THE INFLUENCE OF A SMALL Ti ADDITION ON THE HOT DUCTILITY OF Cu CONTAINING STEELS[1]

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Abstract

An investigation into the influence of Cu additions and a small addition of Ti on the hot ductility of C-Mn-Al steels has been carried out. Two levels of copper, 0.1% and 0.5%Cu were examined; the steels having, 0.045%Al and 0.005%Ti. Samples of the steels were tensile tested after heating to 1300°C in an argon atmosphere and cooling to the test temperatures in the range 800°C to 1000°C at two cooling rates of 25°C/min. and 100°C/min. Samples were strained to failure and the hot ductility curves obtained using reduction of area as a measure of ductility. Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) analyses were also carried out. The results show a trough in the hot ductility between temperatures of 800°C and 900°C. Increasing the amount of Cu from 0.1% to 0.5% was found to have only a small detrimental influence on the hot ductility if the cooling rate was high, 100°C/min, but a significant deterioration in ductility was noted at the slower cooling rate. Increasing the cooling rate led to a slightly deeper trough. Although precipitates of copper sulphide and aluminium nitride were found these were too few and coarse to have any influence on ductility. However, copious precipitation of TiN was found in both steels, these being finer in the higher Cu containing steel, thus accounting for its deeper trough. The displacement of the hot ductility curve to lower temperatures in the higher Cu containing steel is probably because of the steels lower transformation temperature due to its higher Cu and C content.

Key words: Copper; Steels; Hot shortness; Ductility; Precipitation; TiN; CuS.

INFLUÊNCIA DE PEQUENAS ADIÇÕES DE Ti DUCTILIDADE À QUENTE DE AÇOS CONTENDO Cu

Resumo

Foi realizada uma pesquisa sobre a influência de adições de Cu e pequenas adições de Ti na ductilidade à quente de aços C-Mn-Al. Duas adições de Cu, 0.1% e 0.5%Cu foram examinadas; os aços contendo, 0.045%Al e 0.005%Ti. Amostras dos aços foram rompidas por tração, depois de aquecidas a 1300°C em atmosfera de argônio e resfriadas até a temperatura de ensaio, na faixa de 800°C a 1000°C, em taxas de resfriamento de 25°C/min. e 100°C/min. Foram obtidas as curvas de ductilidade à quente, medida pela redução de áreae também realizados ensaios de Microscopia Eletrônica de Transmissão (MET) e Varredura (MEV). Os resultados mostram um "poço" na curva de ductilidade entre 800°C e 900°C. Aumentando-se o teor de Cu de 0.1% para 0.5% causou uma pequena queda na ductilidade à quente, quando a taxa de resfriamento é alta, 100°C/min, mas uma queda significativa foi notada para taxa de resfriamento baixa. O aumento da taxa de resfriamento causou um leve aprofundamento do "poço". Embora tenham sido encontrados precipitados de CuS e AlN, eles foram poucos e grosseiros para que causem qualquer influência na ductilidade à quente. Contudo, uma copiosa precipitação de TiN foi encontrada em ambos os aços, sendo mais finos no aço com Cu mais alto, sendo isto considerado como a causa do "poço". O deslocamento da curva de ductilidade à quente para mais baixas temperaturas no aço com Cu mais alto é provavelmente por causa do abaixamento da temperatura de transformação devido ao maior teor de Cu e C.

Palavras-chave: Cobre; Aços; Fragilidade à quente; Precipitação; TiN; CuS

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INTRODUCTION

The environmental pressure for recycling as well as the diminishing supplies of sufficiently pure iron ore for modern integrated steelworks is increasing the use of scrap in steel making, leading to an increase in the residual Cu content. Copper in the scrap cannot be oxidized in the refining stage but remains in the bath as an impurity. Copper is present in steels either as an addition or as a residual element. Small Cu additions (0.2%) are often added to HSLA steels to increase strength without impairing impact behaviour and higher additions such as 1-2% can be used to improve the impact behaviour in Thermo-mechanical Precipitation Control Processed Steels (TPCP steels).(1) Another advantage of adding Cu is that it improves the corrosion resistance for unpainted welded structures. Unfortunately, it is also a known fact that copper can cause low ductility behaviour and hot shortness in carbon steels under oxidation conditions. A Cu film with a low melting point can then form which when molten penetrates along the austenite grain boundaries, leading to inter-granular failure.(2)

