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Effect of copper additions in directly quenched titanium–boron steels

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Abstract The present study concerns the effect of copper additions on the microstructural evolution and mechanical properties of directly quenched Ti–B steels. Ti and B are added as microalloying elements with an aim of achieving adequate austenite hardenability and Cu is added to retard the austenite (γ) $\rightarrow$ ferrite (α) transformation. Therefore, the microalloying and Cu additions together allow the transformation of austenite to occur at a lower temperature, resulting in a finer microstructure containing martensitic constituents. The direct-quenching route is adopted with an aim of facilitating the nucleation of the constituent phases from the deformed austenite. In order to circumvent the hot-shortness due to the Cu addition, 0.79 wt% Ni has been added to one of the 1.5 wt% Cu microalloyed steels. The present study has demonstrated that the Ni-containing 1.5Cu–Ti–B steel is capable of providing an attractive combination of strength and ductility comparable to the high strength varieties of HSLA steels in directly quenched condition.

Introduction

The transformation of austenite during continuous cooling changes from diffusional to displacive mode depending on the alloy content, cooling rate and amount of deformation in the austenite. The microalloying elements (Ti, B) expectedly shift the transformation temperature ranges downwards resulting into delay in $\gamma \rightarrow \alpha$ transformation [1].

When the deformation of austenite is completed at a temperature lower than the recrystallisation temperature, deformation bands dividing the austenite grains into numerous sub-grains are created [2, 3]. Thus, the large amount of heterogeneity in the deformed austenite results in a finer microstructure facilitating precipitation hardening, tempering resistance and secondary hardening [4, 5]. Deformation within the intercritical region followed by direct-quenching (DQ) induces finer and more copious ε-Cu precipitation due to the low solubility of Cu in ferrite [3, 6]. The DQ and tempering process as applied to high strength steel offers a better strength–toughness balance, improved weldability and lower manufacturing cost than the conventional reheat quenching and tempering process [6, 7].

Depending on the acquired hardenability, austenite transforms into a low temperature ferritic constituent of widely varying morphology [8] in low carbon steel during continuous cooling. In addition to the temperature of transformation, presence of dislocation substructures within the austenite grain exerts significant influence on the nucleation and growth of ferritic phases and, hence, determines their morphology [9, 10].

In continuously cooled low carbon steels, it is difficult to distinguish between the bainitic and martensite laths [11]. Moreover, in directly quenched steels, the carbon atoms do not precipitate on the dislocations within the bainite and martensite laths, and this results in continuous yielding [11]. Therefore, it is apparent that DQ of microalloyed steel containing a precipitate-forming element like Cu is conducive to the formation of a finer martensitic

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microstructure suitable for achieving an attractive strength–ductility combination.

In the present study, an attempt has been made to develop a pearlite-free directly quenched microstructure composed of bainitic and/or martensitic micro-constituents in Cu-containing Ti–B microalloyed steels by utilising a simple thermomechanical processing schedule. An attempt has also been made to understand the role of Ni on the microstructural evolution and mechanical properties of Cu-bearing microalloyed steels.

Experimental procedure

A series of steels were prepared in order to evaluate the effect of Cu on a Ti–B microalloyed steel. The alloys were prepared in a laboratory-scale induction-melting furnace (5 kg crucible capacity). Table 1 presents the compositions of the alloys as measured by spectroscopic analysis using an Optical Emission Spectrometer (SPECTROLAB-M8). The ingots were cast into a preheated cast iron mould with approximately 50 mm^2 section. After homogenisation at 1,200 °C for 120 min in a resistance-reheating furnace, the cast ingots were forged into bars of 12.5×12.5 mm section. The forged bars were soaked at 1,200 °C and hot-rolled down to a thickness of approximately 6 mm in three passes in a laboratory scale two-high rolling mill (10 HP) with a finish rolling temperature (FRT) of 750 °C. The FRT was determined in a manner such that approximately 10% deformation can be accomplished within the two-phase ($\gamma + \alpha$) region. After completion of rolling, the samples were quenched in water.

