Precipitation Behavior of Boron in High Strength Steel*

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Synopsis

The hardenability of boron steel is affected by the precipitation behavior of B. Precipitates in the B containing steel were studied by extraction replica technique at the successive manufacturing steps from hot-rolling to heat treatment.

When steels are hot-rolled after heating at 1 300 °C for 1 h, changes of B precipitates with the cooling rate after hot-rolling are as follows:

(1) When steels are water-quenched (cooling rate of 90 000 °C/min) after hot-rolling, no precipitates can be observed on γ grain boundaries.

(2) When steels are air-cooled (cooling rate of 300 °C/min) after hot rolling, BN precipitates on γ grain boundary region.

(3) When steels are furnace-cooled (cooling rate of 0.67 °C/min) after hot-rolling, AlN grows radially from BN which has precipitated before the nucleation of AlN. AlN formed on BN during furnace-cooling is dendritic.

By reheating at a rate of 15 °C/min a specimen which has been water-quenched after hot-rolling (above-mentioned as (1)), the following B precipitates appear depending upon the temperature range:

(1) Below 880 °C, $M_{23}(CB)_6$ precipitates and coagulates on prior grain boundaries.

(2) Above 900 °C and below about 1 000 °C, BN appears on prior grain boundary region which has been previously occupied by $M_{23}(C, B)_6$. $M_{23}(C, B)_6$ is no longer observed at this stage.

(3) Heating at around 1 000 °C, AlN which is not dendritic but acicular grows radially from BN. The size of BN diminishes with growth of acicular AlN.

The formation of AlN on BN is interpreted as a transit from the non-equilibrium to equilibrium state in Al-B-N system in steels.

According to Pease, BN (hexagonal close packed) has the same crystal structure as that of graphite. Because BN in steels was revealed to have spherulite morphology such as spherical graphite, it is considered that $[00.1]$ axes of BN are arranged in radial fashion and (00.1) planes are perpendicular to them, by an analogy to the crystal arrangement of spherical graphite. As the growth direction of AlN is $[0.01]_{AlN}$, it is considered that an orientation relationship of $(00.1)_{BN} \parallel (00.1)_{AlN}$ is satisfied when AlN grows on BN.

I. Introduction

The use of B treated steel is expected to increase from the view point of saving resources but much care is necessary to manufacture B added steels. For example, there is a phenomenon that the hardenability of B treated steels decreases by over-heating.¹⁻⁵⁾ Many papers have been reported concerning with this phenomenon and at present it appears difficult even to reproduce experimentally the same results.

Authors deduced that the phenomenon depends on the precipitation behavior of B precipitates such as BN, $M_{23}(C, B)_6$, etc., during the manufacturing processes.^{6,7)} This paper deals with the different kinds of B precipitates which change their state depending on the heating temperature before rolling, cooling rate after rolling and quenching temperature during heat treatment of Al-B treated steels. This paper also discusses microstructures of BN, as few papers have reported about the microstructure of BN in steels.

II. Experimental Procedures

The chemical compositions of materials are shown in Table 1. Steel X is Cu-Ni-Cr-Mo-V-0.0025%B-0.0107%N 80 kg/mm² grade high tensile strength steel and steel Y is 0.0096%B-0.0326%N-Fe. Steel X was heated at 1 300 or 1 000 °C for 1 h and reduced its thickness by hot-rolling from 30 to 5 mm and afterwards cooled at a cooling rate of about 90 000 °C/min (water-quenched), 300 °C/min (air-cooled) or 0.67 °C/min (furnace-cooled). The water-quenched specimens were reheated at a rate of 15 °C/min and quenched immediately after reaching determined temperatures. Steel Y was forged after heating at 1 300 °C for 1 h and air-cooled. Replicas extracted from these specimens were observed by the electron microscope with an accelerating voltage 100 kV.

III. Results

1. Boron Precipitates during Hot Rolling

Replicated microstructures extracted from the specimens which were hot-rolled after heating at 1 300 °C for 1 h and air-cooled from 900 °C after rolling are shown in Photo. 1. Precipitates in dotted line are identified as BN from the interplaner intervals calculated from diameters of electron diffraction rings.⁸⁾ It is known that BN has several crystal structures in atmosphere. Interplaner intervals measured from Photo. 1 show that BN in steel agrees with the hexagonal one found by Pease⁹⁾ who made samples by

Table 1. Chemical compositions of materials. (wt%)

Steel	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	V	Sol. Al	Total B	N
X	0.11	0.29	0.85	0.009	0.008	0.25	1.02	0.39	0.46	0.03	0.074	0.0025	0.0107
Y	0.004	<0.01	>0.01	0.002	0.005	0.02	<0.01	<0.01	<0.01	<0.01	<0.001	0.0096	0.0326

* Originally published in *Tetsu-to-Hagane*, **62** (1976), 1851, in Japanese. English version received December 22, 1981. © 1983 ISIJ
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Photo. 1. Precipitates in steel X air-cooled from 800 °C after heating at 1 300 °C for 1 h and hot-rolling. Diffraction rings identify the precipitates as BN.

reacting B and N₂ gases directly at high temperatures. Throughout the present experiment diffraction patterns of single crystal were not obtained but showed only diffraction rings characteristic of polycrystalline structure.

