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Microstructural Evolution of Boron Nitride Particles in Advanced 9Cr Power Plant Steels

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ABSTRACT

B and N can be used to increase the creep strength of advanced 9Cr power plant steels by means of microstructural stabilisation and precipitation strengthening, however, the formation of boron nitride (BN) particles removes B and N from solution and reduces the strengthening effect of B and N simultaneously. In the current work, the BN precipitation/dissolution conditions in 9Cr-3W-3Co-V-Nb steels have been investigated in order to understand how to prevent the formation of BN.

A series of austenitisation heat treatments have been designed using thermodynamic predictions as a guide in an attempt to dissolve the BN present after the production of 9Cr-3W-3Co-V-Nb type steels and also to prevent the precipitation of BN during the subsequent heat treatments. Advanced electron microscopy has been carried out to investigate the evolution of the BN particles in relationship to the austenitisation temperature. Energy Dispersive X-ray spectroscopy (EDS) has been used to identify the B containing phases, and a method has been developed using secondary electron images to quantify the amount of BN present within the microstructure.

It has been found that BN solubility is sensitive to the B and N levels in the steel composition, as indicated by thermodynamic calculations. However, it is proposed that austenitisation heat treatments at 1448-1473 K (1175-1200°C) with durations from 1 to 7 hours can effectively prevent the precipitation of BN as well as dissolving most of the BN particles formed during initial steel manufacture.

1 Introduction

Various types of heat resistant steels, such as Grade 91 and 92 have been developed in recent years driven by the need to reduce fossil fuel consumption and hence CO₂ emission during power generation, through an increase in the thermal efficiency of steam power plants by elevating the allowable steam pressure and temperature [1, 2]. The recently developed ferritic 9Cr-3W-3Co-V-Nb steels with controlled additions of B and N have shown superior creep resistance at elevated temperatures compared to other conventional 9 wt.% Cr steels and are considered to be future candidates for 923 K (650°C) applications [3-6]. The microstructure of the 9Cr-3W-3Co-V-Nb steels after the pre-service heat treatment is generally similar to that of conventional 9-12 Cr steels, which typically exhibit a tempered martensite matrix with a fine dispersion of secondary phase particles [3, 7-9]. Due to the high normalising temperature used with the 9Cr-3W-3Co-V-Nb steels, the prior austenite grain size of these steels after heat treatment is much larger compared to conventional 9-12 Cr steel. The large grain size is believed to be beneficial to the creep resistance of weld joints [4]. In addition to the large grain size, two of the important alloy design concepts behind the ferritic 9Cr-3W-3Co-V-Nb steels are: a) B is added to stabilise both Cr-rich carbides ($M_{23}C_6$) against coarsening and grain boundaries during creep [10, 11], and b) the addition of N is carefully controlled to produce a fine dispersion of MX (where M is V or Nb, and X is N or C) particles to strengthen the martensitic microstructure [10,11]. The levels of B and N need to be carefully optimised to avoid the formation of boron nitrides (BN), which, if formed, can offset the beneficial effects induced by B and N additions simultaneously.

In this study, BN particles were observed in two 9Cr-3W-3Co-V-Nb type steels after a standard normalising heat treatment. Previous studies carried out by Abe and co-workers [10,13] have shown that BN can be avoided by carefully controlling the B and N levels in the steel making process. However, this approach normally requires the suppression of N to a level of ~100 ppm or lower, which can be difficult for large scale air castings. Therefore, in

the current study, attempts have been made to both prevent the precipitation of BN and also to dissolve the BN present after normalising in two steels which contain higher N than the suggested maximum [13] by altering the heat treatment conditions. Thermodynamic calculations were first employed to assist in the design of the new heat treatment conditions. Then, a series of heat treatments with different austenitisation temperatures and holding times **have** been carried out. The identification of B containing phases and the quantification of the amount of BN **have** been carried out using advanced electron microscopy techniques.

