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# Development of high strength hot rolled low carbon copper-bearing steel containing nanometer sized carbides

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ABSTRACT

A low carbon ferritic steel was alloyed with Ti, Mo and Cu with the intention of achieving greater increment in strength by multiple precipitate strengthening. The steel is hot rolled and subjected to interrupted cooling to enable precipitation of Ti–Mo carbides and copper. Thermodynamic calculations were carried out to determine equilibrium phase fractions at different temperatures. Microstructure characterization using transmission electron microscopy and composition analysis revealed that the steel contains ~5 nm size precipitates of (Ti,Mo)C. Precipitation kinetics calculations using MatCalc software showed that mainly body centered cubic copper precipitates of size < 5nm form under the cooling conditions in the present study. The steel has the high tensile strength of 853 MPa and good ductility. The yield strength increases by 420 MPa, which is more than that achieved in hot rolled low carbon ferritic steels with only copper precipitates or only carbide precipitates. The precipitation and strengthening contribution of copper and (Ti,Mo)C precipitates and their effect on the work hardening behavior is discussed.



## 1. Introduction

The long-standing goal in research on high strength steels has been to increase the strength while maintaining the ductility, toughness, weldability and cost effectiveness. In low carbon ferritic steels the strength–ductility combination is achieved by microalloying with elements such as Nb, V or Ti in the mill processed condition without the requirement of an additional heat treatment. The microalloying elements form nanocrystalline carbides/carbonitrides which strengthen the ferrite matrix by grain size refinement and precipitation strengthening. The conventional microalloyed steels typically possess yield strengths in the range 450–550 MPa [1,2], however significant improvements in strength can be achieved by a combination of alloy design and thermo mechanical processing followed by controlled cooling.

Recently, Funakawa et al. [3] reported an increase in yield strength of 300 MPa in the hot rolled low carbon steel microalloyed with Ti and Mo in equiatomic concentration. The hot rolled sheet was air cooled to 620 °C where phase transformation ($\gamma \rightarrow \alpha$) was accompanied by precipitation of alloy carbides. The high strength of the steel was due to ferrite grain size refinement (~3 μm) and precipitation of nanometer size (Ti,Mo)C carbides (~3 nm). Chen et al. [4] compared carbide size and hardness of three continuously cooled ferritic steels containing the microalloying elements Ti, Ti–Mo and Ti–Nb respectively. They reported that the Ti–Mo steel had the finest carbide size and highest hardness. The relatively lower change in carbide size and hardness measurements after different cooling rates lead them to conclude that the carbide formed in the Ti–Mo steel was relatively thermally stable.

Copper addition in amounts of 1–2 wt% has also been used for precipitation strengthening in low carbon structural steels [5–9]. Commercially available copper containing low carbon steels such as ASTM A710 or HSLA80, also contain microalloying elements such as Nb and have yield strength between 450 and 520 MPa [10,11] in the as-rolled and air-cooled condition. The higher strength of these steels is because of the formation of nanosized copper precipitates in ferrite and grain refinement brought out by microalloy carbides in prior austenite. Misra et al. [12] studied the effect of copper addition on the mechanical properties of hot rolled V–Nb microalloyed steels. They reported that increasing the copper content from 0.22 to 0.63 wt% increased the yield strength by ~25 MPa in the as rolled condition. In

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order to increase the strength further they microalloyed the Cu–Nb–V steel with Ti and Mo. The yield and tensile strength improved to 554 MPa and 658 MPa, respectively after aging the as-rolled specimen. The improvement in strength was due to ferrite grain refinement (2–10 μm), and nano sized precipitates of copper and the carbides: NbC, VC, $Mo_2C$, Ti(Nb)C. The % elongation decreased with increase in strength. Their results show that multiple carbide precipitates may not guarantee the yield strength superior to that obtained in steels with fewer type of carbide precipitates [3,13].

In the present study the low carbon steel is alloyed with both copper, and titanium and molybdenum with the intention of synergizing their beneficial effect on mechanical properties. The structure and properties of Ti–Mo and Cu–Ti–Mo microalloyed steels were investigated to determine the contributions to strength by Ti–Mo carbides individually and together with copper precipitates. The thermo-kinetic software MatCalc has been used to calculate evolution of copper precipitates in Fe–1.4% Cu alloy [14] and in austenitic heat resistant steels by this paper's co-authors [15]. In the present study MatCalc was used to calculate the phase evolution and size distribution of copper precipitates.

## 2. Experimental and computational details

The compositions of steels designated as CMn, TiMo and CuTiMo are given in Table 1. CMn is the base low carbon steel without any precipitate forming elements. TiMo and CuTiMo are the CMn steel microalloyed with titanium and molybdenum, and microalloyed with copper, titanium and molybdenum respectively. The alloys were prepared using vacuum induction melting into 5.7 kg ingots. The ingots were forged and rolled at 1100 °C into 15 mm thick slabs. The slabs were then heated to 1250 °C and held for 30 min to dissolve any precipitates and then rolled to 75% reduction at 900 °C. After rolling the specimens were first air cooled to 650 °C and held for 5 min, followed by air cooling to 500 °C where it was held for 60 min and then furnace cooled to room temperature. The precipitates viz. (Ti, Mo)C carbide and Cu rich phase are expected to form at 650 °C [3,4,16] and 500 °C [17,18] respectively.