To study the microstructures, the samples were etched with Vilella's reagent (1 g picric acid, 5 mL hydrochloric acid and 95 mL ethyl alcohol) [12]. The microstructures of the etched samples were examined under an optical microscope (Versamet-II) and scanning electron microscope (SEM) (Model: JEOL, JSM-5510, operated at 20 kV). Transmission electron microscopy (TEM) examination of samples was performed using a PHILIPS: CM-200 analytical electron microscope equipped with an EDAX energy dispersive X-ray spectrometer and was operated at 200 kV. Thin slices of the samples were cut parallel to the rolling plane with a slow speed diamond cutter and manually ground down to 0.1 mm thickness. About 3 mm diameter discs were punched out of the thin strips and were further electrolytically polished by twin-jet polishing technique using a mixture of 90% acetic acid and 10% perchloric acid, using 60–70 V at a temperature of about >12 °C.

Hardness measurements were conducted using a Brinell-cum-Vickers hardness tester (Model: BV-250 (SPL)). Room temperature tensile testing was performed using a computer-controlled Instron-4204 testing machine with a crosshead velocity of 0.5 mm/min as per ASTM Standard (ASTM: Vol. 03.01: E8M-96). The error in hardness, YS and UTS measurement was noted as approximately ±3% and the same for percent elongation was ~±5%. Charpy V notch impact testing of the samples was conducted at 25, 0, –25 and –50 °C following the ASTM standard (ASTM: Vol. 03.01: E23-96). The sub-size samples were prepared with $55 \times 5 \times 5$ mm dimensions. The average of three consistent test results was recorded as the impact value for the corresponding samples. The error for Charpy V notch values was approximately ~±10%.

Results

Hardness measurements

Figure 1 shows that the hardness values of the directly quenched Cu–Ti–B microalloyed samples are consistent with the increase in Cu content. It is apparent that presence of Ti and B in 1.5 wt% Cu containing steels increases the hardness value from 292 to 323 VHN. Addition of 0.79 wt% Ni in 1.5 wt% Cu-added Ti–B microalloyed steel has further enhanced the hardness value from 323 to 332 VHN. In order to examine the role of Cu precipitation in DQ steel, a 2.0 (wt%) Cu–Ti–B steel sample was subjected to solution treatment at 1,200 °C followed by water-quenching. It was observed that the directly quenched 2.0 (wt%) Cu–Ti–B steel exhibited a hardness value of 331 VHN, which is significantly higher than that obtained

Table 1 Chemical composition of the investigated steels (wt%)

Steel Identification	C	Mn	Si	S	P	Ti	B	Cu	Ni	N
Ti–B	0.04	1.60	0.49	0.021	0.013	0.028	0.0009	–	–	0.0056
1.5Cu	0.04	1.60	0.48	0.022	0.014	–	–	1.51	–	0.0051
1.0Cu–Ti–B	0.04	1.48	0.42	0.022	0.013	0.047	0.0025	1.09	–	0.0065
1.5Cu–Ti–B	0.04	1.69	0.57	0.021	0.013	0.032	0.0013	1.54	–	0.0080
2.0Cu–Ti–B	0.05	1.63	0.47	0.022	0.014	0.047	0.0015	2.17	–	0.0062
1.5Cu–Ti–B–Ni	0.04	1.68	0.53	0.020	0.013	0.032	0.0012	1.55	0.79	0.0058

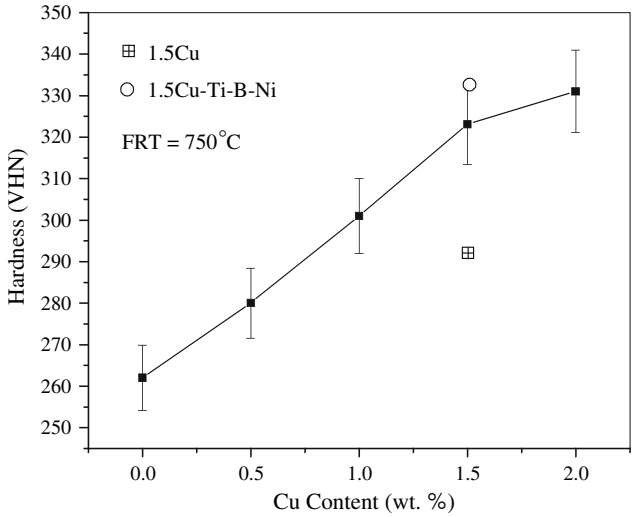

Fig. 1 Variation of hardness values with Cu content in Ti–B microalloyed DQ steels. The hardness values of 1.5Cu alloy and Ni containing 1.5Cu–Ti–B alloys are appended for comparison

in the solution-treated sample followed by water-quenching (280 VHN).