The phenomenon of hot shortness is known to cause cracks in the continuous casting and hot rolling of copper containing steels. Its cause has been reported(3) to be due to enrichment of copper in the preferential oxidation of iron and to its limited solubility in the austenite.(2) Under oxidising conditions, this enrichment causes the solubility limit to be exceeded and therefore copper precipitates on the austenite grain boundaries, forming low melting point compounds. These compounds melt in the normal hot rolling temperature range causing cracks to form on rolling.

It is also known that copper precipitates in the steels as CuS. These fine precipitates have also been shown to reduce the hot ductility and encourage the transverse surface cracking of slabs during continuous casting.(4)

Grain boundary precipitates and inclusions, their size and volume fraction, are fundamental to the understanding of the hot ductility of steels.(5) Fine precipitates/inclusions and high volume fractions give the worst hot ductility in micro-alloyed steels. Higher test temperatures and slower cooling rates to the test temperature result in coarser precipitation and better hot ductility.(6)

Recently, it has also been shown that a combination of a slow cooling rate and the addition of copper or nickel encourages the coarsening of the precipitates in micro-alloyed steels.(7,8)

Hot tensile testing, in which the hot ductility is being measured as the reduction in area, is one of the various simulations that can be used to investigate the problem of cracking at high temperatures. Much research work has been carried out into understanding the ductility problems and many recommendations from this work have been given to improve industrial practice to avoid hot shortness and or transverse cracking.(9) In the case of hot shortness it has been found that nickel alloying helps to prevent hot shortness as this element increases the solubility of copper in austenite, preventing pure Cu from precipitating out.(10)

It has also been suggested that the poor hot ductility in Cu-bearing steels is not always associated with conventional hot shortness, but ductility can be impaired by the precipitation of fine CuS particles, leading to poor surface quality and enhanced transverse cracking. Again, it has been found that Ni additions can improve the ductility by preventing CuS precipitation.(4,11)

However, the exact role of copper on hot ductility is still unclear and a better understanding is essential for dealing with the problem effectively. In this work, as an attempt to clarify the matter, an investigation has been carried out into the influence of cooling rate on the hot ductility of a Ti-treated steel with different Cu additions using an inert atmosphere as the testing medium.

EXPERIMENTAL

Two C-Mn steels with 0.5%Cu and 0.1%Cu additions were tested over the temperature range of 750°C to 950°C in an argon atmosphere. The steels also contained a small addition of Ti (0.005%). The compositions of the steels are given in Table 1. Samples were machined from an ingot (as cast initial condition) and reheated to 1330°C, for 3 min to dissolve precipitates and cooled to the test temperature, at cooling rates of 100°C/min and 25°C/min. After a further 3 min holding to stabilize the temperature, samples were strained to failure at a strain rate of $3x10^{-3}s^{-1}$. Scanning electron microscopy (SEM) investigations were carried out on the fractured surfaces and on longitudinal sections (not shown in this work). Transmission Electron Microscopy (TEM) was also employed on carbon replicas taken close to the fracture.

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

	C	Si	Mn	P	S	Al	Cu	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

RESULTS

Hot Ductility

The curves of reduction of area against the test temperature for the two cooling rates and copper additions are shown in Figure 1.

