THE INFLUENCE OF COOLING RATE ON THE HOT DUCTILITY OF CU CONTAINING STEELS[1]

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Abstract

An investigation into the influence of Cu additions 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 as well as a small amount of Ti, 0.005%. 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% does not have any influence on the hot ductility if the cooling rate is high but a small deterioration was noted at the slower cooling rate. Although precipitates of copper sulphide and titanium nitride were found these were too coarse to have any influence on ductility. The troughs are interpreted in terms of the transformation temperature and the precipitation of AlN. Steels with as high as possible transformation temperatures, i.e. low C and low Mn, are recommended to ensure AlN precipitation is coarse and is not detrimental to hot ductility.

Key words: Copper; Steels; Hot shortness; Ductility.

INFLUÊNCIA DA TAXA DE RESFRIAMENTO NA DUCTILIDADE À QUENTE DOS AÇOS CONTENDO CU

Resumo

Foi realizada uma investigação sobre a influência da adição de Cu na ductilidade à quente doa aços C-Mn-Al. Dois níveis de composição de cobre, 0.1% e 0.5% Cu foram investigados, sendo que os aços continham 0.045%Al e também uma pequena quantidade de Ti (0.005%). Os corpos-de-prova foram ensaiados à tração à quente, depois de aquecidos a 1300°C em atmosfera de argônio e resfriados até a temperatura de ensaio, que estava na faixa de 800°C to 1000°C, em duas taxas de resfriamento de 25°C/min. e 100°C/min. Os valores da redução de área, medidos na ruptura dos corpos-de-prova, foram usados como medidas de ductilidade à quente para a construção das curvas. Foram também executadas análises de Microscopia Eletrônica de Transmissão (MET) e Microscopia Eletrônica de Varredura (MEV). Os resultados mostram um vale de ductilidade entre as temperaturas de 800°C e 900°C. Nenhum efeito foi observado aumentando-se a quantidade de Cu de 0.1% to 0.5% em altas taxas de resfriamento, porém uma pequena redução da ductilidade foi notada em taxas de resfriamento mais baixas. Embora precipitados de sulfeto de cobre e nitreto de titânio tenham sido encontrados, eles eram muito grosseiros para causar qualquer influência na ductilidade. Os vales de ductilidade das curvas são interpretados em termos da temperatura de transformação do aço e precipitação de AlN. São recomendados aços com temperatura de transformação mais alta possível, i.e. baixo C e baixo Mn, são recomendados para garantir precipitação grosseira de AlN que não é nociva à ductilidade à quente.

Palavras-chave: Aços; Fragilidade à quente; Ductilidade; 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 the steel industry. This increased usage of scrap in steel making is leading to an increase in the residual Cu content. Copper in the scrap cannot be oxidized in the refining steel process and 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 larger additions (1-2%) of copper 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 known that copper can cause low ductility behaviour and hot shortness in carbon steels submitted to oxidation conditions. A low melting point Cu film can then form and this has been shown to penetrate along austenite grain boundaries when molten, 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 as a consequence of the building up of its concentration after 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 copper is precipitated at the austenite grain boundaries, forming low melting point compounds. These compounds melt at 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, their size and volume fraction, are fundamental to the understanding of the hot ductility of steels.(5) Fine precipitates and high volume fractions give the worst hot ductility in micro-alloyed steels. Temperature and cooling rate have been shown to influence the size and the volume fraction of the precipitates.(6) Slow cooling rates coarsen the precipitates and improve the hot ductility.

Recently,(7,8) it has 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.

The hot ductility, measured as reduction in area in the hot tensile test, 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 problems and many recommendations have been made to improve industrial practice so as to avoid hot shortness and or transverse cracking. In the case of hot shortness it has been found that adding nickel helps to prevent hot shortness as this element increases the solubility of copper in austenite, preventing pure Cu from precipitating out.(9)

It has also been suggested that the poor hot ductility on adding Cu to steel is not always associated with conventional hot shortness and that 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 in this case CuS precipitation.(4)

The mechanism of how the build up of the concentration of copper causes this precipitation is still unclear, so a fuller understanding is essential for dealing with the problem effectively. In this work, an investigation has been carried out into the influence of cooling rate on the hot ductility of steels with different Cu additions using an inert atmosphere as the testing medium.

