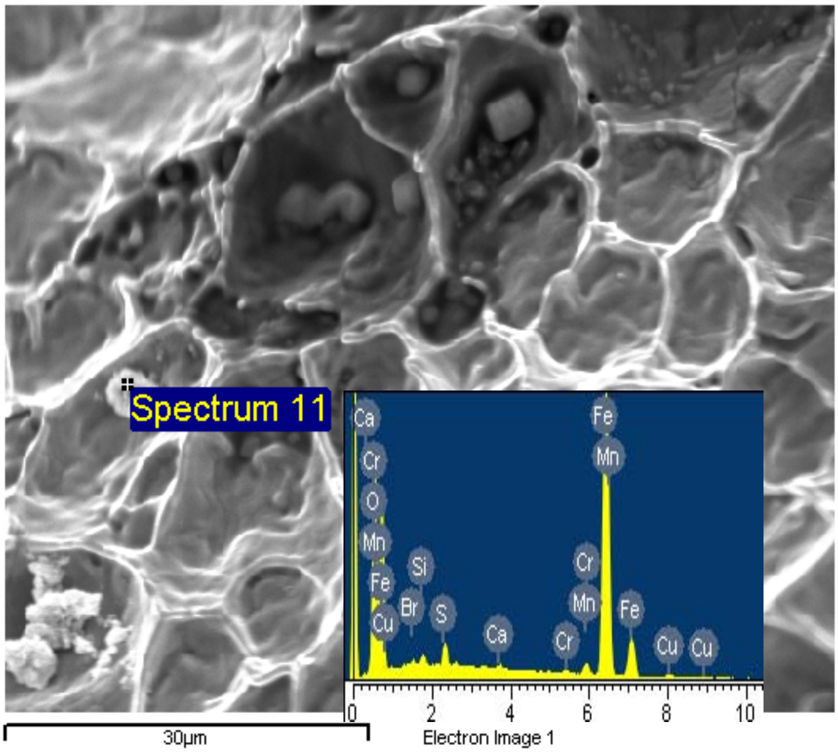

Figure 1 - Cu segregation around Ca/MnS inclusion and respective X ray analyse, 0.5%Cu steel, IL0088, as cast, tested at 25°C/min, 800°C – Reduction of Area 16%

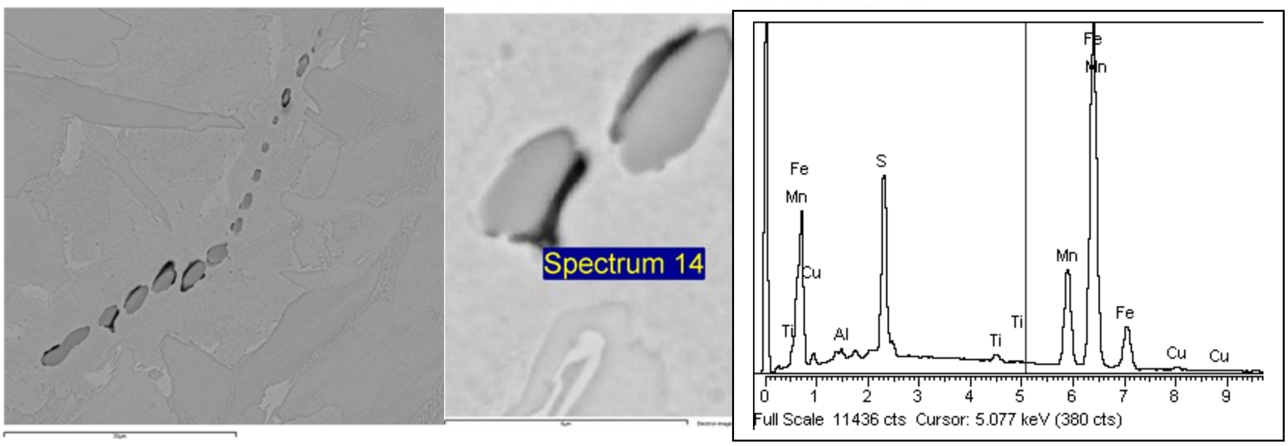

Figure 2 - SEM of same steel (IL0088) and temperature of Figure 1, but faster cooling rate of 200°C/min. – on left - line of MnS inclusions; on centre - detail showing Cu segregation on border of MnS inclusion and - on right - respective spectrum – R of A 25%