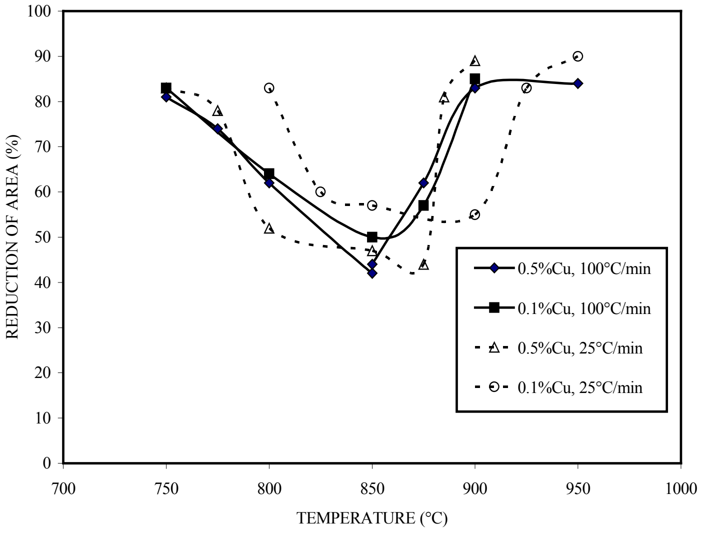

Figure 1 - Hot ductility curves for the steels investigated for cooling rates of 25 and 100°C/min

The hot ductility of the higher Cu containing steel (0.5%Cu) tested at the slower cooling rate (25°C/min) gave worse hot ductility than the lower copper (0.1%Cu) containing steel tested at the same cooling rate; dashed curves. Increasing the amount of Cu from 0.1 to 0.5% displaces the curve to a lower temperature range as well as deepening the trough.

At the higher cooling rate, 100°C/min similar trends are noted but the changes are much smaller.

Transmission Electron Microscopy (TEM)

In spite of the steels having a low sulphur content (0.0018%S), some CuS precipitation was observed, Figure 2, even though infrequently and particles were always coarse. TEM investigation of carbon replicas taken from close to the point of fracture in the tensile specimens revealed coarse CuS, isolated coarse AlN and fine TiN precipitation in the matrix, Figures 2 to 6. As the precipitates of CuS and occasional AlN are so coarse, they would be expected to have little or no effect on the hot ductility(6). Similarly, some very coarse TiN particles were observed but as can be seen from the background in Figure 3 and in Figures 4 and 5, copious precipitation of very fine TiN particles could also be seen which were at the size that would be likely to influence the hot ductility. The spectra for the very fine TiN particles (6-7nm) found in the 0.5%Cu containing steel cooled at 25°C/min and tested at 850°C are given in Figure 6.

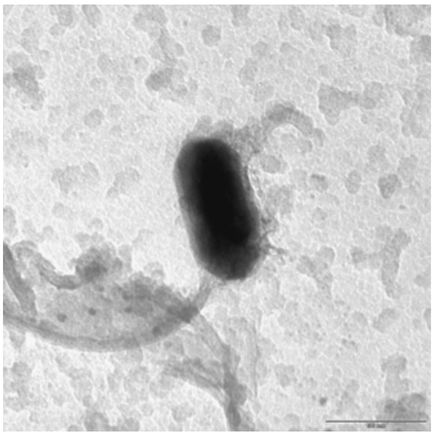

Figure 2 - Coarse CuS particle found in 0.5%Cu steel tested at 100°C/min, 850°C - CuS - PS 100nm; RA 44%, 200,000X.

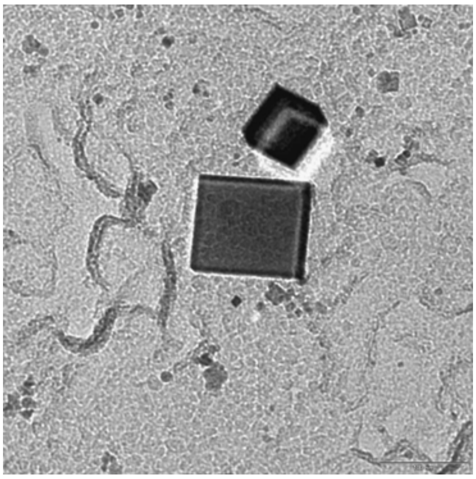

Figure 3 - Coarse TiN particles found in 0.1%Cu steel tested at 100°C/min, 800°C - PS100nm and 130nm RA 64%. Very fine TiN particles are also present in the background, 150,000X.

