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Influence of Cu alloying on hot ductility of C-Mn-Al and Ti-Nb microalloyed steels

O. Comineli*, H. Luo**, H.M. Liimatainen*** and L.P. Karjalainen***

Abstract

A beneficial effect of the copper on the hot ductility was observed in Ti-Nb microalloyed steels over the temperature range 800-1,000 °C at the cooling rate of 0.4 °C/s, but no influence at the cooling rate of 4 °C/s. Precipitates containing Nb and Ti were present whose size was coarser in the Cu-bearing grade as cooled at 0.4 °C/s. Cu-bearing precipitates were not found. In the C-Mn-Al steel, no influence of the copper on the hot ductility was recorded, but CuS particles were detected. Two mechanisms are proposed to explain the positive influence of the copper in the microalloyed steel. The first is that the copper atoms in the solid solution affect the activity of the carbon and the nitrogen analogically to the previously observed effect of the silicon, enhancing the precipitation at high temperatures, and another mechanism that the copper atoms can prolong the lifetime of vacancies generated by straining assisting the formation of TiNb-vacancy complexes and thereby coarsening the precipitates.

Keywords Continuous casting. Hot ductility. Precipitation. Copper. Microalloyed steel. Tensile test.

Influencia del Cu sobre la ductilidad en caliente de aceros Cu-Mn-Al y microaleados Al Ti-Nb

Resumen

Se ha observado un efecto beneficioso del cobre sobre la ductilidad en caliente del acero microaleado al Ti-Nb, en el rango de temperaturas 800-1.000 °C. La influencia fue observada a velocidades de enfriamiento bajas, 0,4 °C/s, mientras que a 4 °C/s no se aprecia. En el acero C-Mn-Al, la influencia de cobre no fue detectada. En el acero microaleado se detectó la presencia de precipidados que contienen niobio y titanio, la dimensión de los cuales es mayor cuando se enfría a 0,4 °C/s. En este acero no se detectó la presencia de precipitados con contenidos de cobre, en contraste con el acero C-Mn-Al, donde sí se observaron partículas de CuS. Se proponen dos mecanismos para explicar la influencia positiva del cobre en aceros microaleados. El primero es el aumento de la actividad de carbono y nitrógeno en austenita debido a presencia de átomos de cobre en solución sólida, con el mismo efecto que el silicio, el cual aumenta la precipitación a altas temperaturas. El otro mecanismo sugiere que los átomos de cobre pueden prolongar la permanencia de vacantes generadas por deformación, facilitando la formación de complejos de vacantes con átomos de Ti-Nb, y como consecuencia agrandando las partículas precipitadas.

Palabras clave Colada continua. Ductilidad en caliente. Precipitación. Cobre. Acero microaleado. Ensayo de tracción.

1. INTRODUCTION

When iron scrap is used as a raw material in steelmaking, tramp elements such as copper remain in steel because they cannot be preferentially oxidized and removed by slag in the normal steelmaking process. Otherwise, copper can also be used as an alloying element in some steel grades and it is the major cause of hot shortness; while at the temperature range of 1,100-1,200 °C, the Cu-rich phase precipitated under oxidizing conditions of iron is liquid and tends to penetrate along the grain boundaries leading to surface cracking during the subsequent rolling operation[1-3].

Besides this, copper has been reported to cause surface cracking in the continuous casting

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process[1 and 4]. Numerous studies have been reported on the influence of composition on hot ductility and transverse cracking over two decades. However, they only include a few investigations dealing with copper. Hannerz[5] examined its influence up to a level of 1 % on the hot ductility of plain C-Mn steels but could not find any significant effect. These tests were carried out in the argon atmosphere after a solution treatment. Matsuoka *et al* .[6] investigated the influences of copper and tin (Sn) in 0.02-0.15 % C-0.27 % Mn steels, testing them also in the inert atmosphere, and they found that the co-addition of these two elements deteriorated the hot ductility due to the segregation of Sn at the austenite grain boundaries and due to increasing strength difference between austenite and proeutectoid ferrite. The work by Shaker[7] showed that copper caused deterioration in the hot ductility as the ferrite film thickness at the austenite grain boundaries increased and the sulfide precipitation was enhanced. Recent work by Mintz *et al.* [8] has looked into the effect of oxidation in detail. Both C-Mn-Al and C-Mn-Nb-Al steels containing copper and/or nickel up to 0.5 % were examined. It was found that only in the instance when the tensile specimens were re-melted and cooled in air, the significant deleterious effect of the copper on hot ductility was present and it could be prevented by an equal addition of nickel. Moreover, the explanation put forward is not that the molten Cu-rich film penetrates along the austenite grain boundaries, but the precipitation of fine copper sulfides or oxysulfides occurs at boundaries. In order to further clarify the mechanisms of copper its influence on the hot ductility at the austenite regime was investigated in C-Mn-Al and C-Mn-Ti-Nb steels.

