Precipitation behavior during thin slab thermomechanical processing and isothermal aging of copper-bearing niobium-microalloyed high strength structural steels: The effect on mechanical properties

R.D.K. Misra a,*, Z. Jia a, R. O’Malley b, S.J. Jansto c

a Center for Structural and Functional Materials, University of Louisiana at Lafayette, P.O. Box 44130, Lafayette, LA 70503, USA
b Nucor Steel Decatur, LLC Sheet Mill, 4301, Iverson Blvd., Trinity, AL 35673, USA
c CBMM-Reference Metals Company, 1000 Old Pond Road, Bridgeville, PA 15017, USA

Abstract

We describe here the precipitation behavior of copper and fine-scale carbides during thermo-mechanical processing and isothermal aging of copper-bearing niobium-microalloyed high strength steels. During thermo-mechanical processing, precipitation of ε-copper occurs in polygonal ferrite and at the austenite–ferrite interface. In contrast, during isothermal aging, nucleation of ε-copper precipitation occurs at dislocations. In the three different chemistries investigated, the increase in strength associated with copper during aging results only in a small decrease in impact toughness, implying that copper precipitates do not seriously impair toughness, and can be considered as a viable strengthening element in microalloyed steels. Precipitation of fine-scale niobium carbides occurs extensively at dislocations and within ferrite matrix together with vanadium carbides. In the presence of titanium, titanium carbides act as a nucleus for niobium carbidic formation. Irrespective of the nature of carbides, copper precipitates and carbides are mutually exclusive.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

It is now well known that the addition of copper to steels increases the yield strength of base steel via precipitation strengthening [1–7]. There is currently a renewed interest in copper precipitation strengthened steels because of the need to reduce carbon content, particularly in high strength martensitic steels for improved weldability, which is the fundamental basis for HSLA 100 for naval applications [8]. It was observed that during tempering of martensite, copper is precipitated and contributes to yield strength [9]. Consideration of the above concept led to the development of ASTM A710 Grade B steel with a yield stress of 480–550 MPa in as-rolled and air-cooled conditions [10–13]. Similar interest is there in microalloyed steels for structural applications.

The metastable strengthening phenomena during the aging process is associated with the precipitation of copper that occurs in stages and follows the sequence: clustering of Cu atoms \( \rightarrow \) bcc copper \( \rightarrow \) 9R copper \( \rightarrow \) fcc ε-copper precipitates [14–16]. The bcc copper precipitates contain less than 2% iron. The lattice parameter of this phase was estimated to be 0.296 nm. On continued growth, the bcc copper precipitates transform to fcc structure. Electron microscopy suggested a complex fcc-type structure that is twinned and faulted on a very fine scale, and was proposed as a twinned 9R structure [17]. Similar internal structure was observed in large ε-copper precipitates [18]. The bcc copper precipitates are coherent and coplanar with the ferrite matrix and their activation energy is small for nucleation to occur on air cooling from hot rolling. The strength of the steel is further enhanced on aging in the temperature range of 500–550 °C [10–13]. It is pertinent to mention here that according to the Fe–Cu phase diagram, Cu has a relatively high solubility in austenite but has very low solubility in ferrite. Hence, copper precipitation is expected to take place in copper-bearing steels. However, the precipitation of copper in steels with relatively low copper contents (~0.4–0.6 wt%) continues to be a subject of discussion, particularly, in the presence of other microalloying elements, such as niobium.

In addition to the effect of copper on strength, the copper precipitates improve the mobility of screw dislocations at low temperatures, resulting in lower ductile-to-brittle transition temperature and higher impact toughness [19]. Another theory on the effect of copper on steels relates to the proposition that nanometer-sized copper precipitates are misfit centers that increase the strength at room temperature but decrease the yield strength at low temperatures, consequently decreasing the ductile-to-brittle transformation temperature (DBTT). According to Weertman, the stress (Peierls stress)

* Corresponding author. Tel.: +1 337 482 6430.
E-mail address: dmisra@louisiana.edu (R.D.K. Misra).