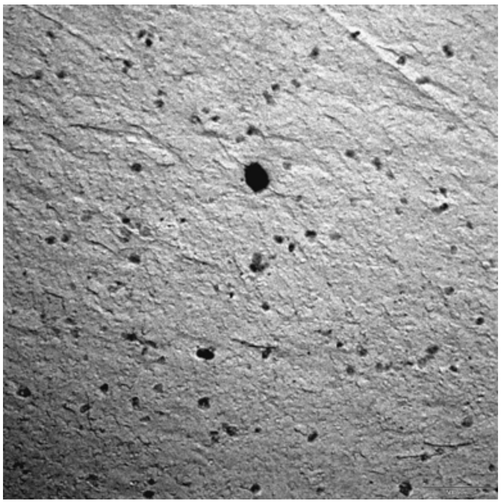

Figure 4 - TiN particles found in 0.1%Cu steel tested at 25°C/min, 800°C. PS - 50nm -TiN; RA 83%, 220,000X

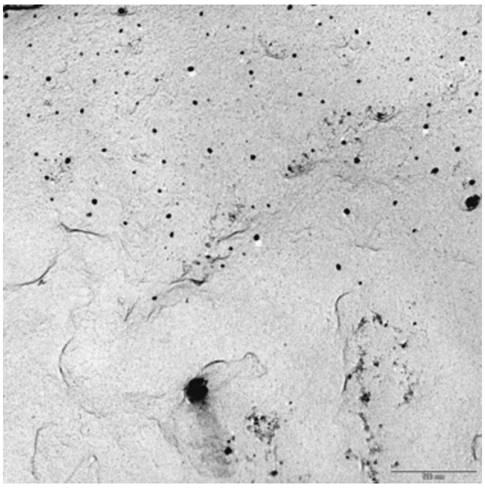

Figure 5 - Finer TiN precipitation found in 0.1%Cu steel tested at 100°C/min, 800°C - PS 25nm; RA 64%, 200,000X.

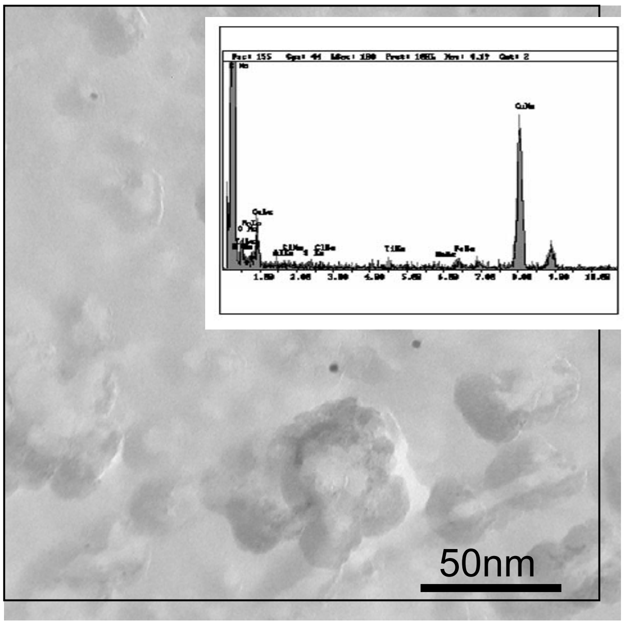

Figure 6 - Fine TiN precipitation found in 0.5%Cu steel cooled at 25°C/min and tested at 850°C - PS 6-7nm; RA 47%.