Tensile properties

Figures 2–4 present the variation of tensile properties with respect to the variation of the alloying and microalloying elements. The increase in the YS and UTS values with increasing Cu content as shown in Fig. 2 corroborates the observed variation in hardness (Fig. 1). However, in contrast to the hardness measurements, the addition of microalloying elements to the 1.5 wt% Cu steel and the

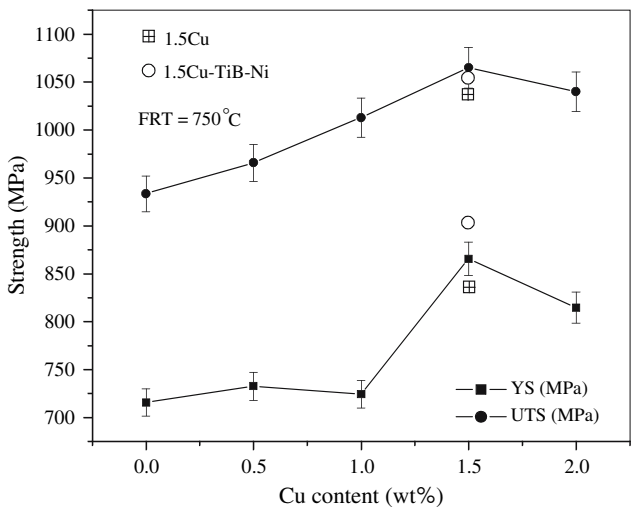

Fig. 2 Variation of strength i.e. YS and UTS (MPa) with Cu content in Ti–B microalloyed DQ steels. The YS and UTS values of 1.5Cu alloy and Ni containing 1.5Cu–Ti–B alloy are appended for comparison

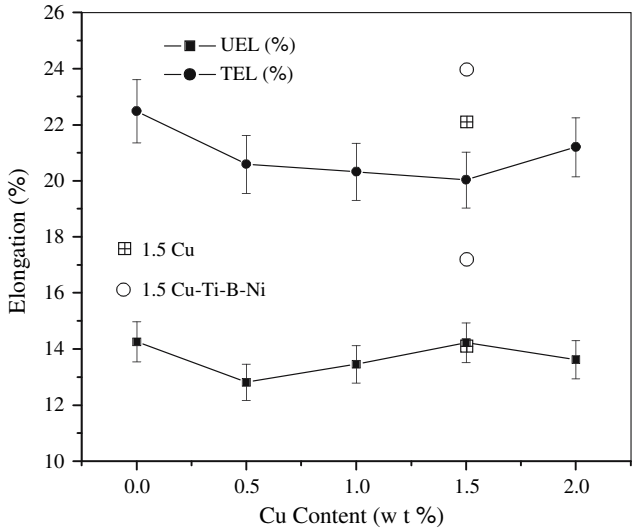

Fig. 3 Variation of elongation (%) i.e. UEL (%) and TEL (%) with Cu content in Ti–B microalloyed DQ steels. The UEL and TEL values of 1.5Cu alloy and Ni containing 1.5Cu–Ti–B alloy are appended for comparison

