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Effect of Niobium and Titanium Addition on Formation of Second Phase Particles in CHQ Steel Using Transmission Electron Microscope

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ABSTRACT

It is common practice that formation of second phase particles such as nitrides or carbides in the steel matrix has significant role to control the grain size of steel. An attempt is made in the present research work to find out the role of nitrogen to form the nitride particles either with Al, Ti, B, Cr or Si. Two steel samples Steel-A and Steel-B with same titanium and aluminum weight percent in the chemical composition were obtained in hot rolled conditions from international market with only the difference of presence of Niobium in Steel-A. Solution heat treatment was performed at 1350°C with 60 minutes holding time in protherm heat treatment furnace available locally was used to dissolve the particles and then steel samples were reheat treated at 800°C with holding time of 60 minutes and water quenched and microstructure was revealed. Transmission electron microscope connected with Ehlers-Danlos Syndrome (EDS) was used to reveal the morphology of second phase particles. Both samples for a high resolution power Transmission Electron Microscopy (TEM) (Jeol JEM 3010) analysis were prepared by using carbon extraction replica method in 5% Nital solution as an etching technique. Both samples were then caught in copper grid of 3mm for using TEM analysis. TEM micrographs clearly revealed the second phase particles in the matrix of steel. The EDS peaks were studied and it was found that the peaks showed the titanium peaks in both the samples A and B and surprisingly there was no any peak found for aluminum. Stoichiometric calculations were carried out and it was found that weight percent nitrogen required for forming TiN is 0.0073, however the total nitrogen present in both the steels A and B is 0.0058 and 0.0061 respectively. That means that all the nitrogen present in the steel matrix was consumed by titanium to form the Titanium Nitride (TiN) so there was no nitrogen remain to fulfil the requirement of aluminum to form the Aluminum Nitride (AlN) particles.

Keywords: Cold Heading Quality Steel, Second Phase Particles, Transmission Electron Microscopy, Niobium.

1. INTRODUCTION

The Cold Heading Quality (CHQ) steels are assumed to be non-heat treatable so strengthening by cold forming which is a quick and mass production makes these steel a low cost solution for various applications. The micro-alloying addition of various elements, especially Al, has significant effect on the quality of CHQ steel. With respect to addition of Ti, Nb or V aluminum nitride and their precipitation in steel the precipitation of AlN has strongly influence on end mechanical properties. Due to difficulty in forming precipitates, of AlN, it is unavoidable to produce thermo-mechanical treatment to give rise to accelerate the precipitation kinetics. Gong *et al.* [1] studied the dissolution and precipitation behaviour in micro alloyed steels of Nb steel and Nb-Ti steel, both steels indicated the dissolution of Nb in austenite upon reheating in both the Nb and Nb–Ti steels but the dissolution was faster for Nb steel as

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compared to the Nb–Ti steel. Titanium micro-alloying when adding to Nb contained steel result in a substantial increase of the yield strength due to refinement of grains, contribution of precipitation hardening was small [2]. Strain plays an important role in precipitation of Nb-Ti-V steel [3]. In high Nb steel the Nb does not completely dissolve in the reheating processes, the un-dissolved precipitates act as heterogeneous nucleation sites for the strain induced precipitates [4]. Carbon and manganese can also effect the precipitates sizes in high Nb steels [5]. Addition of Nb can significantly improve the impact toughness of 25CrMo48V steel due to grain refinement and final martensitic structures [6]. Different other researchers have also studied the various aspects of Nb addition in steel [7-17]. None of anyone has studied this effect in CHQ steels.

In this research work effect of Nb addition of precipitation behaviour of micro alloyed CHQ steel is carried out to study the nature of precipitated formed when other elements such as Al, Si, Ti and Cr are also present. The sample also contains small quantity of Nitrogen.

2. EXPERIENTIAL PROCEDURE

Grain size control is always a superior priority for researchers to obtain the small grains which simultaneously increase the hardness as well as toughness. Second phase particles are therefore useful source for the steel to control the grain growth and grain growth is deciding factor to increase the strength. When aluminum and titanium combines with nitrogen in the chemistry can form the aluminum nitrides and titanium nitrides particles respectively because nitrogen has good affinity with both elements. Whenever titanium and aluminum are the alloying elements at the same time, there is quite difficult to find out that nitrogen will either combines with only aluminum or only titanium or with both elements to form the nitride particles which are known as second phase particles and due to their higher melting point and stability they remain in the solution in the solid state when steel is cooled from its melting point. The investigations of two steels were carried out in the present work to understand this effect. In this connection two steels as shown in Table 1 were collected in hot rolled condition in two high rolling mills from POSCO steel plant available at Korea Advanced Institute of Science & Technology (KAIST) Laboratory. The hot rolling process cycle is shown in Fig. 1.