DISCUSSION

Hot Shortness – Hot Ductility Behaviour

Many authors(9,12) have in the last few years investigated the problem of transverse cracking in continuous casting. For simple plain C-Mn steels, the problem occurs when a thin film of ferrite forms surrounding the austenite grain, while the transformation from austenite to ferrite occurs on cooling between the Ae_3 and Ar_3 temperatures. This film always forms on cooling but often as-deformation induced and it can then be present over a very wide temperature range. When austenite and ferrite are present together at high temperatures, ferrite is very much softer than austenite so all the strain concentrates within these films causing voiding at inclusions, the voids joining to give inter-granular failure. Previous work(5,9) has also reported that the presence of precipitates on the grain boundary encourage the formation of the cracks that link up to each other and impair the hot ductility and this can both deepen the trough and extend the trough to temperatures above the Ae_3. This is a particularly serious problem in micro-alloyed steels that form fine precipitates at the grain boundaries making it easier to unzip the boundary and propagate cracks. In these steels, increasing the cooling rate always reduces the hot ductility as the faster cooling rate produces finer precipitation.(5,6)

On the other hand, the problem of cracks in copper containing steels (hot shortness) is reported to be a consequence of the enrichment of copper on the surface, caused by the preferential oxidation of iron, since copper is a nobler element than iron. This Cu rich phase region can be melted at the test temperatures causing the ductility to decrease.

However, Mintz et al.,(11) have pointed out that the increase in transverse cracking observed when Cu is added to steels may have a very different explanation to that commonly used to explain hot shortness. They have suggested that it is due to the fine precipitation of copper sulphide particles formed according to the reaction

$2MnS + 4Cu + O_2 = 2\,Cu_2S + 2MnO$. In their work copper was found to be only effective in reducing the hot ductility under an oxidising atmosphere and when cast directly. No effect of copper on the hot ductility could be found when tests were carried out on solution treated samples or when tested in an argon atmosphere. The work was carried out both on C-Mn-Al-Nb and C-Mn-Al steels, the manganese level of the steels being 1.4%.

Japanese work(13) has confirmed by electron microscopy that copper does segregate at the atomic scale, forming clusters similar to Guinier-Preston zones.

Although copper sulphides were found in all conditions in the present work, the particles were few in number and coarse and therefore unlikely to influence hot ductility, Figure 2. The changes that have been observed in the hot ductility cannot therefore be ascribed to copper forming a low melting point compound or fine extensive precipitation of copper sulphide.

Very few AlN precipitates were found and these were also too coarse to influence the hot ductility. Of all the particles present, the only particles that were found which could influence hot ductility were Ti N and these were often present in abundance and in a very fine form, Figures 3 and 6.

It can be seen from Figure 7 taken from previous work(5) that for precipitates to influence hot ductility they must be less than 15nm in size. Of all the particles examined only the TiN particles were within the size range which can influence hot ductility and therefore the electron microscope studies were concentrated on these fine precipitates. A summary of these results for the two Cu containing steels for the slower cooling rate which gave the most marked changes in hot ductility behaviour are given in Table 2.

Table 2 - Summary of size and distribution of the finer TiN particles found in the Cu containing steels at the slower cooling rate

Steel	Temperature°C	Particle size nm	Density	R of A %
0.1%Cu	850	10-15	Numerous	58
"	900	6-7	Numerous	56
0.5%Cu	850	6-7	Numerous	47
"	900	7	Few isolated	90

This table indicates that at 850°C, which is in the trough for both steels, the 0.5%Cu containing steel has finer TiN particles present than in the 0.1% Cu containing steel (6-7nm compared to 10-15nm).

At 900°C the 0.5%Cu containing steel has fully recovered its ductility giving 90% R of A and there are now very few fine TiN particles. However, at this temperature, a copious fine TiN distribution is still present in the 0.1%Cu containing steel which accounts for the extension of its trough to temperatures above the Ae_3.

Influence of Cu.