Replicated microstructure extracted from steel X which is furnace-cooled from 900 °C after heating at 1 300 °C and hot-rolled is shown in Photo. 2. There observed many complicated precipitates which are composed of globular precipitates at the core and dendritic ones radially grown from the core. Electron diffraction patterns resulted from the vicinity of the core (Photo. 3), are the superposed ones which are composed of AlN spots and BN rings. Because electron diffraction patterns resulted from radially grown parts indicate only AlN, it is concluded that AlN grows radially on the core of BN. The morphology of AlN which precipitates and grows during furnace cooling is dendritic.^{9,10)} When steel X is hot-rolled and then cooled after Al, B and N dissolved

Photo. 2. Precipitates in steel X furnace-cooled from 800 °C after heating at 1 300 °C for 1 h and hot-rolling.

Photo. 3. Precipitates in steel X furnace-cooled from 800 °C after heating at 1 300 °C for 1 h and hot-rolling. AlN grows radially on BN. AlN observed in Photos. 2 and 3 is dendritic.

into solid solution by heating at 1 300 °C, the state occurs in which BN precipitates on austenite grain boundaries although Al is in solid solution. During cooling B and N atoms segregate to austenite grain boundaries due to their high diffusion velocity, so that concentration of B and N atoms at grain boundaries increases and exceeds the solubility product while Al atoms distribute homogeneously and do not prevent BN to precipitate. As mentioned later, the effect of B on the hardenability almost disappears at this stage. It is supposed that the stage corresponds to the non-equilibrium state of Al-B-N-Fe system. Habu *et al.* showed,⁵⁾ by calculating B content in solid solution in the equilibrium state of Al-B-N-Fe system, that Al protects all of B from precipitating as BN by fixing N as AlN, so that B in solid solution necessary for increasing hardenability is obtained.

If the cooling rate is very slow like furnace-cooling, Al atoms migrate into grain boundaries and precipitate as AlN on the surface of BN particles. Al-B-N-Fe system approaches the equilibrium state at this stage. There observed no evident B precipitate in the samples which are water-quenched after heated at 1 300 °C × 1 h and hot-rolled.¹¹⁾

Photograph 4 shows the extraction replicated microstructure of steel X which is water-quenched after heating at 1 000 °C for 1 h and hot-rolled. Many rectangular AlN indicate that AlN scarcely dissolves into solid solution at 1 000 °C.¹²⁾

2. Boron Precipitates during Heat Treatment

Photograph 5 shows replicated microstructure of steel X which was heated at a rate of 15 °C/min and quenched immediately after reaching at 880 °C. Preceding to the heat treatment, steel X was water quenched from finishing temperature after heating at 1 300 °C and hot-rolled.

There observed precipitates on prior austenite grain boundaries identified as $M_{23}(C, B)_6$.^{13,14)} Cementite within the grains dissolves into solid solution and martensite forms by water quenching.

It is supposed that $M_{23}(C, B)_6$ precipitates during heating below A_{c1} and remains over A_{c3} temperature. A_{c3} temperature of steel X is about 850 °C. BN is not observed in Photo. 5. The replicated microstructure of steel X which is heated up to 930 °C and quenched is shown in Photo. 6. Precipitates on prior austenite grain boundaries are identified as BN and $M_{23}(C, B)_6$ is no longer observed. When the specimen is reheated in which B, N, C and Al atoms are in solid solution, the precipitate that forms on prior austenite grain boundaries below A_{c1} is not BN but $M_{23}(C, B)_6$. $M_{23}(C, B)_6$ does not dissolve into solid solution even after completely austenitized, but heating at higher than 900 °C, $M_{23}(C, B)_6$ dissolves and free B atoms combine with remaining free N and precipitate as BN.

Heated at 1 000 °C, AlN precipitates and grows radially on BN particles as shown in Photo. 7. The morphology of AlN formed on BN during reheating is not dendritic but acicular.

The growth direction of AlN is determined as iden-

Photo. 4. Precipitates in steel X water-quenched from 800 °C after heating at 1 000 °C for 1 h and hot-rolling.

Photo. 5. Precipitates in steel X reheated at 800 °C after heating at 1 300 °C for 1 h, hot-rolling and water-quenching.

$M_{23}(CB)_6$ forms on prior γ grain boundary region.

tical with $[00.1]_{AlN}$ after compensating the rotating angle of intermediate lens of electron microscope.

The precipitation of AlN on the surface of BN during reheating is the necessary stage for Al-B-N-Fe system to approach the equilibrium state after hot-rolling as with the case of slow cooling.