Table 1: Composition of Alloy A and Alloy B

Steel	C	Mn	Al	Ti	Nb	B	N_2	Si	Cr
A	0.202	1.04	0.042	0.025	0.047	0.0018	0.0058	0.25	0.144
B	0.2	1.04	0.042	0.025	-	0.0019	0.0061	0.251	1.21

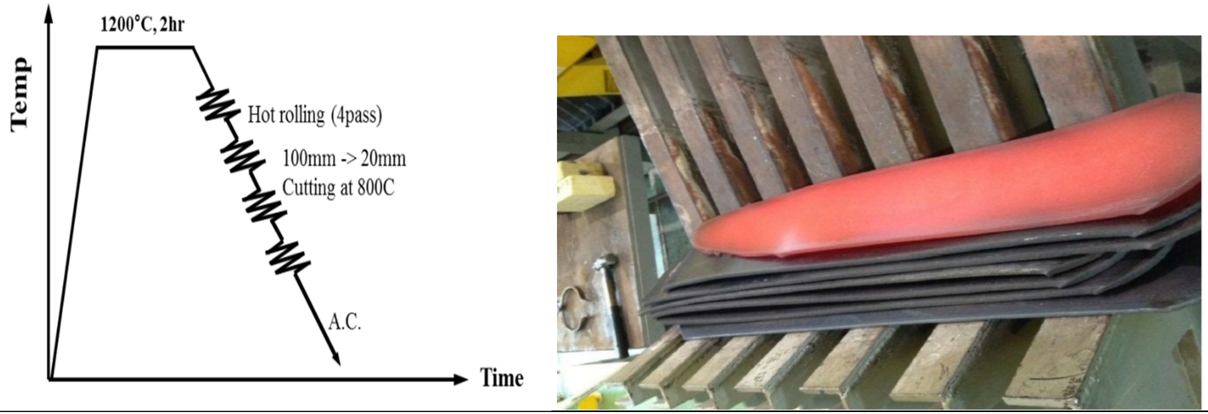

Fig. 1: Hot Rolling Process Cycle

After hot rolling both samples A and B were solution heat treated at 1350°C and 60 minutes holding time in order to dissolve the particles in the solution at elevated temperature, if present any. After holding, samples were fast cooled in tap water. To investigate the effective influence of particles, both the samples were re-heated at moderate temp: of 800°C for one hour and then quenched. After the heat treatment process the samples were then brought to reveal the microstructures with utilizing the conventional grinding and polishing steps followed by etching in 2% Nital, all the metallography steps were performed locally, Optical microscope Olympus 1000x. Immediately after using optical metallurgical microscope to investigate the microstructures of the Sample-A and Sample-B. Both samples were further prepared for TEM by using carbon extraction replica method, as shown in Figs. 2-3.

3. RESULTS AND DISCUSSION

Optical Micrographs of Sample-A as visible in Fig. 4 at 800°C and 1350ºC, which indicated that for lower temperature of 800ºC, the grain size is small as compared to the sample at 1350ºC. It is to be noted that second phase particles can only be seen at higher magnification which is not possible for optical micrographs. The particles that were shown in the Sample-A might be oxide particles or some other inclusions. Similar trend was found in Sample-B, Figs. 5-6 in SEM.

The TEM analysis in Fig. 7 shows the particles in Sample-A as revealed through carbon replica method. It was found that particles are in the range of Nano meters with the morphology of square, rectangular, or and some small particles were also showing spherical shape. It was found from TEM analysis in the Steel-A, that contain Nb, the precipitates are showing presence of Nb as well as Ti, while there was no evidence of Si, Al and Cr in EDS peaks.