0921-5093/– see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.msea.2011.08.047
to move a long dislocation segment from a deep crystallographic energy valley is such that a high Peierls energy dislocation is most likely to move by first forming a double kink [20]. In the bcc metals, the kink side edges are in the edge orientation and hence mobile. A subsequent proposition was that a misfit center interacts with a dislocation to help pull it from its Peierls energy valley [21]. A misfit center increases yield stress at elevated temperatures, where thermal energy is adequate to nucleate double kinks along the dislocation line but reduces the yield stress at low temperatures where the thermal energy is small. The misfit center helps the applied stress displace the dislocation escape from the deep energy valley.

The objective of the present work is to understand the effect of copper precipitation, in particular, on mechanical properties in the as-hot-rolled and aged condition in thin slab processed niobium-bearing high strength steels for structural applications.

2. Experimental

Microalloyed steels of three different chemistries (low Cu–Nb–V; high Cu–Nb–V; and high Cu–Nb–V–Ti–Mo) produced using the thin slab direct hot charge process were studied for copper and fine-scale carbide precipitation behavior. The chemical composition range of the investigated steels is listed in Table 1. The three different chemistries are aimed at obtaining different levels of strength. The carbon content was maintained at ~0.05% while the sulfur, phosphorous and nitrogen content was controlled at ~0.003%, 0.01% and 0.008%, respectively, through selection of feedstock (e.g. selected scrap, direct reduction iron, hot briquetted iron) during steel making. The thickness of the near-net-shaped casting slab was 90 mm for tundish temperatures in the range of 1540–1560 °C (superheat of 20–40°C). The casting speed was approximately 3.3 m/min. The microalloyed steels discussed here were industrial heats that were continuously cast and hot rolled to the desired thickness.

Standard tensile tests were conducted at room temperature on longitudinal specimens machined according to ASTM E8 specification (dimensions 225 mm × 12.5 mm, gauge length, 50 mm) using computerized tensile testing system. Impact toughness was measured using standard Charpy V-notch impact test (ASTM 23) at −20 °F.

Transmission electron microscopy was carried out on thin foils prepared by cutting thin wafers from the steel samples, and grinding to ~45 μm in thickness. Three millimeter discs were punched from the wafers and electropolished using a solution of 20% perchloric acid in ethanol. Foils were examined by Hitachi H7600 TEM operated at 120 kV.

3. Results

3.1. Mechanical properties

The mechanical properties, namely, yield strength, tensile strength, and % elongation of the three different microalloyed steels are presented in Table 2. In Fig. 1, we present the data for high Cu–Nb–V microalloyed steel that was subjected to isothermal aging after thermo-mechanical processing. The objective of the three different chemistries was to obtain yield strength in the range of 500–700 MPa. The yield strength, tensile

Table 1
The chemical composition of Cu-bearing Nb-microalloyed high strength steels.

<table>
<thead>
<tr>
<th>Steel Description</th>
<th>%C</th>
<th>%Si</th>
<th>%Mn</th>
<th>%Cu</th>
<th>%Ni</th>
<th>%Ti</th>
<th>%Mo</th>
<th>%V</th>
<th>%Nb</th>
<th>%P</th>
<th>%S</th>
<th>%Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Cu–Nb–V</td>
<td>0.05</td>
<td>0.24</td>
<td>1.36</td>
<td>0.22</td>
<td>0.047</td>
<td>0.01</td>
<td>0.01</td>
<td>0.07</td>
<td>0.04</td>
<td>0.01</td>
<td>0.003</td>
<td>Balance</td>
</tr>
<tr>
<td>High Cu–Nb–V</td>
<td>0.04</td>
<td>0.50</td>
<td>1.20</td>
<td>0.63</td>
<td>0.32</td>
<td>0.01</td>
<td>0.01</td>
<td>0.07</td>
<td>0.05</td>
<td>0.01</td>
<td>0.003</td>
<td>Balance</td>
</tr>
<tr>
<td>High Cu–Nb–V–Ti–Mo</td>
<td>0.05</td>
<td>0.48</td>
<td>1.23</td>
<td>0.63</td>
<td>0.33</td>
<td>0.06</td>
<td>0.07</td>
<td>0.08</td>
<td>0.05</td>
<td>0.01</td>
<td>0.003</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Table 2
Mechanical properties of Cu-bearing Nb-microalloyed high strength steels.