Ductility troughs which are controlled by the austenite to ferrite transformation generally exhibit a steep fall in the ductility at temperatures just below the Ae_3 temperature. The ferrite that forms as thin soft films is deformation induced and deformation will often raise the normal Ar_3 temperature to the Ae_3, hence the latter is the temperature of most interest. Because the temperature at which ductility starts to fall at the high temperature end of the trough is generally close to the Ae_3, this temperature can be calculated from the work of Andrews(14) and Ohtsuka et al.(15) The calculated Ae_3 temperatures were 882 and 867°C for the 0.1 and 0.5%Cu steel, respectively.(16) The higher Cu containing steel has also a slightly higher C level and taking both these elements into account the Ae_3 would be expected to be 15°C lower. Examination of the curves in Figure 1 show that for the slow cooling rate, increasing the Cu content from 0.1 to 0.5% gives a 25°C displacement to lower temperatures of the hot ductility curve whilst at the faster cooling rate the displacement is smaller, about 8°C. Hence a significant part of the displacement of the hot ductility curve of the higher Cu containing steels to lower temperature is a result of these compositional differences.

It can be seen from Figure 1 that for the 0.5%Cu containing steel cooled at both cooling rates and for the 0.1%Cu containing steel at the faster cooling rate, ductility starts to deteriorate at ~880°C which is close to the Ae_3 temperatures (870-880°C). Only for the 0.1%Cu containing steel when cooled at the slower cooling rate, does ductility start to deteriorate at a significantly higher temperature of 930°C, Figure 1. This indicates that for this composition and cooling rate the copious fine TiN precipitation is extending the trough to higher temperatures above the Ae_3, as can be seen from examination of Table 2 which shows that there are very fine TiN precipitates present at 900°C in the 0.1%Cu containing steel, when cooled slowly to the test temperature.

Influence of cooling rate

Cooling rate has been reported to have a very important influence on the hot ductility of microalloyed steels, since it can affect the time and temperature available for diffusion and as a consequence, the precipitation size and volume fraction(5,6). It can be seen from Figure 7, that once the precipitate size has grown to be in the region of 25nm there is little further influence on the hot ductility. Slower cooling gives more time for precipitate growth.

Increasing the cooling rate in the present work led to slightly deeper troughs. Only limited TEM studies were carried out at the faster cooling rate but again fine precipitation of TiN was observed and there is some indication that the increased cooling rate had produced a slightly finer TiN precipitation, compare Figures 4 and 5. This would be in accord with results from previous work on Al, Nb and Ti containing steels.(16)

The general effect from previous work(16) of increasing the cooling rate on the hot ductility of microalloyed steels is shown in Figure 8, taking AlN as an example but similar behaviour has been noted for C-Mn-Nb-Al and C-Mn-Ti-Al steels. Increasing the cooling rate by refining the precipitates both deepens and widens the trough. However, in the present instance although there is a slight deepening of the troughs, there is no extension of the trough to higher temperatures as has been noted in the past.(16) In Figure 8 for example increasing the cooling rate for a 1.4%Mn, C-Mn-Al steel from 25 to 200°C/min causes the hot ductility curve to be displaced upwards to higher temperatures by ~50°C, whereas in the present work the curves are shifted for the 0.1%Cu steel by 30°C to a lower temperature and not at all for the 0.5%Cu steel.

The major difference between the present and past work is in the Mn content and of course the presence of Cu. All the previous work was carried out on 1.4%Mn steels in which the Ae_3 temperature is low ~840°C.

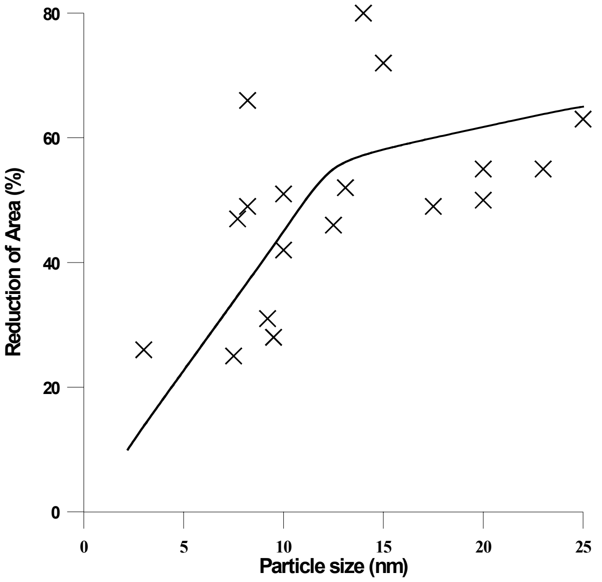

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Figure 7 - Influence of particles size on reduction of area values for Ti containing steels.(5)

Mn is known to increase the solubility of carbonitrides(18) and reducing the Mn level would be expected to speed up precipitation reactions. This may account for the relative insensitivity of the cooling rate to the hot ductility curves in the present instance but clearly more work is required to examine this possibility.