2 Experimental Methods

2.1 *Materials and Heat treatments*

The investigated materials were two 9Cr-3W-3Co-V-Nb steels designated Steel A and B, with different B and N additions. Steel A containing 180 ppm B and 200 ppm N was produced by air melting to simulate industrial manufacturing processes whereas Steel B, which is an experimental alloy produced prior to Steel A containing 90 ppm B and 270 ppm N, was produced by vacuum melting. After initial manufacture, Steel A was kept in the as cast condition, whilst Steel B was hot rolled at an initial rolling temperature of 1523 K (1250°C) to study the effect of rolling on the microstructure. Steel A was subsequently rolled at 1498 K (1225°C). Samples from these two steels were machined into cylinders of 5 mm in diameter and 10 mm in length for subsequent heat treatment in a dilatometer.

Different austenitisation heat treatments were carried out in a Baehr-Thermoanalyse DIL 805 dilatometer to investigate the effect of heat treatment conditions on the BN particles, details of which are shown in Tables 1 and 2. The dilatometer was used due to its ability to control the temperature accurately and monitor the change in length as a result of thermal expansion or phase transformation, and was operated in a vacuum to prevent decarburisation and oxidation. Cooling was carried out using He, using cooling rates of up to 90 K s⁻¹.

2.2 *Thermodynamic Calculations*

Thermodynamic calculations were performed using the compositions of the two steels to give an indication of the phases likely to be present at equilibrium using the software package ThermoCalc for Windows version 5 (TCW5) in conjunction with the thermodynamic database for ferrous materials version 6.2 (TCFE 6.2) [14]. Calculations were carried out over the temperature range 773-1773 K (500-1500°C) with temperature intervals of 5 K. The global minimisation [15] method was used in all the calculations and the miscibility gaps of the predicted equilibrium phases were selected automatically.

2.3 *Scanning Electron Microscopy*

Samples were sectioned after the austenitisation heat treatments using a Struers Accutom saw, using an alumina slitting disk. The samples were subsequently mounted in electrically conductive Bakelite, followed by grinding using 240 to 1200 grit silicon carbide papers, and polishing on standard cloths with diamond suspensions down to 1 µm. Etching was carried out using Vilella's reagent (1 g picric acid, 5 ml hydrochloric acid and 100 ml ethanol) for approximately 15 s.

A field emission gun scanning electron microscope (FEG-SEM, LEO 1530VP) was used to examine the microstructure of the steels. A silicon drift EDS detector (EDAX Apollo XL) attached to a FEG-SEM/FIB dual beam system (FEI Nova Nanolab 600) was used to perform chemical point analysis on the various microstructural features. In order to yield an acceptable X-ray signal intensity and energy resolution, an accelerating voltage of 5 kV was used in conjunction with an aperture size of 50 µm and a working distance of 5 mm.

Due to the strong image contrast between the BN particles and the martensitic matrix, image analysis was carried out on secondary electron images to quantify the area percentage of BN

particles. Analysis was carried out using the UTHSCSA Image Tool 3.0 software package using a minimum of 30 images per sample (covering a total sampling area of $\sim 940,000 \mu\text{m}^2$). The minimum particle size quantified using this technique for BN analysis was set to 550 nm, which is much smaller than the average BN particle diameter ($\sim 3 \mu\text{m}$), to avoid noise and artefacts being included in the analysis.

3 Results and discussion

3.1 Thermodynamic calculations

The formation conditions for BN have been studied using thermodynamic calculations. After a sensitivity calculation study by altering the levels of all the elements in the 9Cr-3W-3Co-Nb-V Steel At the expense of iron, it was found that the predicted BN level is mostly sensitive to the B and N levels in the alloy composition. Therefore, the phase diagrams of a 9Cr-3W-3Co-Nb-V Steel At different temperatures were calculated with the B level varied from 0 to 0.04 wt.% and N level varied from 0 to 0.07 wt.% at intervals of 0.001 wt.%, at the expense of iron, whilst keeping the other elements at normal levels. The predicted BN solubility lines at 1423 and 1448 K (1150 and 1175°C) are plotted in Figure 1. For comparison purposes, the BN solubility product line at 1423 K (1150°C) as reported by Sakuraya et. al [13] has been superimposed in Figure 1.