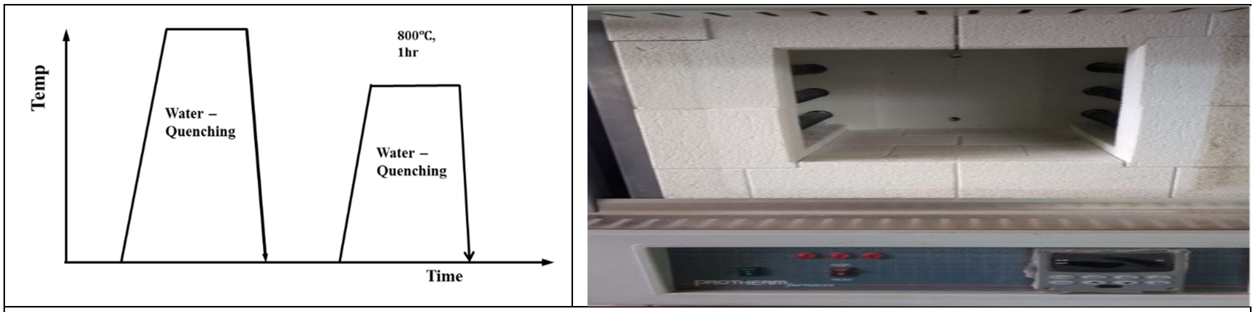

Fig. 2: Up Quenching Cycle

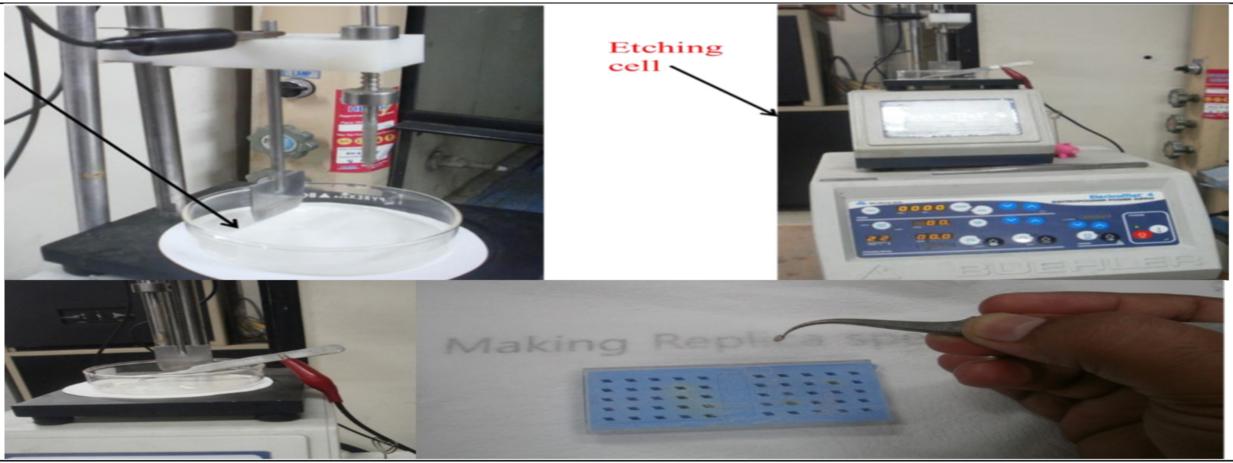

Fig. 3: Extraction of Carbon Replica by Using Etching Cell

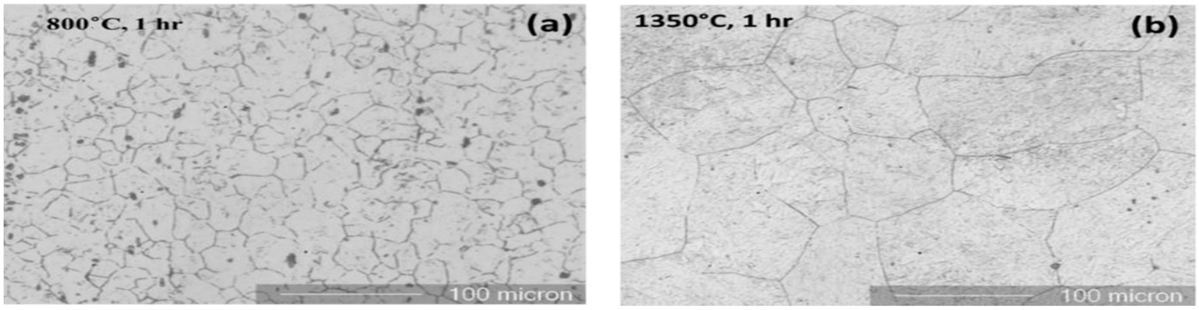

Fig. 4: Optical Micrographs of Sample-A at (a) 800°C and (b) 1350°C

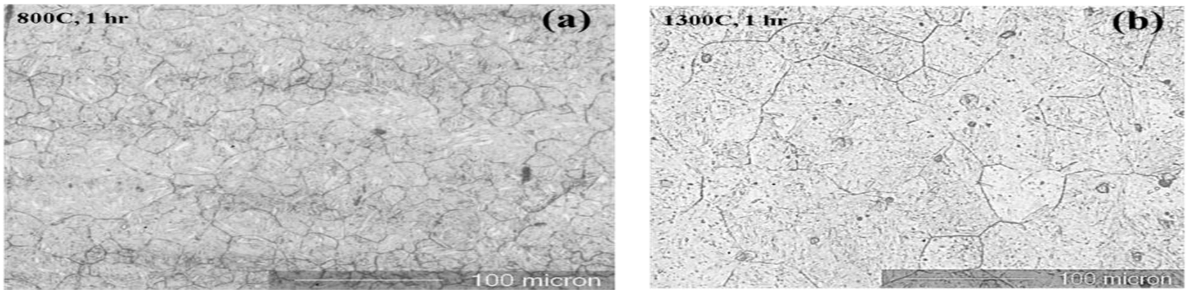