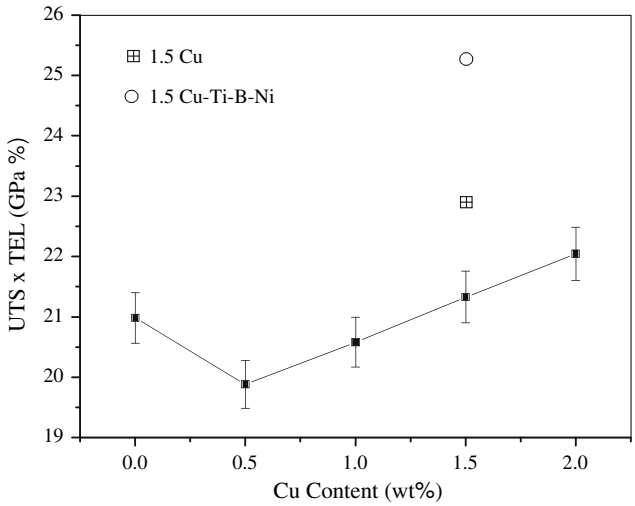

Fig. 4 Variation of strength–ductility combination i.e. UTS × TEL (GPa %) with Cu content in Ti–B microalloyed DQ steels. The UTS × TEL values of 1.5Cu alloy and Ni containing 1.5Cu–Ti–B alloys are appended for comparison

addition of Ni to the 1.5 wt% Cu microalloyed steel do not alter the strength values to any appreciable extent.

It is interesting to note that the elongation values do not exhibit any significant variation as a function of Cu content (Fig. 3) in the microalloyed steel. The variation in the product of UTS and % total elongation (TEL) values (Fig. 4) as a function of Cu content shows that there is a slight increase with increasing Cu. While addition of microalloying elements to the 1.5 wt% Cu steel has decreased the product of UTS and %TEL compared to the

steel without the microalloying addition, the addition of Ni to the 1.5 wt% Cu microalloyed steel has significantly improved the properties. Results shown in Fig. 4 demonstrate that addition of 0.79 wt% Ni in the 1.5 wt% Cu–Ti–B microalloyed steel has yielded the best combination of strength and ductility.

Impact toughness

Figure 5 presents the variation of Charpy impact toughness values for the Ti–B microalloyed steel, the 1.5 wt% Cu–Ti–B microalloyed steel and the 1.5 wt% Cu–0.79 wt% Ni–Ti–B microalloyed steel. The results demonstrate the effect of Cu in deteriorating the toughness. Figure 5 also shows that toughness of the steels remains almost unaltered as a function of testing temperature, particularly from 0 to –50 °C. Figure 5 indicates that the Cu–Ti–B steels are in the lower shelf region. The Ni–Cu–Ti–B steel appears to be in the lower end of the transition region at the –50 °C test temperature.

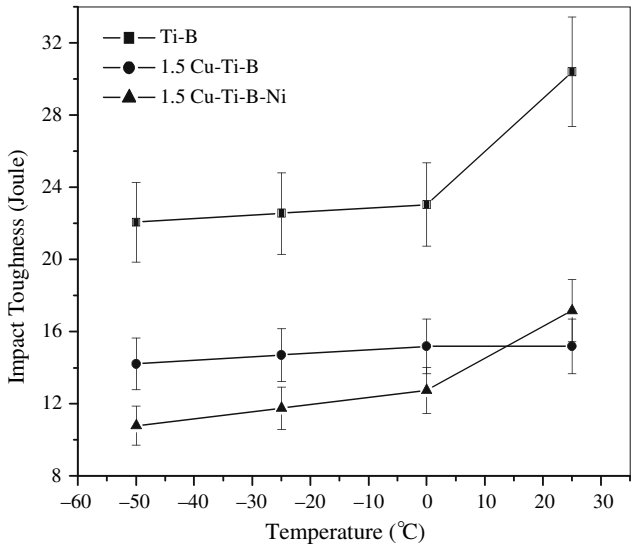

Fig. 5 Variation of Charpy impact toughness (Joule) of DQ steels with the testing temperature

Microstructural studies

Figure 6a contains an SEM micrograph of the Ti–B microalloyed steel obtained after DQ of the hot-rolled sample. The micrograph shows islands of allotriomorphic ferrite (α) distributed along a prior austenite grain boundary. The micrograph also contains blocky ferritic islands along the prior austenite grain boundaries and typical features of acicular (α_a)/Widmanstätten (α_w) ferrite which had nucleated at the grain boundary and grew within the matrix. The TEM micrograph of the Ti–B microalloyed sample quenched directly after hot-rolling is presented in Fig. 6b. The microstructure shows some dislocations in ferritic regions near the martensitic phases.