Comparison between the thermodynamically predicted BN stability line and the BN solubility product reported by Sakuraya et. al [13] shows that the two results are generally consistent with each other since the predicted B and N composition range which results in BN formation is generally comparable. However, Sakuraya et. al [13] calculated the BN solubility product in a Fe-Cr-B-N system whilst the thermodynamic calculation approach used in the current work takes all the elements in the 9Cr-3W-3Co-Nb-V steel into account. As shown in Figure 1, according to the solubility product, when the B addition is between

0.001 wt.% and 0.1 wt.%, BN is predicted in the N range of 0.003 wt.% to 0.03 wt.%. However, thermodynamic calculation in the current work suggests the opposite, as in this composition range, W rich M_2B particles are predicted to be more stable due to the high W content in the alloy. However, current calculations suggest that when the B is less than 0.0005 wt.% (5 ppm), most of the B goes into solution regardless of the N content. Comparing the thermodynamic calculations at 1423 and 1448 K (1150 and 1175°C), it is found that the maximum amount of N which can be added when the B is around 100 ppm (0.01 wt.%) without forming BN increases slightly with temperature. In the case of 1423 K (1150°C), the maximum N which can be added is approximately 280 ppm (**0.028** wt.%), whereas the maximum N that can be added at 1448 K (1175°C) increases to approximately 300 ppm (0.03 wt.%).

Thermodynamic predictions for steels A and B are shown in Figure 2 (a) and (b) respectively, which plots the predicted amount of the two major B containing phases, **a metallic boride** (M_2B , M: Fe, Cr and W) and BN on a log scale as a function of temperature.

According to the thermodynamic predictions shown in Figure 2 (a) and (b), the M_2B phase is expected in the microstructure of the two steels after normalisation at 1423 K (1150°C), as the M_2B phase is predicted to be stable to a temperature of 1533 K (1260°C) in Steel A and 1540 K (1267°C) in Steel B. However, due to the higher level of B in Steel A compared to Steel B, the predicted maximum amount and temperature range of BN is significantly higher in Steel A than in Steel B. The BN phase is predicted to be stable in the range 1303 – 1413 K (1030 - 1140°C) for Steel A and a much reduced range of **1363** – 1376 K (1090°C - 1103°C) for Steel B. In addition, thermodynamic calculations predict that the temperatures at which delta ferrite forms are ~1573 K (1300°C) for Steel A and ~1523 K (1250°C) for Steel B.

3.2 Identification of Boron Nitride and M_2B

An advanced EDS silicon drift detector (SDD) was used to identify B containing phases, the results of which are presented in Figure 3. To confirm that the EDS SDD could detect B, EDS point analyses were performed on pure B_4C powders. It is observed in Figure 3 (b) that a significant B peak was detected in the spectrum of the B_4C powder.

Figure 3 (a) shows a typical BN particle observed in the Steel B as-rolled sample, with the corresponding EDS spectrum produced from the particle shown in Figure 3 (b). In addition, the spectrum from the B_4C particles is superimposed on Figure 3 (b) for comparison.

It can be observed from the spectrum of the BN particle that both the B and the N peaks are evident confirming that this particle is likely to be BN. In addition, the BN particles appear to be much darker in the secondary electron images than the martensitic matrix and other inclusions present in the microstructure, such as Al_2O_3 and MnS. Therefore it is possible to quantify the area percentage of BN particles by using image analysis techniques based on image contrast.

Characterisation of both Steel A in the ‘as-cast’ condition and Steel B in the ‘as-rolled’ condition showed there was a large amount of M_2B present, **an example SEM image of the M_2B particles observed in the as-cast Steel A is shown** in Figure 4 (a). The M_2B particles were identified in a similar way to the BN particles, however, in addition, they were discriminated by their bright appearance in secondary electron images, which is consistent with the presence of W. The spectrum produced from the EDS point analysis is shown in Figure 4 (b). It is shown in Figure 4 (b) that the major metallic elements in the M_2B particles are Fe, Cr and W, which is consistent with the thermodynamically predicted composition for M_2B .