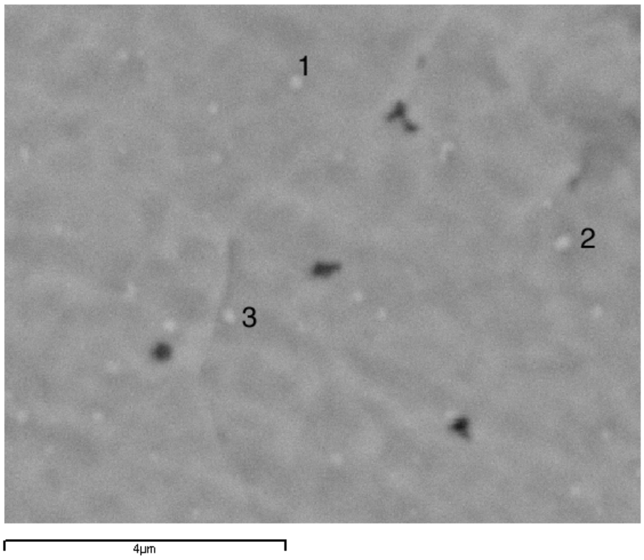

Figure 3 - Cu segregation around inclusions in the same steel (IL0088) as shown in Figure 1 (~15%Cu average in particles 1, 2 and 3) surrounding CaS/MnS particles in the matrix of 0.5%Cu C-Mn-Al steel, tested at 800°C, Particle size 180 nm; cooling rate 25°C/min (SEM-BEI).

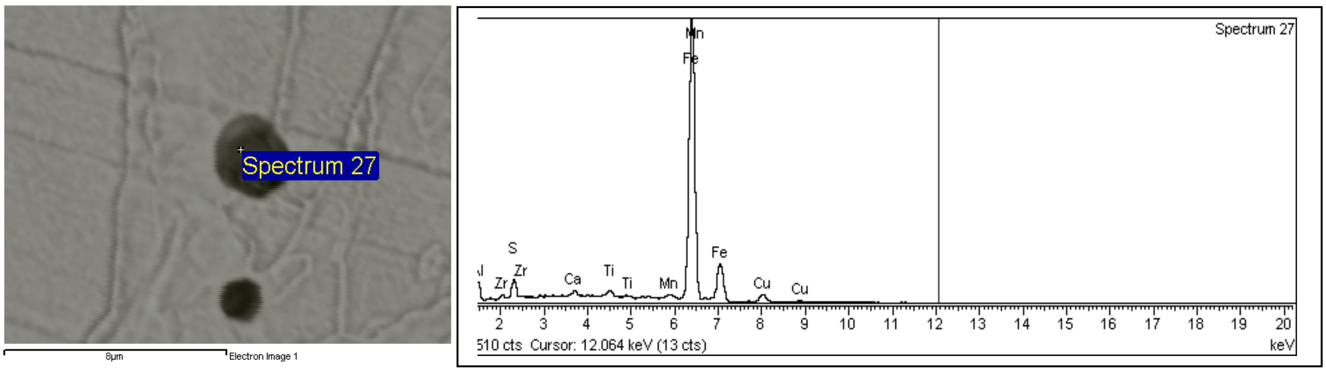

Figure 4 - Cu surrounding a S-containing inclusion (and respective spectrum) (~5%Cu) in the matrix of 0.5%Cu, C-Mn-Al steel (DA0387), tested at 850°C, reheated at 1330°C, cooled at 100°C/min, R of A 44%.