EXPERIMENTAL

Two C-Mn, Al-killed steels with 0.5%Cu and 0.1%Cu additions have been tested over the temperature range of 750°C to 950°C in an argon atmosphere. The steels also contained a very 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 100°C/min and 25°C/min cooling rates. After a further 3 min at the test temperature to allow homogenization, 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) has also been carried out 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 the Figure 1.

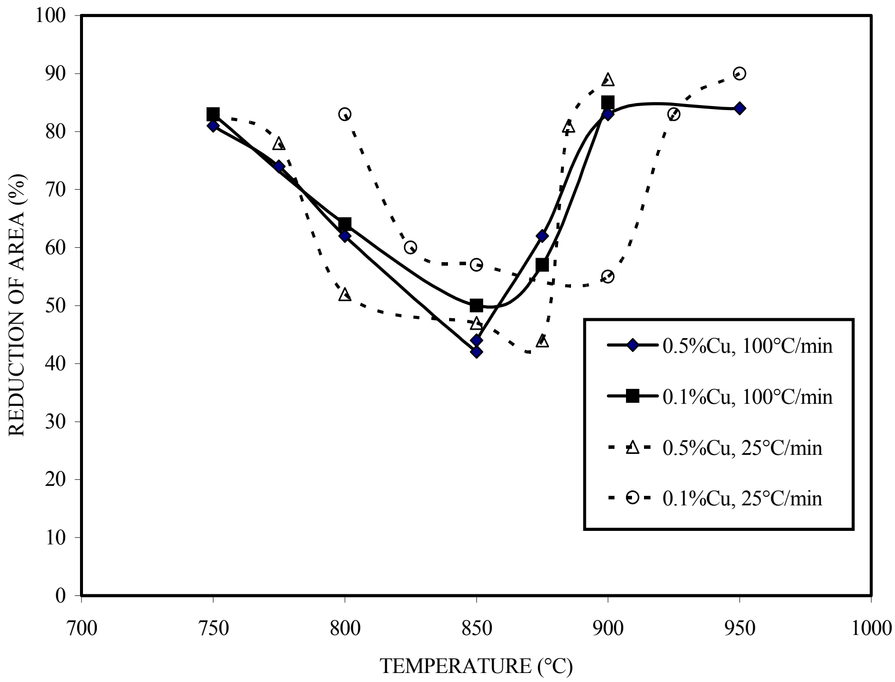

Figure 1. Hot ductility curves for the steels investigated for cooling rates of 25 and 100°C/min.

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 of 100^{o}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, but infrequently and it was always coarse. TEM investigation of carbon replicas taken from close to the point of fracture in the tensile specimens revealed coarse CuS, AlN and TiN precipitation in the matrix, Figures 2 to 8. As the precipitates of CuS and TiN are so coarse, they would be expected to have little or no effect on the hot ductility.[(6)] However, this is not the case for the AlN precipitates as will be discussed later in the paper.