3. The Microstructure of BN

Photograph 8 shows BN in steel Y. It shows that spherical BN is composed of many cone-like crystals radially grown from a common center at which all of

Photo. 6. Precipitates in steel X reheated at 930 °C after heating at 1 300 °C for 1 h, hot-rolling and water-quenching.
BN forms on prior γ grain boundary region.

Photo. 7. Precipitates in steel X reheated at 1 000 °C after heating at 1 300 °C for 1 h, hot-rolling and water-quenching.
Acicular AlN grows on BN.

Photo. 8. BN in steel Y.
BN has spherulite structure such as spherical graphite in iron.

cone tops are located. This is similar to that of spherical graphite.

Owing to this structure, diffraction pattern of BN results in the continuous rings characteristic of a polycrystal.

IV. Discussion

Boron precipitates observed on each stage in the experiment are represented schematically in Fig. 1. Boron precipitates in steel X are BN and $M_{23}(CB)_6$. Hexagonal close packed BN found by Pease⁸⁾ in which B and N atoms form two dimensional nets by covalent bonding and each layer of net combines with others by Van der Waals force similar to graphite. Photograph 8 shows that BN in steel has spherulite morphology such as spherical graphite. According to Morrough and Williams,¹⁵⁾ in spherical graphite, C axes are arranged in radial fashion and (00.1) planes are perpendicular to them. It is supposed by analogy to spherical graphite that BN in steel also has similar crystal orientation arrangement. As shown in Fig. 2, it is thought that [00.1] axes of BN are arranged in radial fashion and (00.1)_{BN} planes are perpendicular to them. As the growth direction of AlN is identical with [00.1]_{AlN}, it is inferred that the orientation relationship (00.1)_{BN}//(00.1)_{AlN} is satisfied locally on the surface of BN. The other precipitate $M_{23}(CB)_6$ forms below A_{c1} during reheating after quenching at so high a cooling rate that B, N and C atoms remain in solid solution. On this stage BN is not observed. It is impossible to estimate which is more stable because formation free energies of BN and $M_{23}(CB)_6$ are not yet obtained below A_{c1} . Over A_{c3} temperature, there are the experimental value of BN by Fountain and Chipman¹⁶⁾ and the calculated one of $M_{23}(CB)_6$ by Hasebe and Nishizawa.¹⁷⁾ Comparing with the two, BN is more stable. So above A_{c3} the estimation accords with this experiment.

In discussing the precipitation behavior of B below A_{c1} , it is necessary to take kinematical consideration into account besides the thermodynamical stability in equilibrium state. That is, for the sake of the precipitation of $M_{23}(CB)_6$, substitutional atoms (mainly Fe atoms) change their place only a very little distance to fit for the atomic arrangement of $M_{23}(CB)_6$. However, as it is supposed that BN contains no or little Fe atoms, it is necessary for Fe atom to diffuse away a long distance to leave the space for the precipitation and growth of BN. On this account, it is thought in the lower temperature range $M_{23}(CB)_6$ predominantly precipitates and grows.

It is well known that B added steel decreases its hardenability after over-heating above 1 150 °C.⁵⁻⁷⁾ Precipitation behavior of B atoms in this experiment has a good correspondence with the phenomenon of hardenability change. That is, the state that B precipitates remain on prior austenite grain boundaries corresponds to that in which B factor for hardenability decreases to almost 1.0 (no effect). Figure 3⁷⁾ shows the influence of the 1st step quenching temperature T on the hardenability of the following 2nd step quenching of B added steel which was precedingly

Fig. 1.
Schematic illustration of precipitation behavior of B in the manufacturing process.

Fig. 2. Schematic representation of spherical BN.
The orientation relationship $(00.1)_{BN} // (00.1)_{AlN}$ exists between BN and AlN when AlN grows radially on BN.

Fig. 3. Influence of 1st step quenching temperature T upon the following hardenability.
The hardenability is evaluated by the distance from quenched end at which hardness is Rockwell C 26.

over-heated at 1 200 °C before forging. In Fig. 3 hardenability is represented by the location of $H_{RC}=26$ measured from the quenched end of Jominy test. In the as forged state the effect of B is not fully obtained. This stage corresponds to the state in which BN forms as shown in Photo. 1 or Photo. 6. The

hardenability on the following step of quenching is recovered after reheating at 1 000 °C for 1 h. This state corresponds to that in which AlN precipitates on the surface of BN and free B increases, owing to the reaction of $BN + [Al] \rightarrow AlN + [B]$, approaching to the equilibrium state of Al-B-N-Fe system.

V. Summary

- (1) The behavior of B atom which changes its state depending on the heating temperature before rolling, cooling rate after rolling and quenching temperature in heat treatment has been almost clarified.
- (2) These results, combining with the observations by autoradiography of B atoms, quite agree with the changes of hardenability in B treated steels.
- (3) The microstructure of BN is deduced to spherulite structure like spherical graphite.

Acknowledgements

The author wishes to thank Dr. K. Nishioka, Managing Director of Sumitomo Metal Industries, Ltd., for his permission to publish this work.

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