Microstructure characterization of Cu-rich B2 intermetallic nanoprecipitates in an austenite-based High specific strength steel

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Abstract. Effects of Cu addition on microstructure and tensile property of a hot rolled austenite-based high specific strength (i.e. yield strength-to-mass density ratio) steel (HSSS) are investigated. The addition of Cu promotes the precipitation of intermetallic compounds (B2), resulting in higher volume fraction of nanoscale B2 particles in the steel. Addition of 2.8wt% Cu improves both the yield strength (by 53MPa) and tensile strength (by 138MPa) of the steel, and maintains high ductility. The yield strength enhancement is predominantly attributed to nanoscale B2 intermetallic precipitation. A high number density of ultrafine (2-10nm) B2 and Cu uniformly precipitates in the austenite matrix with three different types of ultrafine nanoscale particles.

1. Introduction

Ultra-high light-weight steels are one of the strongest ductile bulk materials currently available which have received a growing interest in recent years due to excellent combinations of specific strength and ductility[1-3]. Kim [4] groundbreaking introduce B2 into lightweight steel, show that hard intermetallic B2 compounds with nanoscale can be effectively used as strengthening phase in high Al low density steels. M.X.Yang [5] analyze the strain hardening process in the Fe-16Mn-10Al-0.86C-5Ni(wt%) high specific strength steel, founding that the B2-FeAl and austenite are both deformable with significant strain hardening capability. Alireza Rahnama [6-7] confirm that the ordering in the BCC (α) occurs in two discrete stages, the addition of Ni into the alloys led to the ordering of α phase and its transformation to stringer B2 compounds and prevent the formation of lamellar structure of α+κ. The addition of Ni also resulte in the formation of B2 at coarse grain boundary, which led to the formation of depleted zones and annealing at 900°C and 1050°C alloy exhibited higher strength and smaller ductility due to the fact that Ni-Al bonds are much stronger than Fe-Al bonds formed in B2 intermetallic compounds. Nano scale B2 were observed at austenite grain. Jiang Suihe [8] show a new
variation Ni(Al,Fe)-maraging steel Fe-18Ni-3Al-4Mo-0.8Nb-0.8C-0.01B (wt%). Owing to B2-Ni(Al,Fe) extremely fine size (2.7±0.2 nm) and high density (about 3.7×1024m⁻³), the coherent precipitates strengthen the matrix via dislocation shearing. In addition, the core/shell precipitates comprised of Ni-Mn-Al rich B2 shells and a bcc Cu-rich core has been reported in literatures [9-11]. The intermetallic B2 shells act as a buffer layer to relax the lattice mismatch strain between the bcc Cu precipitates and the steel matrix.

In this paper, Al were design to reduce the density, and the Mn/Ni were added to control the microstructure and morphology. Besides, Cu were added to increase the stability of the B2 as the B2 precipitates nucleate on the Cu alloyed precipitates. The forming of these composite precipitate structures contributes to a high number of ultrafine (2-10nm) B2 precipitates, which has proven to be effective in ferritic steels [8-11]. Therefore, we apply this method to austenitic matrix steels to expect better mechanical properties. [4-7].

2. Materials and experimental procedures

Investigated Ni and Cu added light-weight steel with the chemical composition are shown in Table 1. The steel used in this study were fabricated by a vacuum induction melting method. The ingot was homogenized at 1180°C for 2 h, hot forged between 1150°C and 900°C into slabs with a thickness of 40mm and hot-rolled with a starting temperature of 1100°C into strips with a thickness 4.3mm. Hot-rolled sheets were annealed at 900°C for 15 min and followed immediately by water-quenched.

Table 1. Analyzed chemical compositions of the alloys (wt.%).

| sample     | C   | Al | Mn | Ni | Cu | Si | Fe+others |
|------------|-----|----|----|----|----|----|-----------|
| 2.8Cu      | 0.93| 9.7| 15.5| 4.2| 2.8| 0.2| Bal       |
| Cu-free    | 0.91| 9.5| 15.2| 4.1|-- | 0.2| Bal       |

Scanning electron microscopy (SEM, ZEISS ULTRA 55) was used to characterize the microstructure of the steel before and after tensile tests. A transmission electron microscope (TEM, FEI TecnaiG20 type transmission electron microscope (TEM)) and a high-spatial resolution analytical electron microscope (HRTEM, FEI TecnaiG20) both operated at 200kV were used for examinations of the typical microstructural features in γ and B2 grains. Thin foils for TEM observations were cut from the gage sections of tensile samples, mechanically ground to about 50μm thick and finally thinned by a twin-jet polishing facility using a solution of 5% perchloric acid and 95% ethanol at 20°C. In addition, the microstructural features of B2 precipitates were also examined by electron back-scattered diffraction (EBSD) using a high-resolution field emission Cambridge S-360 SEM equipped with a fully automatic Oxford Instruments Aztec 2.0 EBSD system and X-ray diffraction (XRD) measurements with Cu Kα radiation were performed in a Seifert-FPM URD-6 diffractometer. The density of the experimental steel measured by the Sartorious BSA2245 electronic analytical balance is 6.68g/cm³ about 13% lower than traditional steel. Tensile properties were estimated by the uniaxial tensile test with the gauge length of 25 mm. The tests were performed with a crosshead speed of 1.0 mm/ min at room temperature.