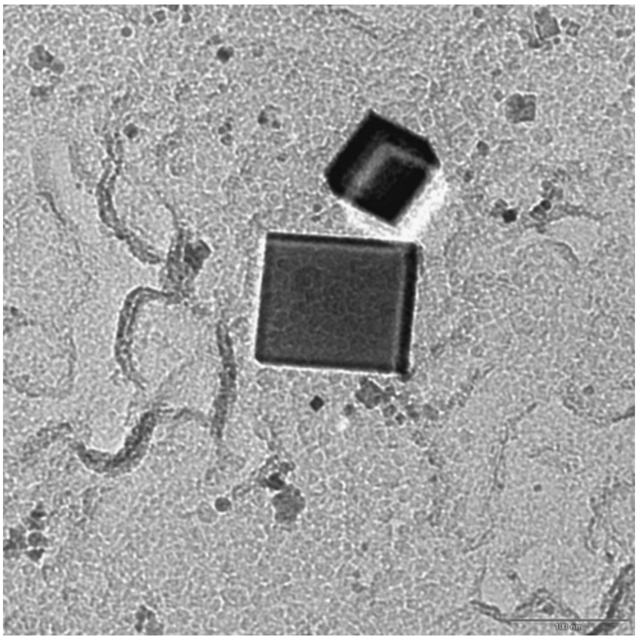

Figure 2. Coarse TiN precipitation found in 0.1%Cu steel tested at 100°C/min, 800°C - PS100nm and 130nm - RA 64%, 110,000X.

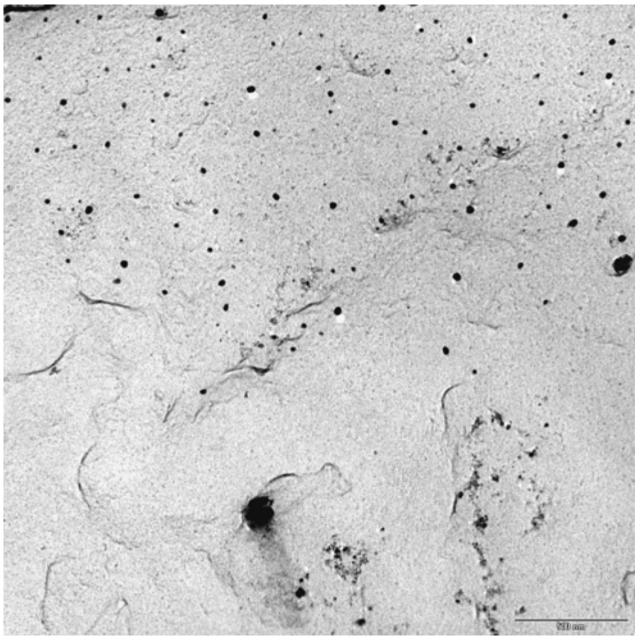

Figure 4. Finer TiN precipitation found in 0.1%Cu steel tested at 100°C/min, 800°C - PS 25nm - RA 64%, 30,000X.

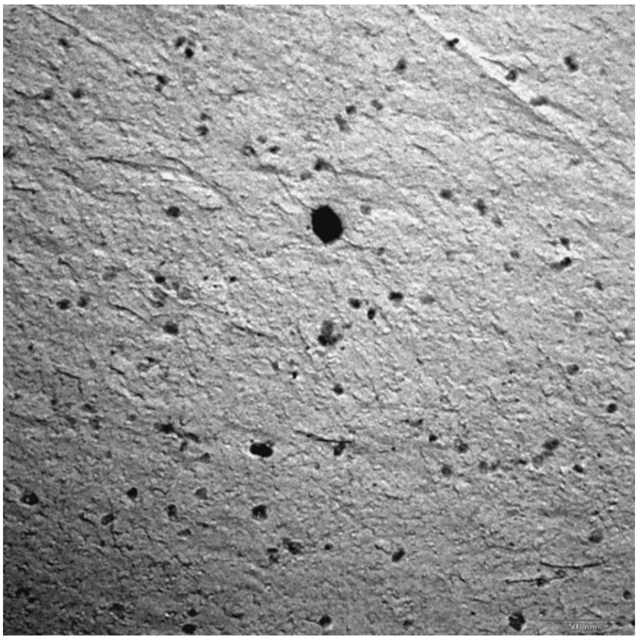

Figure 3. Precipitates found in 0.1%Cu steel tested at 25°C/min, 800°C. mixed Ti N and AlN precipitates - PS 50nm -TiN/AlN - RA 83%, 24,000X.