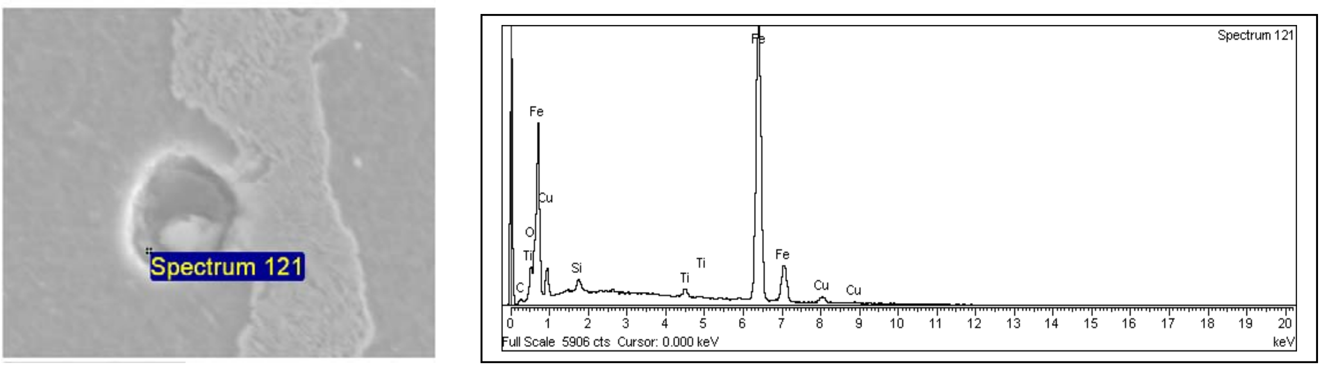

Figure 5 - Cu segregation (~3.5%Cu) around inclusion and respective X ray analyse, 0.5%Cu steel solution treated, cooled at 25°C/min, (DA0387), tested at 850°C – R of A 47%

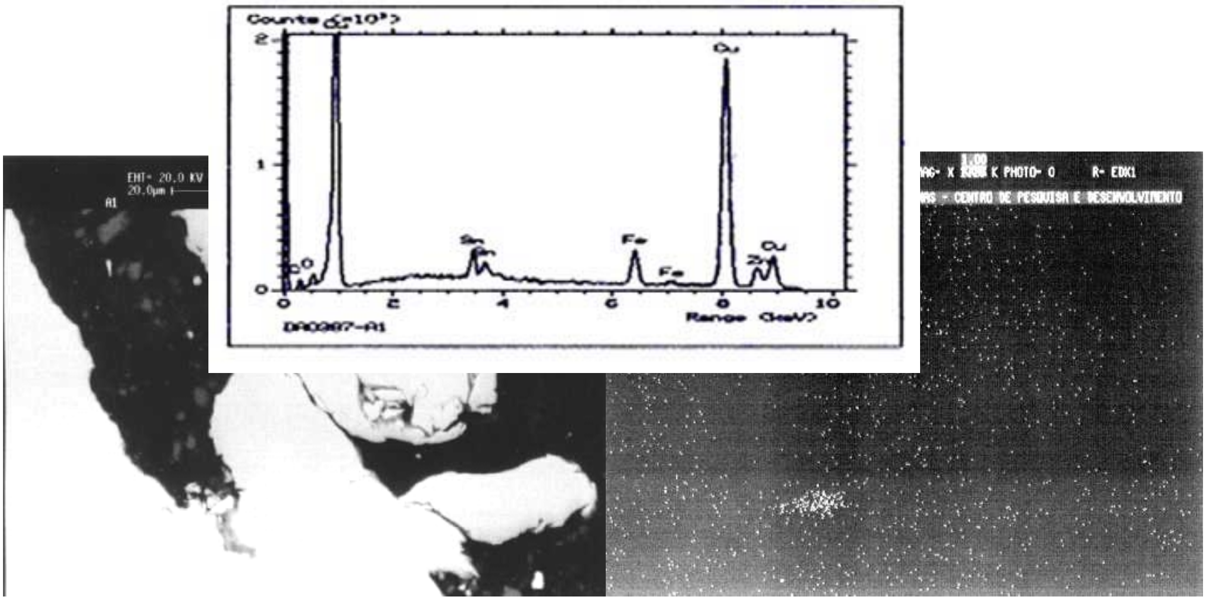

Figure 6 - SEM of internal crack shows Cu segregation, solution treated steel containing 0.5% Cu, (DA0387), X ray map and analyse. CR 25°C/min - 800°C – R of A 52% - 1000X.