2. EXPERIMENTAL

The C-Mn-Al steels had the basic composition (wt %) 0.1 C-0.23 Si-0.5 Mn-0.043 Al-0.006 N with 0.5 % Cu or 0.1 % Cu. Two laboratory heats of Ti-Nb microalloyed steel grade 0.1 C-0.4 Si-1.5 Mn-0.015 Ti-0.03 Nb-0.005 N without Cu (coded here TiNb Steel) and with 0.30 % Cu (coded CuTiNb Steel) were tested.

A GLEEBLE 1500 thermo-mechanical simulator was employed to determine the hot ductility, defined as the reduction of area (RA) in the tensile test. The tensile test specimens were rods of 120 mm length and 10 mm diameter. The specimens were heated at 25 °C/s in the argon shielding gas up to the melting temperature, while a length of 1,520 mm in the middle part of the specimen was supported by a slotted silica tube 60 mm in length. Subsequently, the specimens were directly cooled to test temperatures at the cooling rate of 4 °C/s or 0.4 °C/s (or 200 °C/min and 25 °C/min), and held for 15 s, finally strained to failure at a strain rate of 0.0005 s^{-1}. Tests were repeated for two or three times at temperatures between 800-1,000 °C and the mean values of RA at each temperature were used.

Carbon replicas were taken from samples close to the fracture, etched by the 2 % nital alcohol solution. The replicas were examined by an electron energy filtered, scanning transmission electron microscope (LEO 912), and the composition of precipitates were analyzed by the EDS device attached.