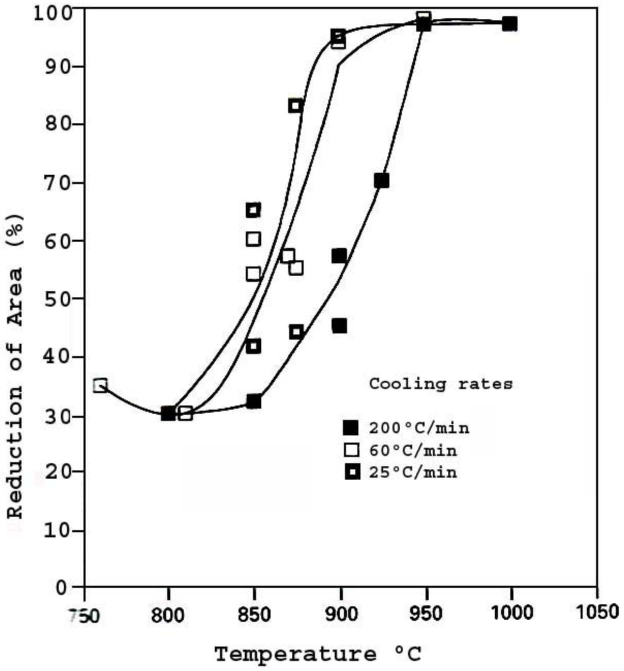

Figure 8 – Hot ductility curves for as cast C-1.4%Mn-Al steel at three cooling rates, 25, 60 and 200°C/min, showing the displacement of the curves to the right.(16)

COMMERCIAL IMPLICATIONS

The present work does not indicate any adverse influence which can be ascribed directly to copper, and this is not surprising considering the samples were not exposed to an oxidising atmosphere. The deterioration in ductility that did occur was due to TiN precipitation and indicates that even this low addition level of 0.005%Ti can cause a significant deterioration in the ductility. However, the higher Cu containing steel did produce a finer TiN precipitation but this may be due to the decrease in transformation temperature from the higher Cu and C content of the steel. Ductility was always in excess of 40% suggesting that there should be no problems in the continuous casting of these steels but given that the conditions were non-oxidising this should be taken with caution. Clearly, the size of TiN precipitates must be very carefully controlled if transverse cracking is to be avoided.

SUMMARY AND CONCLUSIONS

Previous work(11) has shown that oxidising conditions are required in order for substantial copper sulphide precipitation to occur and so be able to influence hot ductility. Such conditions were not present in this work and the ductility will not be influenced by the coarse copper sulphide precipitation that was observed. In the presence examination, fine TiN precipitation (6-10nm) has been found to be responsible for influencing the depth of the trough. This precipitation was found to be finer in the higher Cu containing steel which accounted for its deeper trough.

For the 0.5%Cu containing steel, the temperature at which ductility started to deteriorate at the high temperature end of the trough could be associated with the

Ae_3 temperature when a thin film of deformation induced ferrite first forms around the austenite grain boundaries. This was also the case for the 0.1%Cu steel cooled at the faster cooling rate but not when cooled at 25°C/min, the trough being extended to higher temperatures by the presence of fine TiN precipitation.

Increasing the cooling rate from 25 to 100°C/min led to slightly deeper troughs in accord with previous work(16) .

The copper additions in the present instance are only affecting the ductility by their influence in reducing the transformation temperature and encouraging finer precipitation of TiN.

In the present work, the reduction of area values were always in excess of 40% so that transverse cracking should not occur but this must be treated with caution as testing was carried out in an inert atmosphere.

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