With the ability to identify both BN and M_2B particles independently, further characterisation was carried out on steels A and B to investigate the microstructural evolution of these two B containing phases as a function of heat treatment conditions. The M_2B phase was observed in the as cast condition of Steel A and in the as rolled condition in Steel B. However, contrary to the thermodynamic prediction which indicates that the M_2B phase is stable until 1533 K (1260°C) in Steel A and 1540 K (1267°C) in Steel B, most of the M_2B phase was found to dissolve after normalising at 1423 K (1150°C) in the two steels, which is consistent with the results reported by Horiuchi et al [16]. BN particles were not observed in the as-cast condition of Steel A whilst BN particles were observed in the as-rolled condition of Steel B. After a standard normalising heat treatment performed on the as-cast condition steel (**Steel A**) and the as-rolled condition steel (**Steel B**) at 1423 K (1150°C) (2 hours for Steel A and 1 hour for Steel B), BN particles were observed in both steels. In an attempt to remove the BN phase from the microstructure in these two steels, alternative heat treatment conditions have been designed to prevent the initial precipitation of BN in Steel A during normalising (section 3.3) and also to dissolve the BN formed during initial steel manufacture of Steel B (section 3.4).

3.3 Precipitation of boron nitride as an effect of heat treatment conditions

Steel A was supplied in the ‘as-cast’ condition where no BN particles were found. However, after a standard normalising heat treatment carried out at 1423 K (1150°C), BN particles were observed in Steel A. In order to understand the BN precipitation conditions, various austenitisation heat treatments, as detailed in Table 1, were then carried out on the as-cast Steel A. The microstructures of Steel A after various austenitisation heat treatments are shown in Figure 5 (a) to (d). It should be noted that the term ‘austenitisation’ is used for these heat treatments because they were carried out in a dilatometer in a controlled environment rather than cooling in air.

Observations of the microstructures revealed that **the** austenitising **of** Steel A at both 1373 K (1100°C) and 1423 K (1150°C) resulted in precipitation of BN (Figure 5 a and b), however austenitising at 1448 K (1175°C) and 1473 K (1200°C) resulted in no BN being precipitated (Figure 5 c and d). The experimental results were found to be generally consistent with the thermodynamic calculations which predict that BN will be present only between 1304 and 1413 K (1031 and 1140°C) in Steel A. However, a variation of approximately 30 K between the experimental results and the thermodynamic predictions for Steel A was noted.

3.4 Dissolution of boron nitride as an effect of heat treatment conditions

The dissolution behaviour of BN has been studied in Steel B. The steel was received in the as-rolled condition, during which the steel had been soaked at 1523 K (1250°C) and subsequently hot rolled. A large number of elongated BN particles were observed in the as-rolled condition of Steel B, as shown in Figure 6.

The BN particles observed in Steel B after hot rolling adopted an elongated morphology. Also, it was found that nearly all the BN particles were aligned with the rolling direction, as highlighted in Figure 6. It is worth noting here that although Steel B had been soaked at 1523 K (1250°C) prior to rolling, the temperature of the steel will have decreased from this initial temperature during the rolling process.

Thermodynamic predictions have shown that BN is stable in the relatively narrow temperature range of 1363 – 1376 K (1090 - 1103°C) in Steel B. Therefore, if the steel is austenitised at a temperature higher than 1376 K (1103°C), the elongated BN particles observed after hot rolling may be dissolved. Therefore, a series of heat treatments with different holding temperatures and times (as shown in Table 2) were performed on the as-rolled samples. The samples with the different heat treatment conditions were characterised using FEG-SEM and the area percentage of BN inclusions in each sample was quantified using image analysis software. To achieve statistically valid data for particle measurements,

three individual measurements, each containing ten images from randomly selected areas, covering a sampling area of $313,335 \mu\text{m}^2$, were performed for each sample, resulting in a total sampling area of $\sim 940,000 \mu\text{m}^2$ per sample. The measured values for each sample were averaged and then plotted in Figure 7 against the heat treatment condition. The error bars for each measurement were calculated from the standard deviation of the three individual measurements on each sample. In addition, the change in the BN morphology was also characterised by measuring the elongation of a number of particles. The elongation was calculated by dividing the longest axis of the particle by the shortest axis. The measured BN elongation as a function of heat treatment condition is plotted on the second axis of Figure 7.