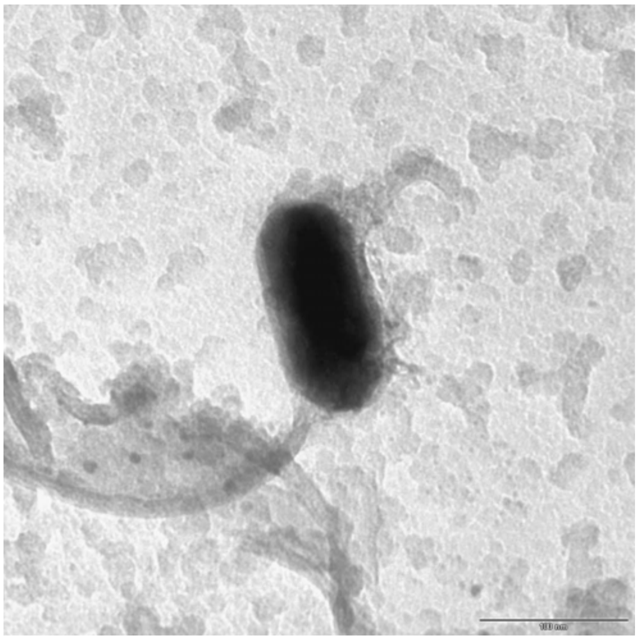

Figure 5. CuS coarse precipitate found in 0.5%Cu steel tested at 100°C/min, 850°C - CuS - PS 100nm - RA 44%, 190,000X.

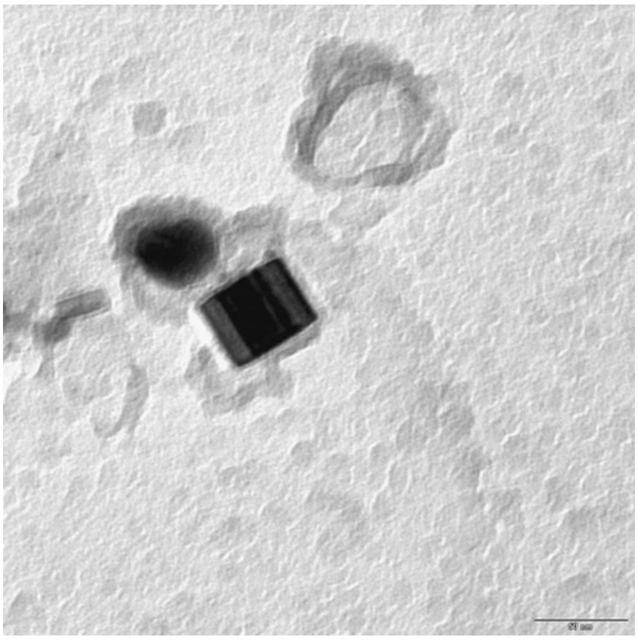

Figure 6. Coarse precipitates found in 0.5%Cu steel tested at 25°C/min, 850°C - diamond shape TiN PS 50nm; round shape CuS - PS 47nm - RA 47%, 240,000X.

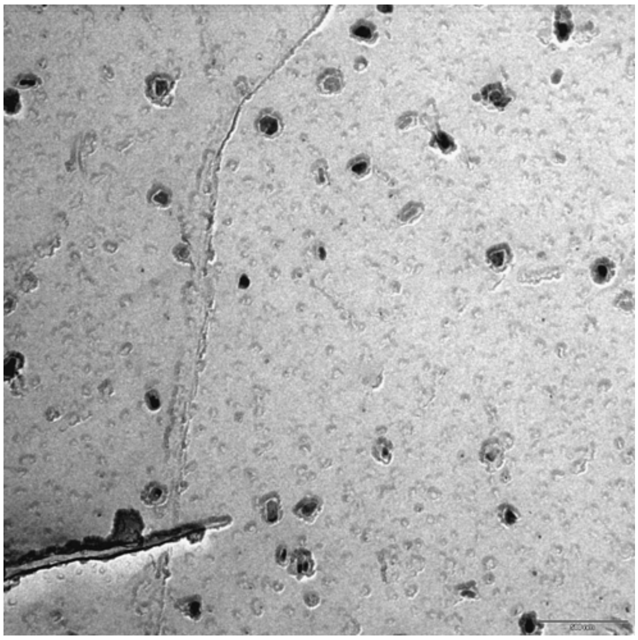

Figure 7. Coarse AlN precipitates found in 0.5%Cu steel tested at 25°C/min, 850°C AlN - PS 70nm; RA 47%, 24,000X.