The specimens for the tension test were prepared from the rolled plates along the rolling direction according to ASTM standard E08-M with gage length of 25 mm, gage width of 6 mm and thickness of 2 mm. The tests were carried out at the constant crosshead speed of 1 mm/min. The tension test experiments were conducted on two specimens for each composition. The microstructure was characterized using scanning electron microscope (SEM), the 200 kV Tecnai 20 transmission electron microscope (TEM) and energy dispersive spectroscopy (EDS). Focused Ion Beam (FIB) technique was used to make thin foil specimens for characterization of precipitates in TEM-EDS. The precipitates were also extracted by dissolution in the electrolyte solution consisting of 4% tetramethylammonium chloride, 10% acetone and 86% methyl alcohol. The grain size was determined from SEM micrographs with help of an image analyzer using the linear intercept method. The precipitate size and distribution were determined from measurements in TEM micrographs on up to 400 extracted particles.

The equilibrium phase fractions at different temperatures were calculated using Thermo-Calc [19,20]. The data set of parameters for the thermodynamic models describing the Fe–C–Mn–Si–Mo–Ti–Cu system used in Themo-Calc was from the TCFE database incorporated in the software. The phases included in the calculations were austenite, ferrite, cementite, fcc-copper, and MC (M=Ti, Mo) carbide. A thermo-kinetic software MatCalc (version 5.30) [21–23] was used to determine the precipitation kinetics and size distribution of Cu precipitates and MC carbides. In MatCalc the microstructure evolution is calculated based on the classical nucleation theory. The evolution equations for the radius and composition of each precipitate are derived from the thermodynamic extremum principle. The thermodynamic and kinetic data required for the simulation are calculated from the MatCalc database 'mc_steel', version 1.18, and the MatCalc mobility database 'mc_sample_fe', version 1.007. The following assumptions were made for the simulation: (i) average grain size and dislocation density of austenite is 50 μm and $10^{12}$ $m^{-2}$, (ii) average grain size and dislocation density of ferrite is 15 μm and $10^{13}$ $m^{-2}$, (iii) nucleation of bcc Cu and MC precipitates occurs on grain boundaries and dislocations, (iv) the austenite–ferrite transformation occurs at 650 °C and (v) the bcc Cu precipitates transform into fcc Cu precipitates when they grow in a range between 3–5 nm.

**Table 1**
Chemical composition (wt%).

| Steel | C | Mn | Si | Mo | Ti | Cu | Al | Fe |
|---|---|---|---|---|---|---|---|---|
| CMn | 0.07 | 1.47 | 0.32 | – | – | – | 0.04 | Bal. |
| TiMo | 0.07 | 1.34 | 0.32 | 0.20 | 0.09 | – | 0.04 | Bal. |
| CuTiMo | 0.07 | 1.53 | 0.34 | 0.21 | 0.09 | 1.17 | 0.04 | Bal. |

## 3. Results

### 3.1. Phase equilibria

The equilibrium phase fractions calculated using ThermoCalc are plotted as a function of temperature in Fig. 1. In all the steels cementite precipitates below ~700 °C and precipitation of face centered cubic (fcc) copper begins at around 750 °C. In steels containing Ti and Mo MC carbide (NaCl structure) precipitates, consisting mainly of TiC, start to form around 1150 °C. In these steels the volume fraction of cementite is relatively lower than that in CMn steel. The lower cementite content is expected because some carbon is used up in the formation of MC type precipitates.

### 3.2. Microstructure

The microstructure in all the steels consists mainly of polygonal ferrite (Fig. 2). In the CMn steel cementite exists in pearlite form whereas in TiMo and CuTiMo steels pearlite colonies are less common. The latter is consistent with the calculations of equilibrium phase fractions (Fig. 1) where it was noted that the lower fraction of cementite was because some carbon was used in the formation of MC carbides. The ferrite grain size of CMn steel is 16 μm whereas both TiMo and CuTiMo steels have relatively finer grain size of 12 μm.

Fig. 3a is a TEM micrograph of the extracted nanometer size carbide particles from TiMo steel. The electron diffraction pattern from the precipitates shows that they have a typical face centered cubic structure (Fig. 3b). The lattice parameter calculated based on the diffraction ring diameter is 0.430 nm which is similar to that of TiC (0.433 nm). The EDS spectrum shows that MC precipitates contains Ti and Mo as main components (Fig. 3c). The copper peak (at ~8 eV) in the EDS spectrum is from the Cu grid that supports the carbon extraction replica. The composition analyses showed that MC precipitates contain molybdenum and titanium in the atomic concentration ratio between 0.2 and 0.4. This indicates that the precipitates are indeed (Ti,Mo)C precipitates. The precipitates have size in the range from 2 nm to 7 nm (Fig. 3d).

Fig. 4 shows the diffraction pattern and bright field and dark field images from the foil specimen of the CuTiMo steel. The diffraction rings for (110)-αFe and for (111) and (200) from TiC are overlaid on the diffraction pattern. The diffraction pattern has been inverted i.e. the