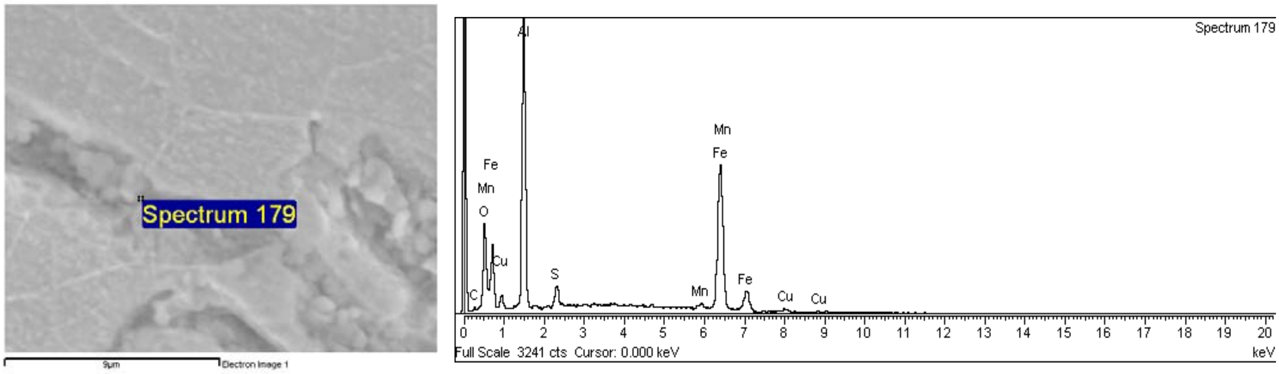

Figure 7 - Cu segregation (~2.3%Cu) and inclusions present in a crack and respective X ray analyse, 0.5%Cu solution treated steel, (DA0387), tested at 25°C/min, 800°C - R of A 52%

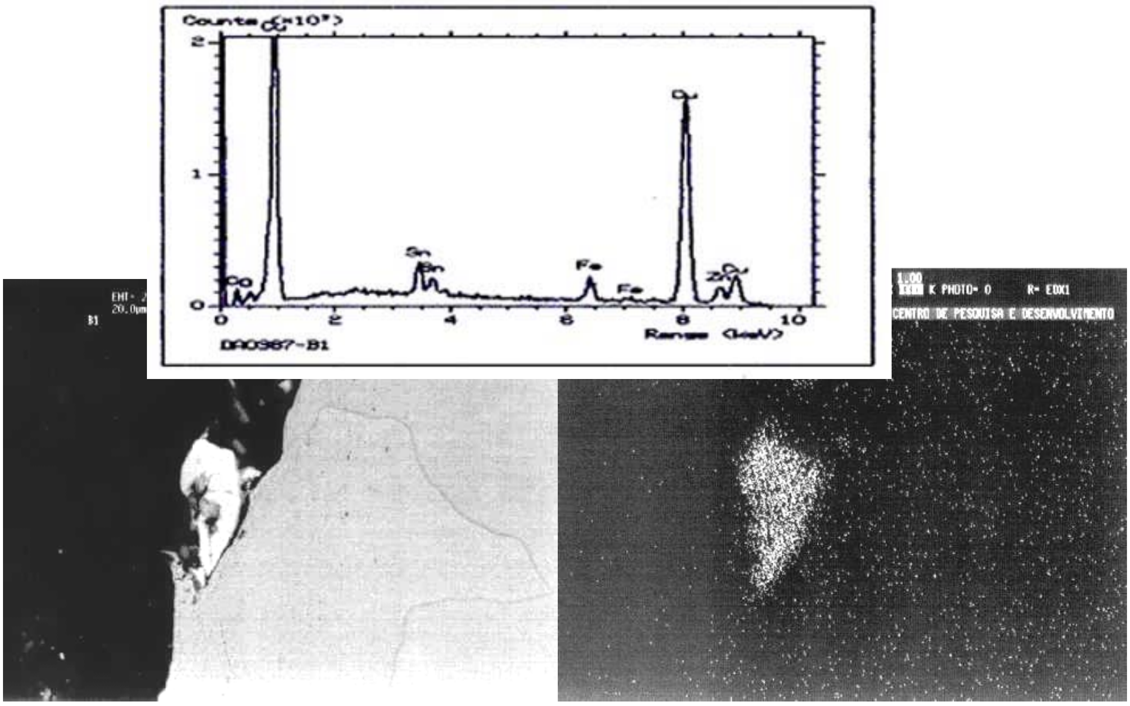

Figure 8 - SEM Cu rich region on the border of the sample of solution treated steel, DA0387, containing 0.5%Cu, CR 100°C/min – Text temperature 800°C – R of A 62% - 1000X.