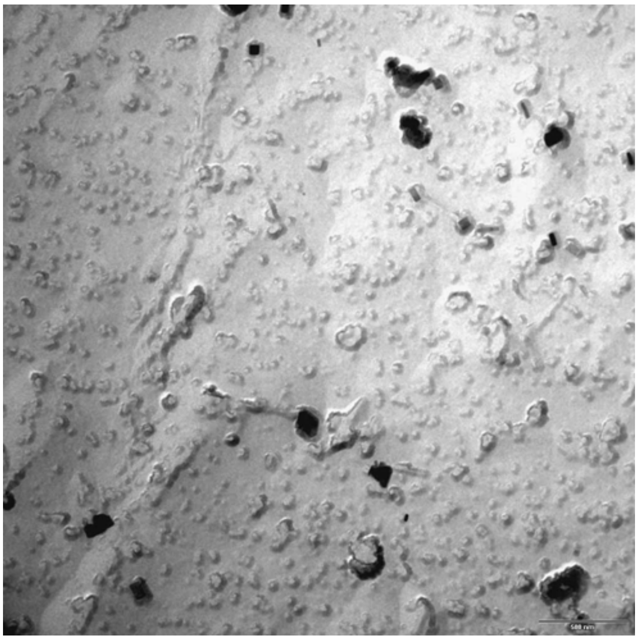

Figure 8. Coarse AlN precipitates found in 0.1%Cu steel tested at 25°C/min, 850°C TiN PS 70nm; AlN PS 110nm; RA 58%, 24,000X.

DISCUSSION

Hot Shortness – Hot Ductility Behaviour

Many authors[10,11] have in the last few years investigated the problem of transverse cracking in continuous casting. For simple plain C-Mn steels as in the present instance, the problem occurs when a thin film of ferrite forms surrounding the austenite grain, when the transformation from austenite to ferrite occurs on cooling. The film forms between the Ae_3 and Ar_3 temperatures. This film always forms on cooling but is often deformation induced and 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 which join up to give inter-granular failure. Previous work[5,6] has also reported that the presence of precipitates in the grain boundary encourage the formation of the cracks that link up to each other and impair the hot ductility. 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.

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[12], 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 by 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 cluster like Guinier-Preston zones.
It is perhaps important to mention that the very small addition of Ti in the steels is unlikely to have any influence on hot ductility particularly as the volume fraction is very low and the precipitates are coarse (>50um), Figs 2 and 6. Similarly, although copper sulphides were found in all conditions, they were generally few and coarse and therefore unlikely also to influence hot ductility, Figs. 5 and 6. The changes that have been observed in the hot ductility can therefore not be ascribed to copper forming a low melting point compound or fine extensive precipitation of copper sulphide.
However, AlN precipitation was very pronounced and extensive and this will have an influence on the hot ductility, particularly as it precipitates at the austenite grain boundaries. Unfortunately, the damaging AlN precipitates at the austenite grain boundaries are also notoriously difficult to detect, forming very thin films, and insufficient time was available to study the boundaries for these particles.

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 this is the temperature of most interest. As 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] In the present instance, the steel with 0.5%Cu will have a lower Ae_3 than the 0.1%Cu containing steel. In addition the higher Cu containing steel has a slightly higher C level and taking both these elements into account the Ae_3 would be expected to be 15^{o}C lower in the 0.5%Cu containing steel. Examination of the curves in Figure1 show that for the slow cooling rate, the 0.5%Cu containing steel gives a 25^{o}C displacement to lower temperatures of the hot ductility curve whilst at the faster cooling rate the displacement is smaller, about 8^{o}C. Hence taking into account that tests are carried out at 25^{o}C intervals these differences are most likely due to experimental scatter, and it is likely that increasing the Cu content from 0.1 to 0.5% leads to an approximate 15^{o}C displacement of the curves to lower temperatures independent of the cooling rate.