The results indicate that the area percentage of BN decreases after an austenitising heat treatment at 1373 K (1100°C) / 1 hour compared to the as-rolled state. In addition, the measured elongation of the BN particles also decreased after the 1373 K (1100°C) austenitisation, which indicated that the morphology of the BN particles changes gradually from elongated rods to spherical particles. This observation is consistent with the thermodynamic calculations, which predicted that the amount of stable BN decreases gradually in the temperature range 1365 – 1376 K (1092 - 1103°C). Both the area percentage and the elongation of BN particles further decreased when the austenitising temperature was increased to 1423 K (1150°C). When the austenitising temperature was further increased to 1448 K (1175°C), significant dissolution of the BN particles occurred within a short time. After austenitising at 1448 K (1175°C) / 10 minutes, the area percentage of BN was very similar to that of the 1423 K (1150°C) / 1 hour sample. The high elongation of BN inclusions in the 1448 K (1175°C) / 10 min sample was also similar to that in the as-rolled sample, which may be due to the limited austenitising time. Both the area percentage and elongation decreased significantly in the 1448 K (1175°C) / 30 min sample, whilst only a very small number of rounded BN particles (diameter 1 - 2 μm) were observed after austenitising at 1448 K (1175°C) / 1 hour. Quantification of the exact area percentage of BN particles in the

1448 K (1175°C) / 1 hour sample was complicated by the very small number of particles present. The estimated area percentage based on image analysis is less than 0.002%, which means over 97% of the BN particles observed in the as-rolled condition were dissolved after the 1448 K (1175°C) / **1 hour** heat treatment. The results suggest that austenitising at 1448 K (1175°C) is very effective at dissolving the BN particles formed during the rolling process, which is lower than the required temperature reported by Sakuraya et al [13]. In their work, it was reported that BN started to dissolve at 1473 K (1200°C), and that 1523 K (1250°C) resulted in complete dissolution of BN, however, the N content (480 ppm) in their steel was approximately double that in Steel B (270 ppm). Thermodynamic calculations have shown that a higher N content will increase the BN stable temperature range significantly. Therefore, the results presented here and in [13] together confirm the thermodynamic prediction that the dissolution temperature of BN is highly dependent on both the B and N levels in the alloy.

3.5 Effect of tempering heat treatment on the boron nitride formation

It has been demonstrated in sections 3.3 and 3.4 that a BN free microstructure can be achieved by using a higher austenitisation temperature **than** the conventional temperature for grades 91 and 92 in steels A and B. However, a tempering heat treatment subsequent to the austenitisation process is necessary to achieve the desired microstructure and mechanical properties for power plant applications. Therefore, it is important to understand if the BN free microstructure achieved after high temperature austenitisation can be retained after the tempering heat treatment.

In order to simulate the manufacturing process of steam pipes and tubes, the as-cast Steel A was first soaked at 1498 K (1225°C) and subsequently hot rolled. A large number of BN particles were found in the as-rolled condition as shown in Figure 8 (a). An extended normalisation heat treatment at 1473 K (1200°C) for 7 hours was then carried out on the as-

rolled Steel A. Microstructure characterisation has shown that all the BN particles formed during rolling were dissolved after the extended high temperature normalisation. Subsequently, a tempering heat treatment at 1053 K (780°C) for 3 hours was carried out on the as-normalised Steel A and, as shown in Figure 8 (b), no BN was found after tempering.

Steel B was previously rolled at 1523 K (1250°C) and it has been demonstrated in section 3.4 that most of the BN particles observed in the as-rolled condition can be dissolved after an 1448 K (1175°C) / 1hr heat treatment. Therefore, a tempering heat treatment at 1053 K (780°C) for 3 hours was performed on the sample which had been austenitised at 1448 K (1175°C) for 1hr. The microstructure after tempering was found to be almost BN free, however, a very small number of rounded BN particles (1-2 μm) were observed after tempering. Figure 8 (c) shows an example image of one of the very few spherical BN particles observed after the alternative austenitisation and tempering heat treatment, these particles are believed to be the undissolved BN particles present after austenitisation.

These results, therefore, indicate that BN particles do not form during the tempering heat treatment in both steels A and B. This finding is consistent with the thermodynamic calculations, which suggest the BN formation temperature range is much higher than the tempering temperature. Therefore, the normalising condition is crucial in dissolving the BN. However the actual condition used is dependent on the B and N levels in the alloy.