2. Steel with low Cu without Ni (0.1%Cu), steel DL0096

SEM examinations of the steel containing 0.1%Cu also revealed segregation on fracture surface around inclusions and also in the longitudinal section taken near the fracture, both at fast and slow cooling rates, as shown in Figures 9 to 11. However, in a particular case, shown in Figure 12, no Cu segregation around inclusions was found in this steel. The reason for this is not clear, but presumably due to the low copper content in the steel or due to presence of coarse AlN particles in addition to MnS inclusions. Also, no segregation was found in X-ray mapping of the fracture for this low-copper steel tested at the fast cooling rate of 100°C/min, but it was present around the inclusions, as shown in Figure 11. In all other cases, the low copper containing steel showed segregation around inclusions. However, the occurrence of Cu segregation does not seem to make significant influence on the ductility of the steels investigated, when they were tested under the inert atmosphere.

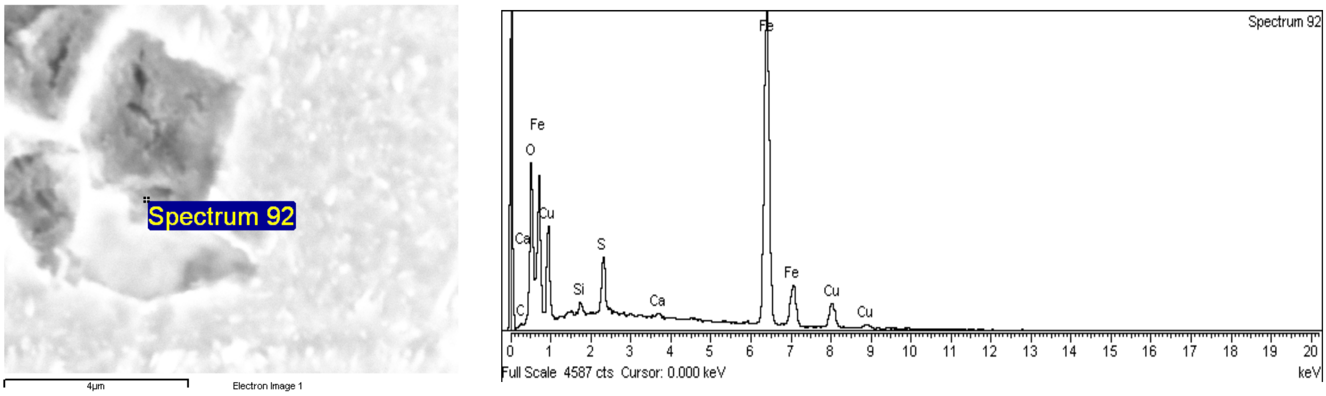

Figure 9 - Cu segregation (~8%Cu) around sulphide inclusions and respective EDS analysis of 0.1%Cu steel, DL0096, CR 25°C/min, tested at 850°C – R of A 58%