<table>
<thead>
<tr>
<th>Steel Description</th>
<th>Yield Strength (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>% Elongation</th>
<th>Impact Toughness (−20 °F)(−28 °C) (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Cu–Nb–V</td>
<td>483–495</td>
<td>587–596</td>
<td>32–33</td>
<td>241–244</td>
</tr>
</tbody>
</table>

![Fig. 1](image-url) (a) Yield strength, tensile strength, and % elongation and (b) impact toughness at −20 °F of high Cu–Nb–V microalloyed steel in the as hot-rolled and aged conditions (510 °C/1 h; 580 °C/1 h).
Fig. 2. General microstructure of Cu-bearing Nb-microalloyed steels illustrating polygonal ferrite structure. (a) 0.22Cu–0.04Nb–0.07V (yield strength: 503 MPa), (b) 0.62Cu–0.05Nb–0.07V (yield strength: 523 MPa), and (c) 0.63Cu–0.05Nb–0.08V–0.06Ti–0.07Mo (yield strength: 584 MPa) microalloyed steels. (i) and (ii) are scanning and transmission electron micrographs, respectively. Detailed chemical composition is listed in Table 1.

strength, and % elongation of low Cu–Nb–V, high Cu–Nb–V, and high Cu–Nb–V–Ti–Mo steels were in the range of 483–636 MPa, 587–728 MPa, 24.5–33.3%, respectively. The actual values are a function of the alloy chemistry. The impact toughness measured in terms of Charpy V-notch toughness at −28 °C was in the range of 143–332 J, depending on the chemistry. In general, the increase in strength was accompanied by a loss in impact toughness.

3.2. General microstructure

Representative scanning electron micrographs (SEM) and bright field transmission electron micrographs (TEM) illustrating the general microstructure of the three investigated steels is presented in Fig. 2. The microstructure of all the three steels is characterized by polygonal ferrite grains with sub-boundaries and dislocation substructure. Some of the ferrite grains contained a high density of...
dislocations in the ferrite matrix. The polygonal ferrite grains were in the size range \(\sim 2-10 \mu m\).

In addition to the strengthening effect of copper, the solute copper in austenite can retard the recrystallization of deformed austenite, which retains more non-crystallized austenite enhancing ferrite nucleation. Furthermore, the solute copper in austenite suppresses austenite-to-ferrite transformation and decreases the transformation temperature and prevents ferrite grains from coarsening. Thus, the fine ferrite observed here can also be attributed to the solute copper, besides grain refinement effect of niobium and vanadium.

3.3. Precipitation of copper and fine-scale precipitation of carbides

3.3.1. Precipitation in the ferrite matrix and interphase precipitation

Figs. 3–5 summarize the precipitation of copper and microalloying elements (Nb, V, Ti, Mo) in the microalloyed steels of different chemical composition. In general, the copper precipitates possessed anisotropic morphology (Figs. 3–5). The different morphology of copper precipitates includes spherical, irregular,
Fig. 4. Representative transmission electron micrographs of hot-rolled 0.62Cu–0.05Nb–0.07V steel illustrating copper precipitation (circled) during thermo-mechanical processing in the ferrite matrix (a) and interphase precipitation of copper (arrow) (b) [(i) bright field, (ii) dark field, (iii) diffraction pattern]. Also, shown is the dislocation structure and precipitation of carbides at dislocations (c–e). c(i) and c(ii) are bright field and dark field images of carbide precipitation.
triangular, and oblong. Two distinct types of precipitation were observed during the thermo-mechanical processing and include random precipitation in the ferrite matrix (Figs. 3a–c, e, 4a, and 5a, b). These precipitates are identified by circles. The second type of precipitates was interphase precipitates, i.e., precipitation at the austenite–ferrite interface. They are delineated by arrows in Figs. 3d, 4b, and 5c.

The large irregular-shaped precipitates that precipitated in the ferrite matrix were in the size range of 40–80 nm. These interphase precipitates were of significantly smaller size (~2–10 nm).