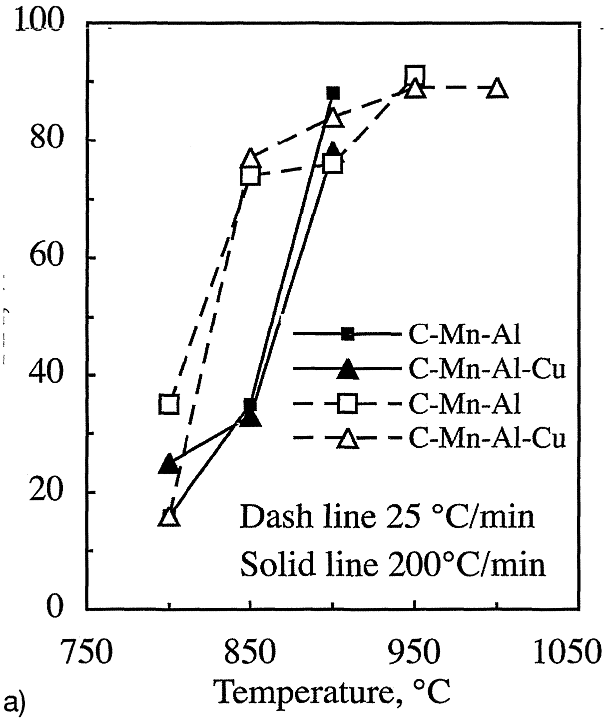
3. RESULTS

3.1. Hot ductility curves

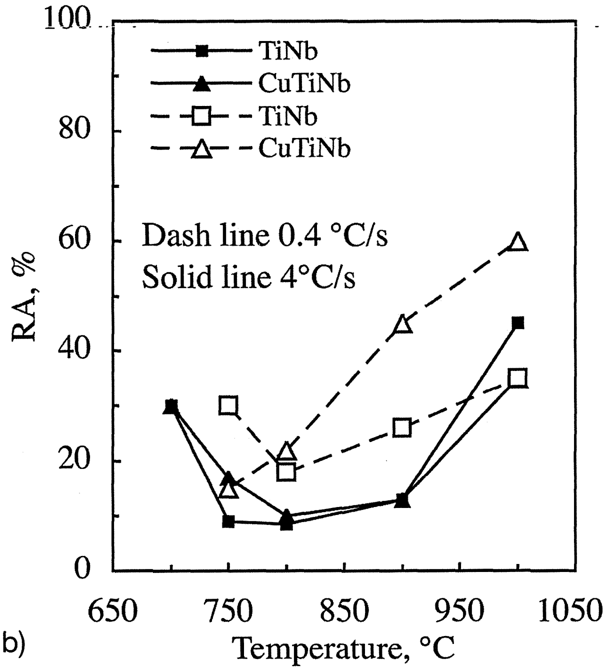
The hot ductility of the steels is shown in figure 1 as the plotted curves RA as a function of the test temperature, for both the C-Mn-Al and the microalloyed steels. As seen, the effect of cooling rate is very significant, for the ductility is considerably improved at the low cooling rate compared to that at the high cooling rate, a phenomenon often observed earlier[1, 9 and 10]. Particularly, the cooling had a very prominent effect at 900 C on the ductility of CuTiNb Steel, whose ductility increased from 14 % to 44 % with the decreasing cooling rate. It can be noted that the effect of cooling rate is present in the both C-Mn-Al steels, i.e. for the steel without Cu as well (Fig. 1a). Further, it is seen that the Cu addition does not affect the ductility of the microalloyed steel at the high cooling rate, but there is a distinct improvement over the temperature range of 800 to 1,000 °C at the low cooling rate (Fig. 1b). However, in the C-Mn-Al steel, the copper seems to have no influence.

3.2. Precipitation structure

A profound precipitation was seen in the microalloyed steel specimens tested at 900 °C. The analysis showed both the presence of titanium and niobium in particles, with the average size of 10 and 15 nm after the fast cooling and the slow cooling in TiNb steel, respectively, as shown in



a)



b)

Figure 1. Effect of the cooling rate and the addition of copper on the hot ductility of a) C-Mn-Al steel b) Ti-Nb micro-alloyed steel.

Figura 1. Efecto de la velocidad de enfriamiento y la adición de cobre sobre la ductilidad en caliente de aceros a) C-Mn-Al b) microaleado al Ti-Nb.

figure 2. This indicates that the fast cooling leaves more solute in the matrix for the subsequent strain-induced precipitation, which leads to a worse ductility.

In the CuTiNb steel, the cooling rate affects the TiNbCN particle size very significantly. The addition of copper seems to have coarsened the precipitates especially at the slowcooling rate (Fig. 2c).

In the 0.5 % Cu-bearing C-Mn-Al grade, particles containing copper and sulphur were observed. Their size was quite coarse, order of 100-200 nm. Typical precipitation structure is shown in figure 3. The investigation on the precipitation behaviour in Cu-bearing C-Mn-Al steels continues and the results will be presented in a future paper.

4. DISCUSSION

At high temperatures, the hot ductility of austenite is controlled by precipitation, the formation of microalloy carbonitrides in microalloyed steels and AlN in C-Mn-Al steels[1 and 8]. A low cooling rate provides more time for diffusion resulting in coarser particles and consequently to a better ductility. In Cu-bearing C-Mn-Al and C-Mn-Al-Nb steels, the copper has been found to have a detrimental influence on hot ductility as cooled in air, but in the inert atmosphere the effect observed was only minor[8]. However, a small improvement of the ductility of TiNb Steel by the addition of 0.3 % Cu was observed in the present tests in the argon shielding gas at the low cooling rate of 0.4 °C/s, which seems to be attributed to the coarsening of Ti-Nb-containing carbonitride precipitates, evidently formed during cooling at higher temperatures. No particles containing copper were detected in this steel. A slow cooling could provide a longer time to enhance precipitation at high temperatures. Hence, the influence due to the addition of copper would be more obvious during the slow cooling than during the fast cooling.