Figure 7a contains a SEM micrograph of the directly quenched samples containing 1.5 wt% Cu. The presence of Cu has apparently reduced the amount of grain boundary ferrite (Fig. 6a vis-à-vis Fig. 7a). The TEM micrograph of the same steel shown in Fig. 7b reveals a martensitic lath structure.

From the SEM micrographs of the Ti - B microalloyed steels containing 1.0–2.0 wt% Cu (Figs. 8a–10a), the micro-constituents were identified as predominantly lath martensite (α'). The extent of the lath constituent in the microstructure appeared to increase as the Cu content increased. The phases with darker contrast and acicular morphology, identified as ferrite, formed at the prior austenite grain boundaries and triple points, and grew within the austenite grains during rolling in the intercritical temperature region. TEM images of the martensitic lath structures observed in the 1.0, 1.5 and 2.0 wt% Cu Ti–B steels are shown in Figs. 8b–10b, respectively. The darker contrast within the laths is due to heterogeneously formed finer Cu precipitates.

The microstructure of the 1.5 wt% Cu–0.79 wt% Ni Ti–B steel is shown in the SEM and TEM micrographs of Fig. 11. This specimen was characterised by a very fine martensitic lath structure, consistent with the TEM micrograph shown in Fig. 11b.

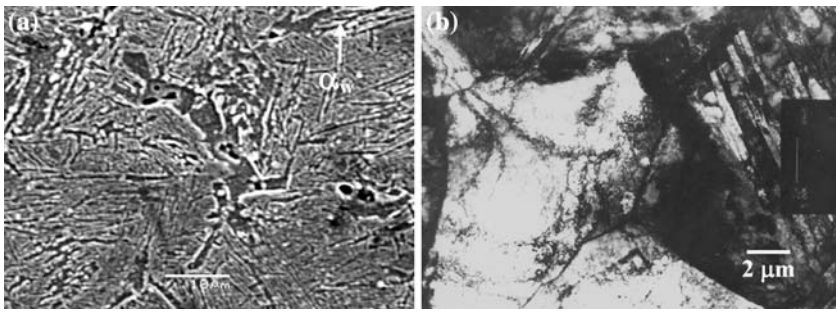

Fig. 6 (**a**) SEM micrograph of Ti–B microalloyed sample showing the allotriomorphic ferrite (α) and Widmanstätten ferrite (α_w) and (**b**) TEM micrograph of same sample showing ferrite with dislocation concentration near martensite laths

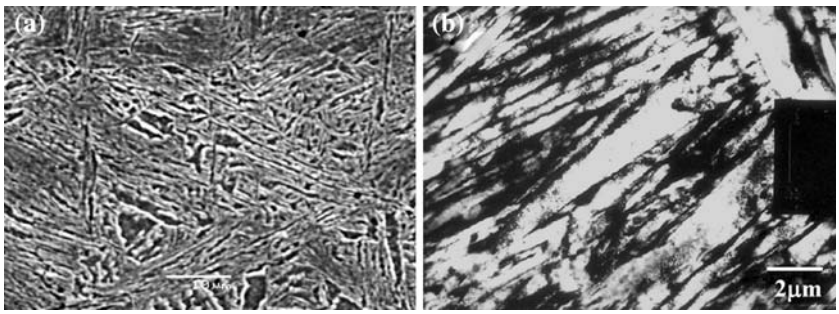

Fig. 7 (**a**) SEM micrograph of 1.5Cu steel sample showing random distribution of ferrite along with martensitic laths and (**b**) TEM micrograph of the same sample showing martensite lath