Fig. 4b(i–iii) are bright field, dark field micrographs of copper precipitates, and the electron diffraction pattern. The analysis of the diffraction pattern confirms e-copper. Also, presented in Figs. 3–5 is the dislocation structure and strain-induced precipitation of carbides at dislocations (Figs. 3f, 4c, 4d, and 5d). These strengthening precipitates were of size similar to interphase precipitates. We will briefly describe the carbide precipitation at dislocations because we have recently discussed the effect of Nb, V, and Ti on precipitation of mixed carbides [22]. Figs. 3f, 4c–e, and 5d identify the nature of carbides in the ferrite matrix and at dislocations that contribute to strengthening. In addition to precipitation of NbC and VC in the matrix and at dislocations in Cu–Nb–V steels, fine-scale precipitation of Mo2C and Ti(Nb)C occurred in Cu–Nb–V–Mo–Ti steels. While each of these precipitates were in the size range of 2–4 nm, NbC and VC exhibited near spherical morphology, Mo2C was characterized by rod-like morphology, and Ti(Nb)C were irregular. The Ti(Nb)C is not surprising because according to solubility calculations, microalloying elements, Ti and Nb, are interchangeable in the precipitate lattice in view of similarity in the crystal structure and lattice parameter.

Irrespective of the nature of the copper precipitates (precipitation in the ferrite matrix or interphase precipitation), the copper precipitates must be formed during or soon after the decomposition of austenite. The formation of e-copper at the ferrite–austenite interface during the decomposition of austenite is expected to take place according to the following reaction [23]:

\[ \gamma \rightarrow a + \text{e} + \text{iron} \]

Unlike precipitation within the ferrite matrix where multiple variants are expected, the interphase precipitates at the ferrite/austenite interface exhibited crystallographic orientation relationship different from Kurdjumov and Sachs and was \[ [1 1 1]_e/Cu//[0 1 1]_a/Fe \] and \[ (1 0 1)_{e/Cu}//(1 0 0)_{a/Fe} \] (Fig. 4b(iii)).

**Fig. 5.** Representative transmission electron micrographs of hot-rolled 0.6Cu–0.05Nb–0.08V–0.06Ti–0.07Mo steel illustrating copper precipitation (circled) during thermo-mechanical processing in the matrix (a, b) and interphase precipitation of copper (arrow) (c). Also, shown is the dislocation structure and precipitation of carbides at dislocations (d).
Copper Precipitates Prior to Aging (in the sample subject to aging 510°C)

Fig. 6. Representative transmission electron micrographs of 0.6Cu–0.05Nb–0.07V steel illustrating copper precipitation during thermo-mechanical processing in the ferrite matrix (a, b) (circle) and interphase precipitation of copper (arrow) (c, d) prior to aging. Also, shown is the bright field d(i), dark field d(ii) and diffraction pattern d(iii) of selected interphase precipitates. Micrographs (e–g) correspond to the precipitation of copper during aging of the same sample at 510°C. During aging, copper precipitates at dislocation (e, f) in conjunction with ε-copper with faults (g).

Copper Precipitates During Aging at 510°C

is generally true for interphase precipitation and the variant is one that corresponds to minimum energy for nucleation [24]. The interphase precipitates were noted to have no correlation between the matrix precipitates and dislocations within the ferrite. This is consistent with the previous studies [23,25–28]. One may expect this behavior because the interfaces are more effective in reducing the energy of formation for a critical nucleus in comparison to the dislocations.

3.3.2. Precipitation during isothermal aging: precipitation of copper at dislocations

A comparison of tensile strength, yield strength, and Charpy v-notch energy in a specific Nb-microalloyed steel (0.6Cu–0.05Nb–0.07V) prior to and after aging (aged at 510°C/1 h, and aged at 580°C/1 h) is presented in Fig. 7. The yield strength of the selected steel increased from 527 MPa to 578 MPa on aging at 580°C for 1 h. Similarly the tensile strength increased from
Copper Precipitates Prior to Aging (in the sample subject to aging at 580 °C)

![Representative transmission electron micrographs of 0.6Cu–0.05Nb–0.07V steel illustrating copper precipitation during thermo-mechanical processing in the ferrite matrix (a, b) (circle) and interphase precipitation of copper (arrow) (c, d) prior to aging. Micrographs (e–g) correspond to the precipitation of copper during aging of the same sample at 580 °C. During aging, copper precipitates at dislocation (e, f) in conjunction with ε-copper with faults (g).]