Several researchers[11-14] have suggested that the activity of carbon and nitrogen is affected by the solute atoms in the austenite and consequently the precipitation kinetics of carbo-nitrides. Akben *et al.* [13] observed a retarded precipitation of TiC in steels with increasing manganese (Mn) concentration, and Dong *et al.*[14] recorded an increased rate of niobium (C, N) precipitation due to silicon alloying, both contributing to the changes of the activities of the carbon and the nitrogen in the austenite. It can be proposed that Cu atoms are able to change the activities of the carbon and the nitrogen and the diffusion rate of niobium and/or titanium to an extent that leads to enhanced precipitation of TiNbCN. Unfortunately, the Wagner interaction parameters needed to

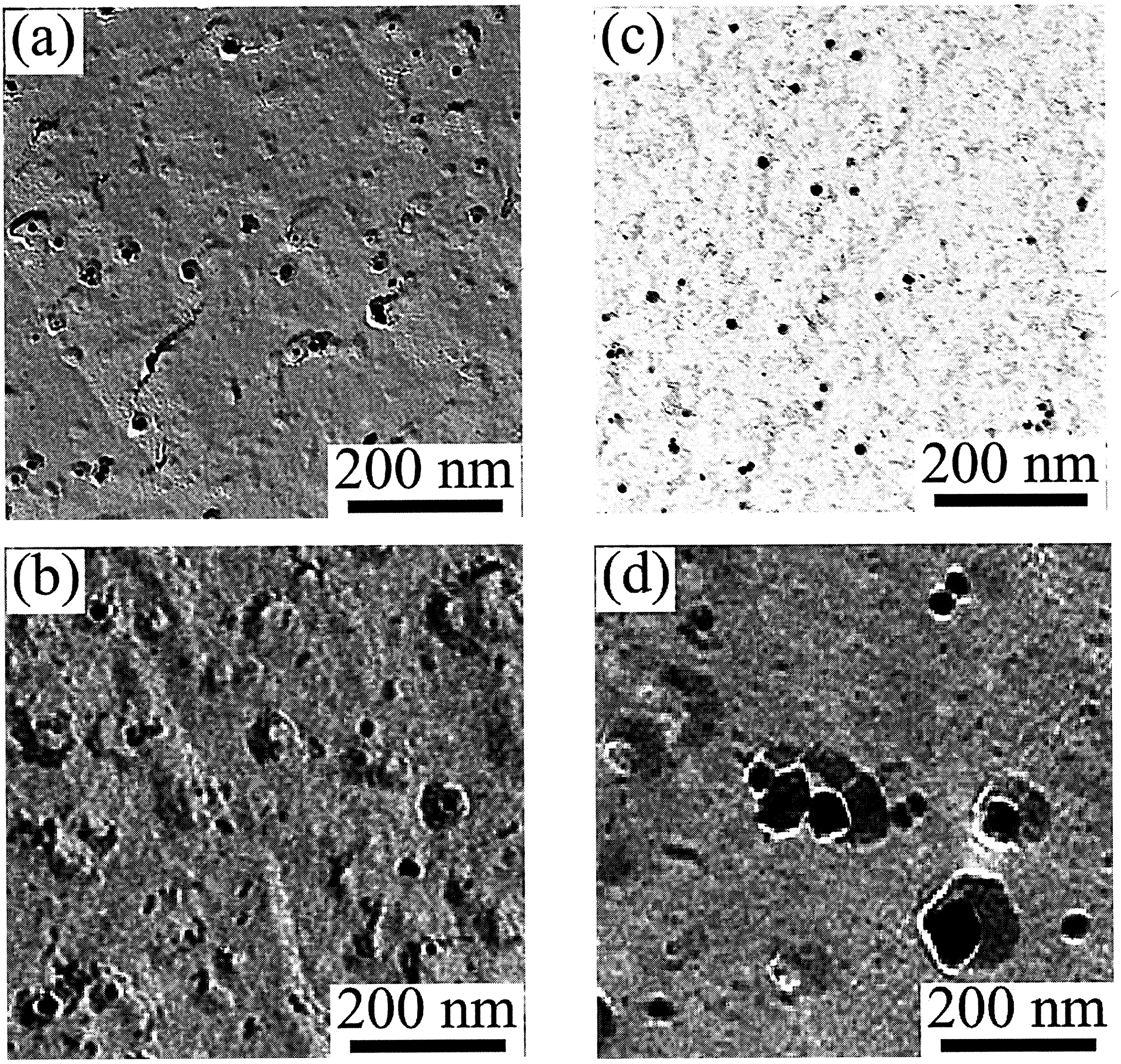


Figure 2. Precipitates of TiNbCN in the microalloyed steels tested at 900 °C: a) TiNb Steel, cooling at 4 °C/s, average particle size 10 nm, RA = 13 %; b) TiNb Steel, at 0.4 °C/s, average particle size 15 nm, RA = 26 %; c) CuTiNb Steel, at 4 °C/s, average particle size 14 nm, RA = 14 % and d) CuTiNb Steel, at 0.4 °C/s, average particles size 23 nm, RA = 44 %.