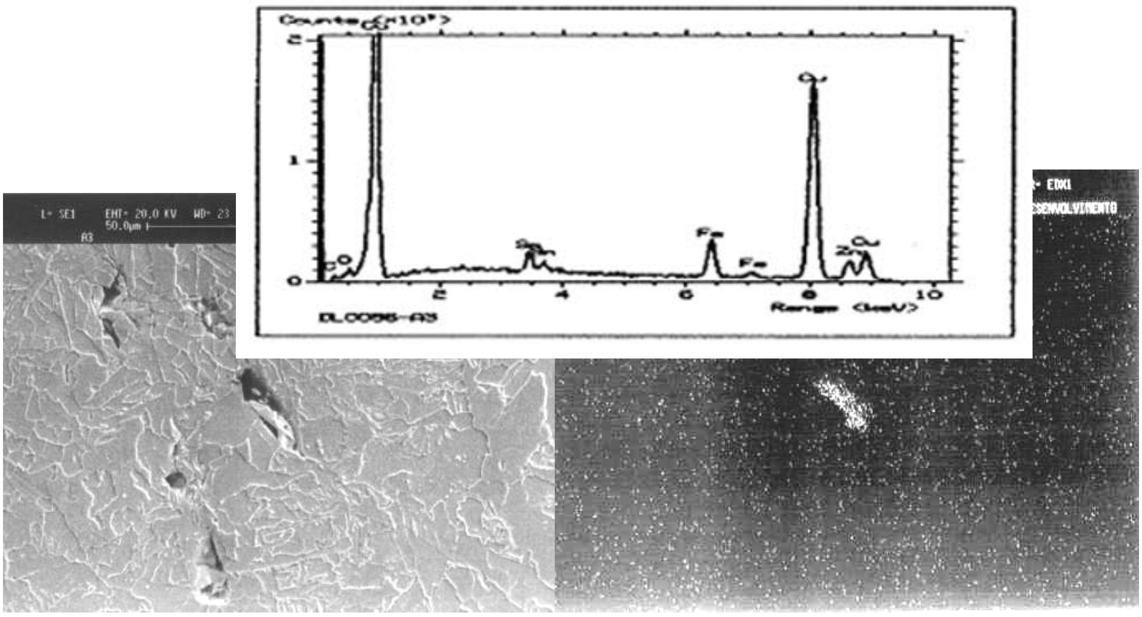

Figure 10 - SEM of internal crack showing Cu segregation in the 0.1% Cu steel, DL0096. X-ray map and analysis attached. CR 25°C/min - 800°C – R of A 83% - 500X.

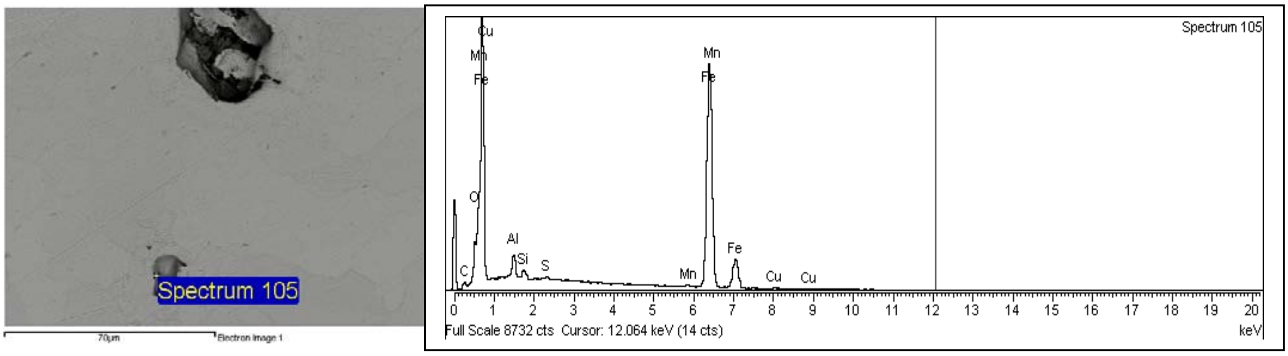

Figure 11 - SEM and respective X ray analyse shows Cu segregation (~1%Cu) around inclusions, 0.1%Cu steel, DL0096, tested at 100°C/min, 850°C – R of A 50%, inside the trough

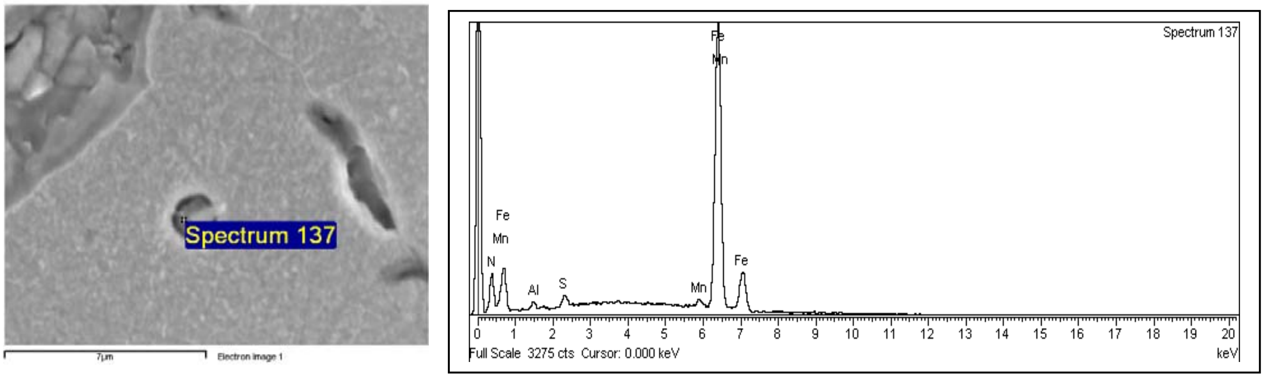

Figure 12 - SEM and EDS- analysis showing AlN around MnS inclusion, but no Cu segregation. The 0.1%Cu steel cooled at 25°C/min, tested at 800°C, DL0096, RA 83%, note the good R of A value (outside the trough).