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]The importance of precipitate size in controlling ductility can be seen from Figure 9 taken from previous work.[5] However, it can be seen from this figure 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. However, even at the faster cooling rate the precipitate size for the TiN and CuS particles is rarely below 25nm, Figures 2,4 and 5, so these particles would not be expected to influence the hot ductility. Increasing the volume fraction of precipitates will also cause ductility to deteriorate and in the case of AlN, there is a large volume fraction that is precipitated out, Figures 3,7 and 8.

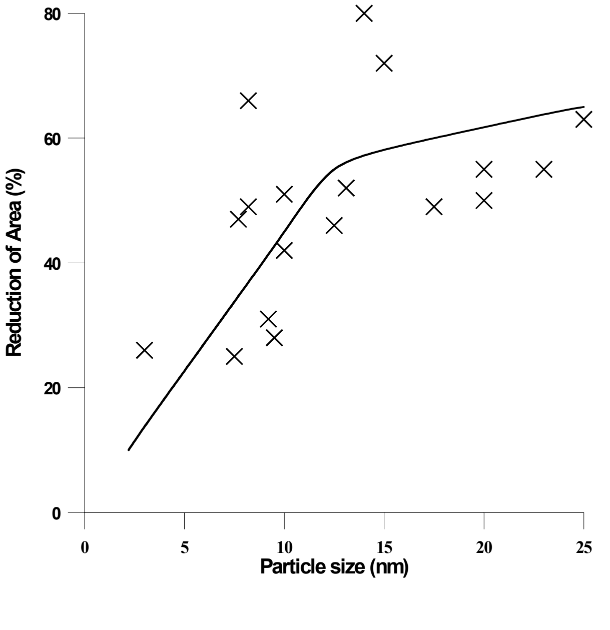

Figure 9. Influence of particles size on reduction of area values for Ti containing steels.[5]

It is interesting to compare the influence of cooling rate on the hot ductility curves for previous work [5] with the present as this gives some incite as to what might be responsible for the changes in hot ductility behaviour shown in Figure 1.

In Cu free, C-Mn-Al steels, increasing the cooling rate can be seen from Figure 10 to impair the hot ductility since it produces a finer AlN precipitation. In this previous work on hot ductility, increasing the cooling rate always resulted in a widening of the hot ductility curve, and the temperature at which ductility starts to fall at the high temperature end, is observed to move to higher temperatures as in Figure 10, not lower as in the present instance, Figure 1.

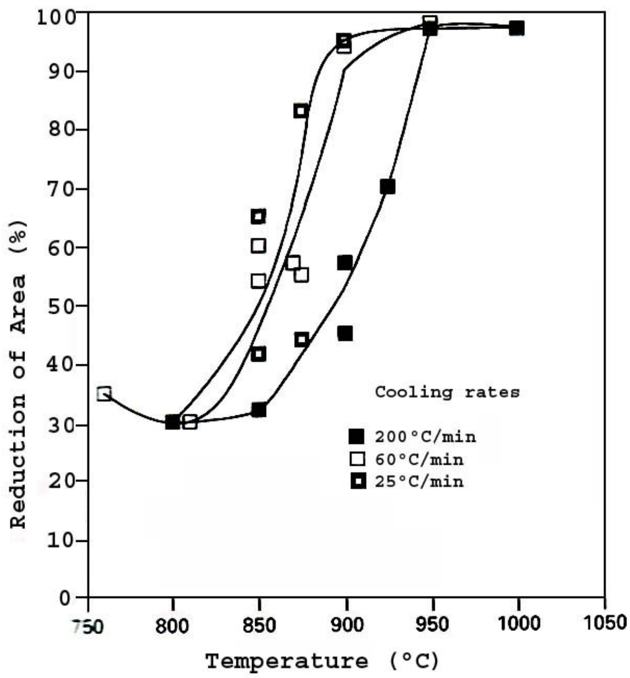

Figure 10. Hot ductility curves for as cast C-1.4%Mn-Al steel at three cooling rates, 25, 60 and 200°C/min and shows how the curves move to the right.[16]