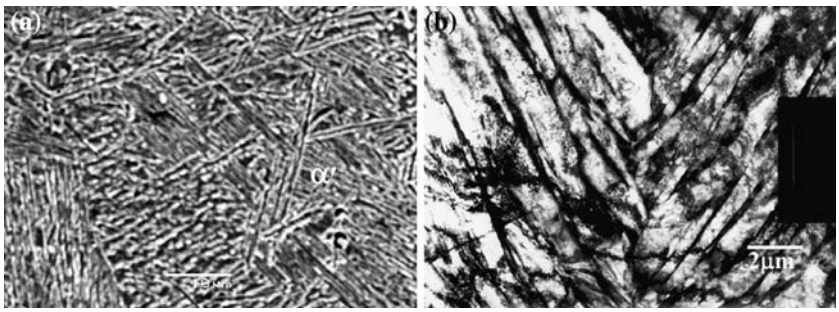

Fig. 8 (**a**) SEM micrograph of 1.0Cu–Ti–B microalloyed steel sample showing predominantly lath martensite (α′) phases and (**b**) TEM micrograph of same steel showing lath martensitic phases

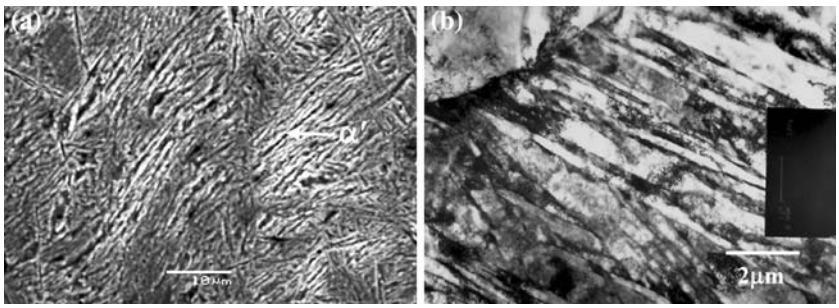

Fig. 9 (**a**) SEM micrograph of 1.5Cu–Ti–B microalloyed steel sample showing lath martensitic (α′) phases and (**b**) TEM micrograph of same sample showing predominantly martensitic region

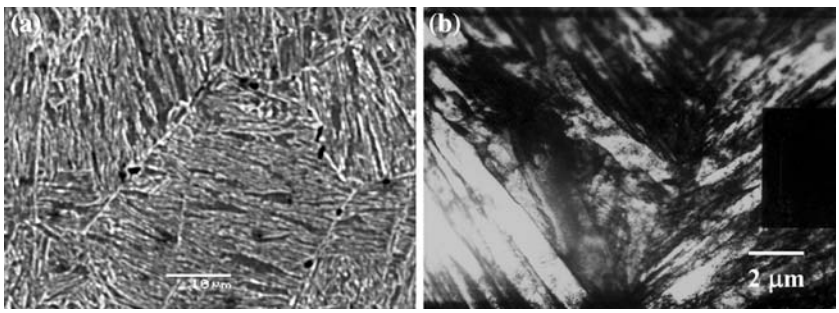

Fig. 10 (**a**) SEM micrograph of 2.0Cu–Ti–B microalloyed steel sample showing comparable microstructure as that of Fig. 9**a** and (**b**) TEM micrograph of same sample showing predominantly lath martensitic structure

Discussion

The addition of Cu to the Ti–B microalloyed steel offers adequate hardenability of austenite, which subsequently results in various low temperature transformation products during DQ. Although the morphological variation among such phases has earlier been elaborated in the ISIJ Bainite research committee report [8], in the present study, the low level of carbon makes the differentiation between bainite and martensite extremely difficult.

The microstructures formed in the case of Ti–B microalloyed steel show a range of ferrite morphologies, which are marked in the micrographs in accordance with the ISIJ Bainite research committee report. It is apparent in Fig. 6a that the transformation products of austenite near the grain boundary are granular in nature. This may be explained by