3. Experimental results

Fig 1(a) and Fig 1(b) are SEM images of the longitudinal section of the 2.8Cu hot forged sample. Microstructure consists of equiaxed recrystallized fcc γ-austenite grains and thick lamellar B2 precipitates at austenite grain boundary. After hot rolled with 90% reduction, the austenite grains...
change from granular to elongate shape as shown in Fig. 1(c). The B2 phase exhibits a much reduced thickness and a large number of granular B2 precipitates from γ-austenite grain boundary. Fig 1(d) shows the SEM images of the longitudinal section of the Cu-free hot rolled sample. Little B2 precipitations are visible inside the interiors of the γ grains. There are two different morphologies of B2: (1) comprising retained big stringer bands,(2) fine particles of size precipitate at the austenite grain boundary. Compared with the morphology and size of the B2 phase in the Cu-free hot rolled sheet (in Fig. 1), the band width of B2 phase in cu-alloyed hot rolled sheet is significantly refined.

![Figure 1](image1.png)

**Figure 1.** (a), (b)SEM micrograph of 2.8Cu hot forged specime. (c) SEM micrograph of 2.8Cu hot rolled specimen. (d) SEM micrograph of Cu-free hot rolled specimen.

![Figure 2](image2.png)

**Figure 2.** Microstructural characterization of steels after annealing at 900°C for 15min.(a)-(c) 2.8Cu steel, (d)-(f) Cu-free steel ; SEM and EBSD micrographs show B2 intermetallic in brighter and color bands respectively.
Heat treatment parameter of holding at 900 °C for 15min has proven to be the best one to obtain the nano-size B2 phase in similar literature[4-7]. Fig 2 shows typical SEM micrographs, and EBSD phase maps of the 2.8Cu and Cu-free steels respectively. The microstructures of steels after annealing at 900°C for 15min are basically banded structures, in which the lighter bands are B2, and darker bands are γ austenite [5-7]. Lighter bands show different variants and morphologies depending on the addition of Cu. In the Cu-free steel, the lighter bands mainly are basically banded structures. There are two different morphologies of B2 phase after annealing at 900°C for 15min (Fig 2de), fine particles of size 500-1,000nm, finer particles of size 100-500nm which is further evidenced by an EBSD image as shown in Fig 2(f). On the contrary, the lighter bands are mainly composed of nanoscale particles in the 2.8Cu steel (Fig. 2a, b). Most of the nanoscale particles are finer particles of size 10-100nm. This is further evidenced by an EBSD image as shown in Fig 2(c). B2 are illustrated in color regions. A large number of nanoscale B2 precipitate at γ-austenite and different type B2 visible inside the interiors of the γ grains. According to EBSD statistical measurements from at least 100 grains for each phase, the γ-austenite grain sizes and B2 are 12.5 ± 5.8µm, 3.8 ± 0.8µm, respectively in the Cu-free steel. While γ-austenite grain sizes of 11.1 ± 5.3µm, B2 of 2.4 ± 0.9µm are found in the 2.8Cu steel.

![Figure 3](image1.png)

**Figure 3.** (a) STEM image, (b) EDS elemental mappings of the clusters, (c) XRD spectrum in the 15min 900 °C annealed 2.8Cu alloy.

Fig 3 represents the STEM and EDS elemental mappings for the 15min annealed 2.8Cu alloy. Fig. 3(a) is a STEM image showing γ and B2 dual-phase. The inset shows the indexed selected area diffraction pattern with electron beam closely parallel to both the [011], and [001]B2 zone axess. Fig. 3(b) showing both the EDS map of precipitates in γ. It can be seen that Ni, Al and Cu elements coexist in the same regions. The partitioning of Al (orange), Mn(green), Ni(red) and Cu (yellow) atoms into the γ phase and NiAl-type B2. Ni, Cu and Al are rich in B2 and Mn is rich in γ. The result showed that the addition of Ni into the alloys led to the ordering of α phase and its transformation to stringer B2 compounds. Essentially that Ni plays an important role in promoting the nucleation reaction for Cu-rich precipitates. It is found that Ni could lower the strain energy for nucleation and the interfacial energy between the matrix and thereby decreasing the critical energy for nucleation [7]. The diffraction peaks of fcc γ-austenite and bcc B2 are clearly identified in Fig 3(c). After annealing at 900 °C for 15 min, the (100) peak of B2 becomes more pronounced in 2.8Cu steel owing to its precipitation.
Figure 4. TEM micrographs of the 2.8Cu steel after annealing at 900°C for 15 min, grains at tensile strain of 19.5%: (a) nano-twin, (b) high density of dislocations in γ, (c) bright-field image of B2, (d) brittle and nonshearable B2, (e) high density of dislocations in B2, (f) dark-field image of B2.