3. Copper-containing steels with nickel addition (steels IL0089 and IL0090)

Additions between 0.3-0.5 % Ni in similar (0.5% Cu) copper-containing steels, (steels IL0089 and IL0090), also showed copper segregations around inclusions, Figures 13 and 14. 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, Figures 13 and 14. 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, so that it is under investigation now.

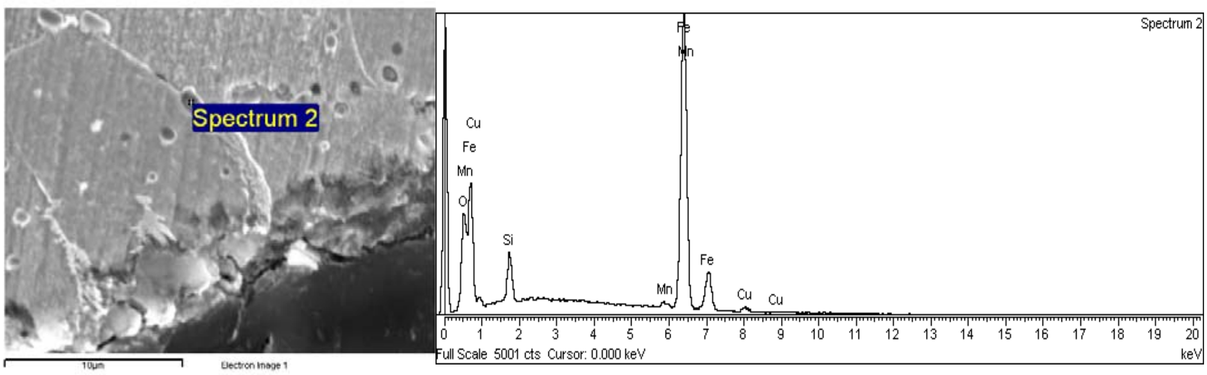

Figure 13 - Copper segregation (~2.5%Cu) surrounding inclusions in the 0.5% Cu-0.3% Ni steel IL0089, as cast, cooled at 25°C/min, tested at 850°C – R of A 74%.

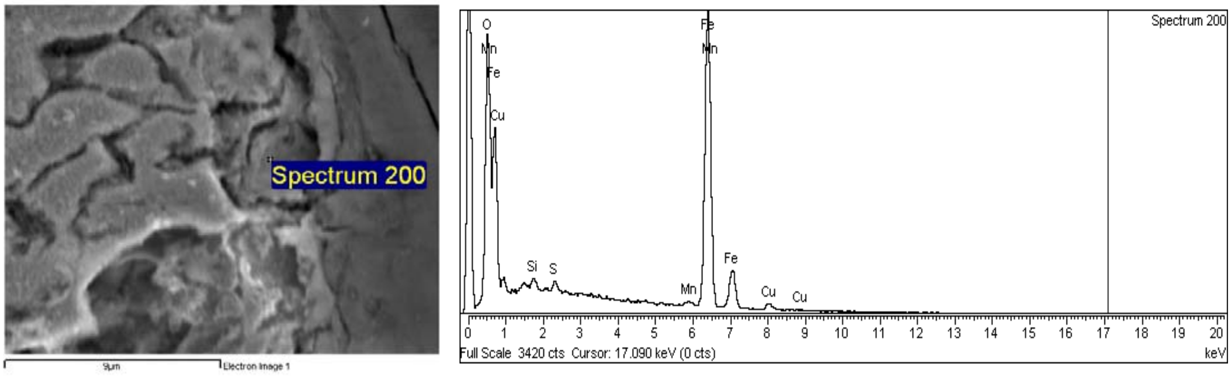

Figure 14 - Copper segregation (~2.5%Cu) in 0.5% Cu-0.5% Ni steel, steel IL0090, as cast, CR 200°C/min, tested at 800°C. R of A 17%.