In Figure 10 for example increasing the cooling rate for a 1.4%Mn, C-Mn-Al steel from 25 to 200^{o}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 to lower temperatures by 30°C for the 0.1%Cu steel and not at all for the 0.5%Cu steel.
So what is the difference?
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. The maximum rate of precipitation for AlN occurs at 815°C, which is close to the Ae_3 temperature of 840°C, see Fig.11, which shows the precipitation kinetics for AlN in a low carbon aluminium killed steel.[17,18]

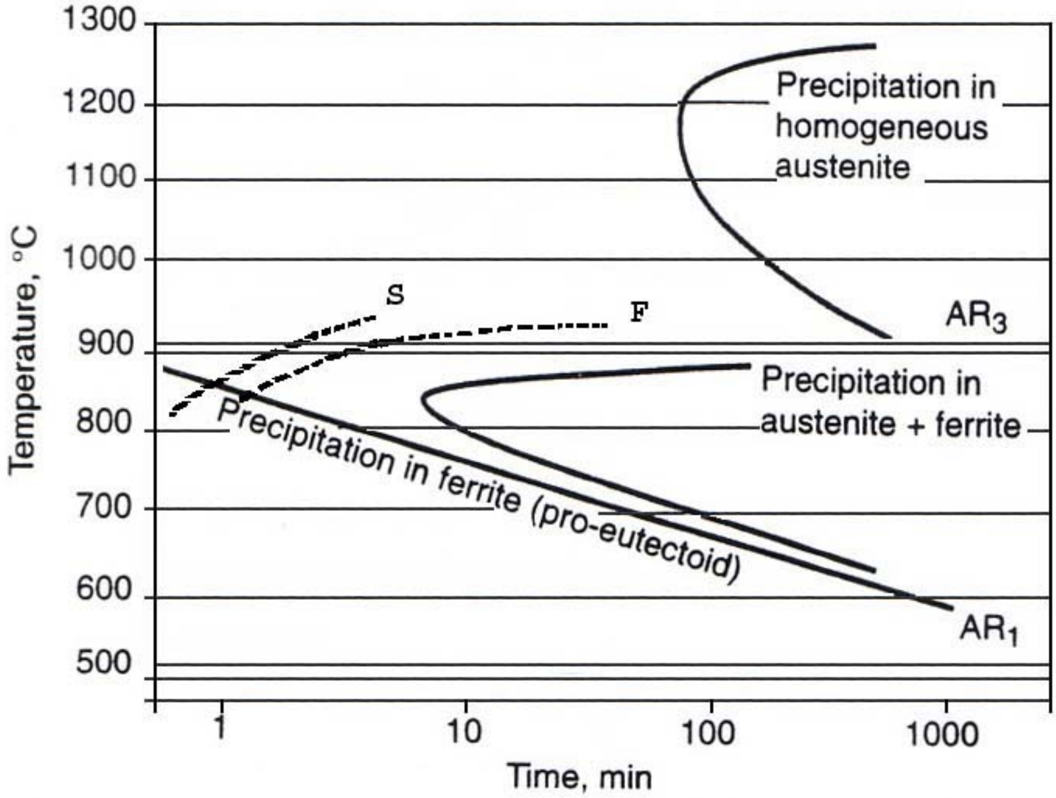

Figure 11. Precipitation kinetics for AlN in low carbon Al-killed steels.[17,18]