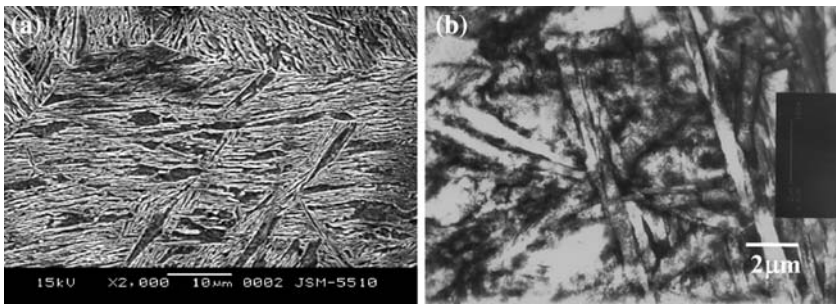

Fig. 11 (**a**) SEM micrograph of 1.5Cu–Ti–B–Ni microalloyed steel sample showing very fine distribution of phases with lath morphology. The dark elongated islands are ferrite and (**b**) TEM micrograph of same sample showing martensitic laths

considering that in DQ steels the ferrite nucleated at the grain boundary of deformed austenite at elevated temperature. The ferrite is blocky because it is a nucleation and growth process and there was insufficient time at temperature for the ferrite to continue to grow.

At the lower transformation temperature (due to presence of ≥1.0 wt% Cu) the subsequent transformation product was martensite formed during cooling.

In the case of Ni–1.5 wt% Cu microalloyed steel, which had been quenched after completion of rolling from the austenite region, acicular laths have formed from the prior austenite grain boundaries, which appear almost parallel (Fig. 11b). The parallel appearance of the laths may merely be a sectioning effect as a series of lath have been intersected. Formation of such martensitic laths has earlier been reported [13].

The microstructural observations indicate that increasing the amount of Cu increases the martensitic lath constituents. In addition, the Cu additions enhanced the strength of the microalloyed steels. The observed mechanical properties of 1.5 wt% Cu steel and Ni–1.5 wt% Cu steel in the present study (UTS = 1,054 MPa, TEL = 24%) is comparable with the high strength categories of HSLA steel (say, HSLA-100) [14].

Although the fact that the dislocation structure formed due to completion of rolling in the non-recrystallisation region of the austenite may induce some Cu precipitation, TEM micrographs of the directly quenched steels did not reveal any appreciable amount of Cu precipitation. However, the difference in hardness between the directly quenched sample (say 331 VHN for 2.0Cu–Ti–B steel) and the same sample subjected to water-quenching after the solution treatment at 1,200 °C (280 VHN) clearly establishes the role of Cu precipitation in improving the hardness. At the same time, difference in hardness among the directly quenched sample of 1.5 wt% Cu (292 VHN), 1.5 wt% Cu–Ti–B (323 VHN) and 1.5 wt% Cu–Ni–Ti–B (332 VHN) steels indicate the role of microstructural features other than Cu precipitation in improving the hardness. The benefit of the Cu addition in respect of improvement in strength may be attributed to the lowering in Ar_3 (≤800 °C for ≥1.5 wt% Cu alloy [15]) and improvement in hardenability of austenite, leading to the transformation of the same at low temperature region. The finer low temperature austenite transformation products primarily contribute to the strengthening effect. The mechanical properties are further enhanced by the dislocation structures present in the deformed ferrite, which are inherited from the deformed austenite during rolling and formed due to subsequent shear driven transformation.

Comparison of the micrographs shown in Figs. 6a–10a show the effect of Cu (≥1.0 wt%) in suppressing the formation of ferrite at the prior austenite grain boundaries and triple points. Based on the high Cu contents of these steels some amount Cu precipitation is expected during thermo-mechanical processing. However, Cu precipitates were not readily visible in the bright-field TEM images, but this may be related to the TEM specimen preparation technique used for these steels.

Conclusions

1. In directly quenched microalloyed steels, the addition of Cu results in comparatively better mechanical properties than the high strength HSLA-100 steels processed by the reheat and quenching route. The attractive mechanical properties are attributed to the formation of finer low temperature transformation products of austenite and Cu precipitation.
2. The addition of Ni not only suppresses hot-shortness in the Cu-containing steels, but also plays favourable role in forming a refined microstructure, thereby improving the total elongation at a given strength level.
3. The 0.79 wt% Ni–1.5 wt% Cu–Ti–B microalloyed steel exhibited the most favourable combination of strength and ductility among the investigated steels.

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