DISCUSSION

Steels Investigated in Current Work

The influence of the particular effect of Cu in steels with microalloying have already been previously investigated.[1,8,12] Also, some preliminary work about the role of nickel on preventing that problem has been reported.[9] Accordingly, this investigation was focused to the problem of sulphide inclusions influencing the segregation of Cu and its consequence regarding the hot shortness and low ductility in carbon steels. As shown in Table I, the compositions of the present C-Mn-Al steels were varied considerably.

Hot Shortness – Hot Ductility Behaviour

Several works[6,7,10,13] have dealt with the problem of cracking in continuous casting over last decades. 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. At high temperatures, this ferrite film is very weak and concentrates the stress that initiates cracking resulting finally to failure. The presence of precipitates on the grain boundaries encourages the formation of cracks and thereby impairs the hot ductility.[6,7] 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.[14]

On the other hand, in copper-containing steels the problem of cracking is more serious. 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 rich phase region can be melted at straining temperatures and impair the ductility, which makes Cu-containing steels more difficult to produce by continuous casting.

Mintz et al.[15] have pointed out that copper is only effective in decreasing the hot ductility of cast structure and under oxidising conditions. No effect has been detected in other conditions. In the same work, no influence was found in C-Mn-Al-Nb and C-Mn-Al steels, while tested in the argon atmosphere and having the equal Cu content as in this work. In that work, the cooling rate was relatively fast (60°C/min). At lower cooling rate of 25 °C/min, copper has been reported[8] as having beneficial influence on the hot ductility of microalloyed steels, for its addition coarsens Ti/Nb carbonitrides precipitates in those steels. In recent works,[1,12] it has been reported that copper can impair the hot ductility in samples tested in 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.

A Japanese investigation[16] confirmed by electron microscopy that the copper segregation occurs in the atomic scale, forming clusters similar as the Guinier-Preston zones. Also, another recent Japanese study[17] 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.

The present investigation showed that copper segregates around sulphide inclusions both in C-Mn-Al and C-Mn-Al microalloyed steels, both on the fracture surface and inside the matrix. The segregation was evident, even in steels with the copper content as low as 0.1% Cu (Figure 11). Also, increasing the cooling rate up to 200°C/min does not seem to reduce the segregation (Figure 2). On the other hand, the influence of sulphide inclusions on the hot ductility is not clear. However, it can be assumed that since they are coarse, they may slightly impair the hot ductility without affecting seriously 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 oxygen atmosphere, like in the continuous casting. Under this condition, the segregation of copper around the sulphides would make a bigger contribution to the hot shortness. Clearly, having such kind of local segregation of copper, as observed here, more serious hot shortness can be created.

Addition of Nickel

Nickel is reported to be a remedy to the hot shortness, so that its addition to a copper-containing steel is one effective solution for the problem. Nickel has also been reported[11,18] to increase the solubility of copper in the austenite and also trap the pure copper in a Ni-Cu alloy, which has the melting point well above that of the pure copper, so that the problem of hot shortness is delayed by the formation of a more ductile phase.

More recent work[5] has been shown that nickel also can improve the hot ductility by coarsening Ti/Nb precipitates in steels tested at slow cooling rate and inert atmosphere. A study still incomplete[19] suggests that the addition of nickel affects the CuS precipitation and the amount of copper segregated. Further, although the conclusion is still not very firm, the addition of nickel seems to somehow modify the sulphide inclusions. Deeper investigation in this effect can be very important in order to understand the actual role of nickel concerning the problem of hot shortness.

CONCLUSIONS

Some conclusions drawn from this work may have commercial implications, so that suggestions are given to avoid the problem of cracking due to Cu in continuous casting:

1 – Cu precipitates as CuS but it also migrates to the sulphide inclusions forming segregation. It is not clear whether it also segregates around inclusions not containing sulphur.

2 - Variation of the cooling rate from 25°C/min to 200°C/min cannot prevent the segregation.

3 - Cu addition as low as 0.1% is enough to produce segregation.

4 - This Cu segregation has not been found either to have any effect or only slightly impair the hot ductility in steels tested under the argon atmosphere. However, it may play a more important role in producing hot shortness, when the steel is cast under oxidising atmosphere.

5 - Addition of nickel seems to modify the segregation, which may be important for the mechanical properties of the steel.

6 - In order to reduce the problem of hot shortness due to Cu, it is advised to reduce the number of sulphides inclusions to a minimum level. Otherwise nickel addition may be mandatory.

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