It can be seen from this figure that precipitation is very much accelerated when ferrite starts to form as the solubility of Al in the ferrite is very low. Deformation also will further increase the rate of transformation as can be seen from the data of Michel and Jonas[18] which has been superimposed on the data from Ref.18.
It can also be seen from Figure 11 that at temperatures above the nose >840°C the rate of precipitation is very slow, many hours for statically produced AlN. AlN forms much more rapidly under dynamic conditions, as in the present work, as can be seen from the curves of Michel and Jonas, dashed curves in Figure 11.
Under dynamic conditions most of the AlN will have precipitated out in the time of the test but the lower the temperature, the finer is the precipitate and hence the more detrimental it will be to the hot ductility. Increasing the cooling rate will reduce the transformation temperature even more, bringing the temperature even closer to that giving the maximum rate of AlN precipitation. Hence, substantial precipitation of AlN will occur, prior to the transformation temperature being reached in these high Mn steels. The curves in Figure 10 are therefore going to be more controlled by precipitation than the transformation and so will widen as the cooling rate increases, as this brings the transformation temperature closer to 815°C, and the greater cooling rate will give rise to finer precipitates Figure 10.

In the case of the low Mn steels the Ae_3 temperature is much higher at 865°C and is now so far away from the nose temperature of 815°C that the precipitates are too coarse to influence the hot ductility and the trough is controlled by the transformation temperature. Certainly, for the low Cu containing steel given the slower cooling rate, increasing the alloying content by reducing the Ae_3 will displace the curve to lower temperatures and hence finer precipitation. This precipitation is presumably not enough to cause the ductility to fall off at temperatures above the transformation but does lead to a deepening of the trough. Similarly, it would be expected that increasing the cooling rate by bringing the transformation temperature closer to the nose temperature will encourage finer precipitation so again producing a deeper trough. Precipitation is however, not sufficiently fine to influence the temperature at which ductility starts to fall at the higher temperature end of the trough, this being controlled by the transformation temperature. Increasing the cooling rate will again lower the transformation temperature and bring the temperature closer to the nose thus encouraging finer precipitation.

The present work agrees with the previous in that no effect of Cu on hot ductility could be found at fast cooling rates, when tested in an argon atmosphere. There is some evidence that Cu and even Ni may cause some coarsening of Nb and Ti containing precipitates but not in plain C-Mn-Al containing steels.[7,8]

However, it is clear in the present work that it is the AlN precipitation that causes the changes in the hot ductility behaviour and that Cu only influences behaviour because it is influencing the transformation temperature just in the same way as Mn or C. Indeed to coarsen the AlN precipitation so that it has little influence on the hot ductility, the transformation temperature should be as high as possible and this can be achieved by having very low Mn and or C contents in the steel.

Commercial Implications

The commercial implications of this work are important. The work indicates that to produce a coarse AlN precipitation which has little influence on the hot ductility, the transformation temperature for the steel should be as high as possible, preferably >880°C. This means keeping the C and Mn levels as low as is commercially acceptable.

CONCLUSIONS

Previous work[12] 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 are not present in this work.

There is no doubt in these low Mn steels, that it is the precipitation of AlN that is controlling the depth of the trough and the width and the position of the trough is controlled by the temperature for the onset of the transformation from austenite to ferrite.

The present work is of interest because it indicates an important difference in behaviour between high Mn, such as 1.4%Mn steels and the lower Mn steels as in the present exercise.

Whereas with the higher Mn, C-Mn-Al steels, precipitation controls when ductility starts to fall at the high temperature end of the trough, in the lower Mn containing steels it is the transformation temperature that is more important and the presence of the softer ferrite film.

The advantage of a low Mn steel is that, although reducing the Mn level moves the trough to higher temperatures, the temperature range is now so high that coarse AlN precipitation occurs which is too coarse to influence either the temperature at which ductility starts to fall at the high temperature end of the trough or to have much influence on the depth of the trough. A shallow trough is observed, >40% R of A so that transverse cracking should not occur.

Copper and cooling rate in the present instance are only affecting the ductility by their influence in reducing the transformation temperature encouraging finer precipitation of AlN.

Acknowledgements

Authors thank to USIMINAS Steel for supplying the steels, CAPES, the Brazilian Research Agency, for the financial support and also Mr. Seppo Järvenpää of the University of Oulu for his help in the TEM and SEM analyses.

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