It is note that both γ and B2 grains are plastically deformable and can store dislocations, as shown in Fig 4 by TEM observations. Fig4(a) shows a high density of nano-twin and the nano-twin boundaries act as strong obstacles to the dislocation motion, so lead to higher strain-hardening [12]. A high density of dislocations can be observed in both B2 and γ (Fig 4(b,e)), this is the same as M.X.Yang reported [5] that B2 and γ are both deformable with significant strain hardening capability. But Fig 4(d) shows that B2 are brittle, nonshearable as no dislocations can be observed in B2. A lot of dislocation pile up and nets at B2 grain boundary. The result is the same as Kim [4] reported. Hard B2 intermetallic compounds particles are responsible for the high work hardening rate due to their nonshearable nature. Deformable and undeformable B2 were further evidenced by Fig 4(c,f). Fig 4(c) illustrates a TEM bright-field image of B2, as shown in the corresponding center dark-field images (Fig 4(f)). High density dislocations exist in B2-(1), and there are no dislocations within B2-(2) with high density dislocations gathered around it. This implies that both types are visible in 2.8Cu steel.

Figure 5. (a)-(i) HRTEM micrographs of B2 and Cu nanoscale particles in 2.8Cu annealed specimen (15min, 900 °C).
Fig 5 reveals highly uniform precipitation of ultrafine (2-5nm) nanoscale precipitates. Three different types of nanoscale precipitates were found: Cu nanoscale particles with irregular polygon edges (Fig 5(b-d)), B2 particles with an average size of 2-5nm (Fig 5(e-g)) and co-precipitation of disk-like B2 and Cu nanoscale particles with a size of a few nanometers (Fig 5(h-i)). The three types of nanosize particles precipitated in 2.8Cu steel were not reported in the Ref [4-7]. Dislocation movement is difficult along the nanoscale precipitates during the tensile test. As shown in Fig 5a, high density dislocation pileup lies in the second phase (2-10nm) along the γ boundary, which induces the substructure strengthening of the matrix. Thus the γ grain can be effective pinning dislocation slip and improve strength of the 2.8Cu steel matrix [8].

The 2.8Cu steel possesses the tensile strength of 1216 MPa, yield strength of 903MPa and specific strength of 181.7MPa.g⁻¹.cm³, higher than the Cu-free steel by 138MPa (i.e., 12.8% increment), 53MPa (i.e., 5.9% increment) and 20.4MPa.g⁻¹.cm³ (i.e., 12.4% increment), respectively. The total elongations of these two steels are comparable about 25%. Mechanical properties of the steel are shown in Fig 6 in detail. The increment in yield and tensile strength results from the precipitation strengthening effect of ultrafine Cu rich B2 in the steel.

![Figure 6](image_url)  
**Figure 6.** Mechanical properties of the both steels after annealing at 900°C for 15 min

4. Conclusions

In the present study, microstructure properties and strengthening effect of nanoscale precipitation of austenite-based specific steel with dual phase microstructure and ultrafine nanoscale Cu-rich B2 precipitation have been investigated. The main findings are summarized as follows:

1. The density of 2.8Cu steel is 6.68g/cm³, which is about 13% lower than traditional steel. Results show that, the hot-rolled steel has a dual-phase structure, and consists of γ-austenite and B2 intermetallic compound. The ultimate tensile strength of 2.8Cu hot-rolled steel after annealing at 900°C for 15min is 1216MPa, yield strength is 948MPa, elongation is 19.5% and specific strength is 181.7MPa.g⁻¹.cm³. The increment in yield and tensile strength results from the precipitation strengthening effect of ultrafine Cu rich B2 precipitation in the 2.8Cu steel.

2. Nanoscale B2 increases, B2 stringer bands decrease after annealing at 900°C for 15min followed by water quenching in 2.8Cu steel. STEM shows that Ni, Cu and Al are rich in B2 and Mn is rich in γ. A large number of nanoscale B2 precipitate at γ grain boundaries and inside γ grains. The
addition of Cu can promote the precipitation of B2 as shown by the XRD result. Both deformable and nonshearable B2 were observed in the 2.8Cu steel.

(3) The result reveals highly uniform precipitation of a high number of fine (<500nm) B2. There are three different types of the ultrafine (2-10nm) nanoscale particles: Cu nanoscale particles with irregular polygon edges, B2 particles with an average size of 2-5nm and co-precipitation of disk-like B2 and Cu nanoscale particles with a size of a few nanometers.

Acknowledgments
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5. References
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