Figura 2. Precipitados de TiNbCN en aceros microaleados ensayados a 900 °C: a) TiNb, velocidad de enfriamiento 4 °C/s, diámetro medio de partícula 10 nm, RA = 13 %; b) TiNb, 0,4 °C/s, diámetro medio de partícula 15 nm, RA = 26 %; c) CuTiNb, 4 °C/s, diámetro medio de partícula 14 nm, RA = 14 % and d) CuTiNb, 0,4 °C/s, diámetro medio de particula 23 nm, RA = 44 %.

make thermodynamic calculations for that are not known so that quantitative predictions are not possible.

Liu[15] has presented another theory to explain the precipitation kinetics of NbCN in some instances. He expressed that deformation not only accelerates but it can also enhance the precipitation beyond the thermodynamic equilibrium. According to him, non-equilibrium segregation of the Nb-vacancy complexes is considered to be responsible for that. Its extent depends on the concentration of vacancies, which is, in turn, dependent on the degree and the rate of deformation. If a higher number of vacancies from severe deformation could remain for a longer time before annihilation, precipitates would grow coarser, since the solute atoms could be bound to vacancies to form vacancy-TiNb atom complexes,

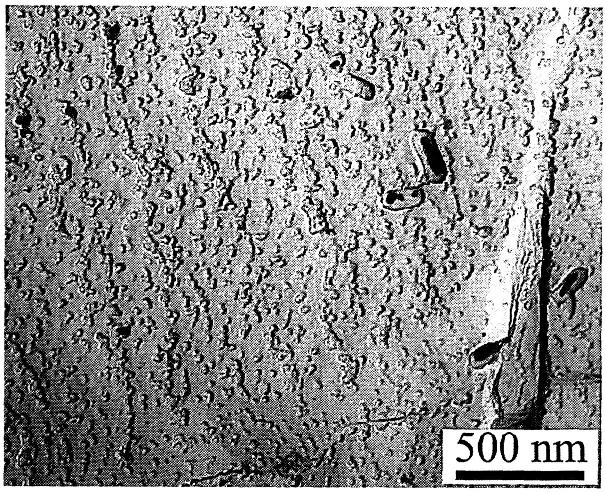


Figure 3. CuS precipitate particles formed in the C-Mn-Al steel with 0.5 % Cu.

Figura 3. Partículas de CuS en el acero C-Mn-Al con 0,5 % Cu.

which can diffuse much faster than plain niobium or titanium atoms. It is known that the copper in the solid solution can retard the dynamic recovery and recrystallisation of austenite due to the solute drag effect[16]. Consequently, it can be expected that numerous vacancies resulting from the tensile straining could remain for a longer time to form the solute atom-vacancy complexes, finally leading to some coarsening of the pre-existing precipitates.

In the C-Mn-Al steel the precipitation of CuS was detected in the present tests under the argon atmosphere. Earlier Mintz *et al.* [8] reported them in a C-Mn-Nb-Al-Cu steel as tested in oxidizing conditions. Anyhow, it seems that these particles are so coarse that they cannot affect the hot ductility significantly, but the effect of cooling rate must be a consequence of some other phenomenon, presumably the precipitation of AlN.

5. CONCLUSIONS

Addition of 0.3 % Cu affects beneficially the hot ductility of Ti-Nb microalloyed steels at the low cooling rate of 0.4 °C/s. In this instance the TiNbCN particles formed have the coarsest size. One explanation for the enhanced precipitation at high temperatures might be that the copper atoms in the solid solution can increase the activity of the carbon and the nitrogen atoms in the austenite. Another explanation could be that the copper atoms in the solid solution can prolong the lifetime of vacancies, generated by straining during the tensile test, to form titanium, niobium atom-vacancy complexes finally leading to some coarsening of precipitates. In C-Mn-Al steels, CuS precipitation can occur in a coarse form, but it seems that the precipitation of AlN is a more important factor than this precipitation.

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