618 MPa to 652 MPa. The Charpy v-notch measurements at −28 °C indicated that the impact toughness decreased slightly from 314 J to 252 J on aging at 580 °C for 1 h. Even with the decrease of Charpy impact fracture energy after aging, it still maintains adequately high value (~250 J) at the test temperature of −28 °C.

Representative transmission electron micrographs summarizing the effect of aging at 510 °C and 580 °C on copper precipitation is presented in Figs. 6 and 7. Also, presented in Figs. 6 and 7 are ε-copper precipitates prior to aging. In a manner similar to the matrix precipitation during thermo-mechanical processing, precipitation during aging at 510 °C and 580 °C was anisotropic or exhibited irregular morphology. The size range was from 2 to 10 nm and is significantly less than the size of the precipitates formed in the ferrite matrix. The different morphology is attributed to different crystallographic variants. In contrast to precipitates formed during thermo-mechanical processing, almost all fcc ε-copper precipitates were observed on α-iron matrix dislocations. It is clear from Figs. 6 and 7 that the majority of the precipitates are either in contact with the matrix dislocations directly or in contact with the dislocation lines normal to the foil surface. This behavior is consistent with the reduction of strain energy for precipitates nucleating at the dislocation lines [23,29].

An intriguing aspect of copper precipitation was the observation of nearly spherical precipitates and are presented in Figs. 6g and 7g.
Some of these precipitates indicated fine structure which appears to contain parallel faults or twins or some other kind of fine structure.

The adequate high toughness in the presence of copper precipitates can be discussed in terms of a theory visited by Fine’s group [21]. They suggested that the coherent and co-planar misfit centers, such as enriched copper clusters, can provide significant twisting of nearby screw dislocations and enhance their mobility in the absence of insufficient thermal activation. This provides a mechanism for making the steel ductile and improving impact toughness at low temperatures.

In summary, $\varepsilon$-copper precipitates formed during the isothermal aging are of two types: the first type of precipitates are associated with $\alpha$-iron matrix dislocations, while the second type of nearly uniform and spherical precipitates are twinned or faulted. An important aspect is that $\varepsilon$-copper precipitates and fine-scale carbides are mutually exclusive and they are not synergistic. The precipitation of carbides does not influence copper precipitation and vice versa. Furthermore, copper precipitates tend to retain the impact toughness of microalloyed steels at adequate values, implying that in the presence of copper precipitation dislocations have the ability to climb or bow and do not pile up.

4. Conclusion

a. During thermomechanical processing, copper precipitation occurred in the matrix and at the austenite/ferrite interface. The interphase precipitates had only one variant.

b. Two types of precipitation occurred in a high-Cu Nb-microalloyed steels isothermally aged at 510 °C and 580 °C. The first one was characterized by precipitation at dislocations and were of 2–5 nm size range, while the second type of precipitates were spherical and nearly uniform and were relatively large (~20 nm). The latter precipitates were twinned or faulted. The precipitation of copper does not influence precipitation of carbides or vice versa, and are therefore mutually exclusive.

c. There was a significant increase in yield and tensile strength on aging between 510 °C and 580 °C, which was accompanied by a small loss in toughness.

d. Irrespective of the precipitation of fine-scale carbides (NbC, VC, Ti(Nb), Mo, C), the precipitation of copper is not affected and vice versa, implying that their respective precipitation is mutually exclusive.

e. The addition of copper in microalloyed steels can be considered as a viable option to increase strength without expecting a significant loss in toughness.

Acknowledgements

The authors are grateful to CBMM, Brazil for financial support of the work presented here. Grateful thanks are due to Z. Zhang for help with metallography.

References