4 Conclusions

Experimental results together with thermodynamic calculations have shown that both the precipitation and dissolution of BN particles in 9Cr-3W-3Co-V-Nb steels are very sensitive to the heat treatment conditions. The N level of Steel A and B investigated in the current study are both higher than the maximum level allowable for complete solid solution suggested by Sakuraya et. al's [13] BN solubility product equation. However, current

research has shown that a BN free microstructure can still be achieved in these high N steels by increasing the austenitising temperature within the range 1448 - 1473 K (1175-1200°C), which is still much lower than the delta ferrite formation temperatures in the two steels. The key conclusions from the current study are summarised below.

1. Thermodynamic calculation is a useful tool in predicting the formation of BN particles using the steels' chemical compositions. Comparison between the experimental observation and the calculation results are generally in agreement with each other.
2. An austenitising heat treatment carried out at elevated temperatures (1448 K to 1473 K) is found to be effective in preventing the precipitation of BN (in Steel A) as well as dissolving the BN formed in the previous hot rolling process (in Steel B).
3. A large amount of BN particles are observed after hot rolling carried out at 1498 K and 1523 K for Steel A and B respectively. However, after applying an alternative austenitising heat treatment at 1473 K for 7 hrs and 1448 K for 1 hr respectively, most of the BN particles formed during the rolling process are dissolved. In addition, it has been found that BN particles are unlikely to precipitate during the subsequent tempering heat treatment (1053K / 3hrs).

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Table 1: Austenitisation heat treatment conditions of Steel A in the ‘as-cast’ condition to investigate the boron nitride precipitation conditions

	Heating Rate	Holding Temperature, K (°C)	Holding time	Cooling rate
Steel A	2 K/s	1273 (1000)	10 min	90 K/s
		1423 (1150)		
		1448 (1175)		
		1473 (1200)		
		1498 (1225)		

Table 2: Austenitisation heat treatment conditions of Steel B in the ‘as-rolled’ condition to investigate the boron nitride dissolution conditions

	Heating Rate	Holding Temperature, K (°C)	Holding time	Cooling rate
Steel B	10 K/s	1373 (1100)	1 h	10 K/s
		1423 (1150)	1 h	
		1448 (1175)	10 min	
		1448 (1175)	30 min	
		1448 (1175)	1 h

Figure 1: Calculated BN solubility line at 1423 K (1150°C) and 1448 K (1175°C) for 9Cr-3W-3Co-Nb-V steel as a function of B and N content. The solubility product reported by Sakuraya et al [13] has been superimposed for comparison purposes.

Figure 2: An equilibrium diagram showing the two major boron containing phases predicted to be present under equilibrium conditions for (a) steel A and (b) steel B.

Figure 3: (a) A secondary electron image of steel B showing the BN particle observed in the as-rolled condition; (b) An EDS spectrum obtained from the BN particle observed in the steel B as-rolled sample; the spectrum of pure B_4C powder is superimposed for comparison.

Figure 4: (a) A secondary electron image of steel A showing the M_2B particles observed in the as cast condition in steel A; (b) An EDS spectrum of an M_2B particle present in steel A in the as cast condition.

Figure 5: Secondary electron micrographs of steel A after austenitising heat treatments at (a) 1273 K (1000°C), (b) 1423 K (1150°C), (c) 1448 K (1175°C) and (d) 1473 K (1200°C) each for 10 minutes; all the heat treatments were carried out on steel A in the 'as-cast' condition in a dilatometer.

Figure 6: A secondary electron image of Steel B after hot rolling at 1523 K (1250°C) showing elongated BN particles; the rolling direction is also illustrated.

Figure 7: Measured BN area percentage and elongation as a function of heat treatment conditions in steel B.

Figure 8: (a) A secondary electron image of steel A showing the BN particles formed after hot rolling at an initial soaking temperature of 1498 K (1225°C); (b) A secondary electron image showing that no BN was found in Steel A after the alternative heat treatment (heat treatments were carried out in the as-rolled steel A with the condition: normalisation at 1473 K (1200°C) / 7 hrs and tempering at 1053 K (780°C) / 3 hrs); (c) An example secondary electron image showing one of the small spherical BN particles found in the Steel B after the alternative heat treatment (normalisation at 1448 K (1175°C) / 7 hrs and tempering at 1053 K (780°C) / 3 hrs)