Fig. 5: Optical Micrographs of Sample-B at (a) 800°C and (b) 1350°C

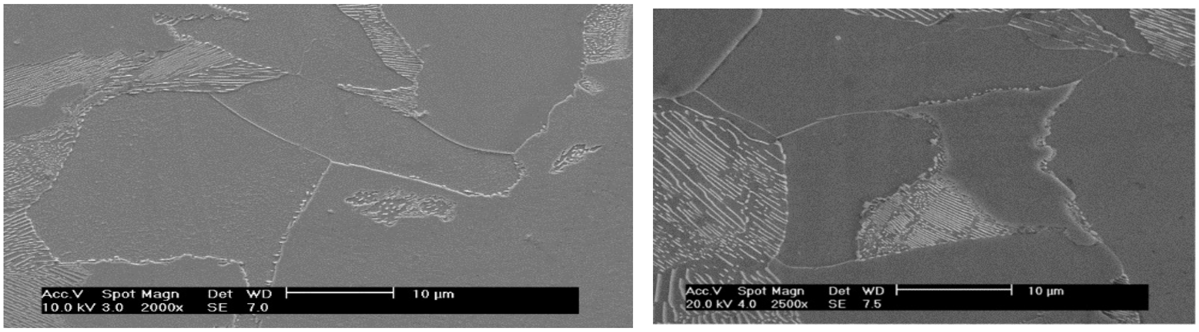

Fig. 6: Initial Sem Micrograhs of Steel-A and Stee-B having Nb and without Nb

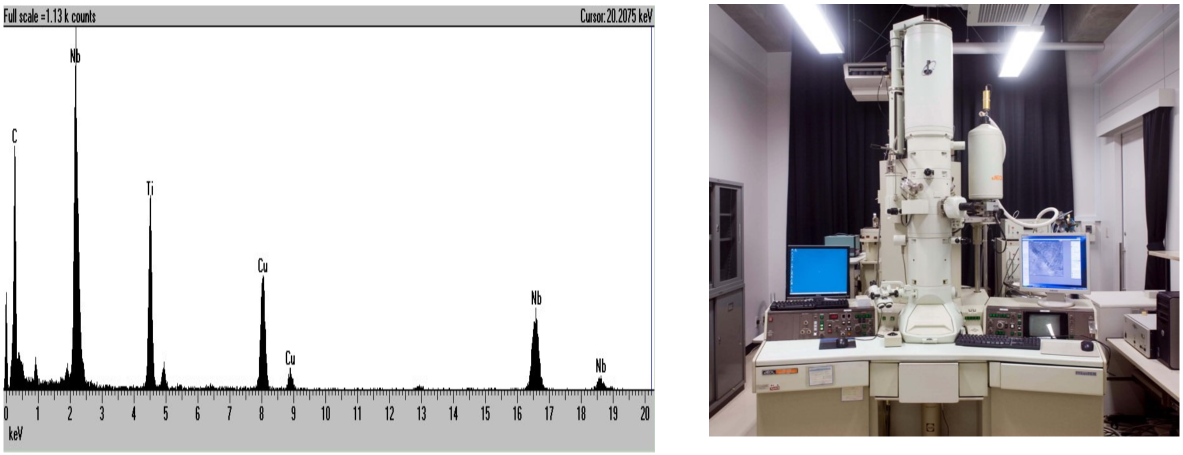

Fig. 7: TEM Micrographs for Sample A. EDS Peaks are shown as well

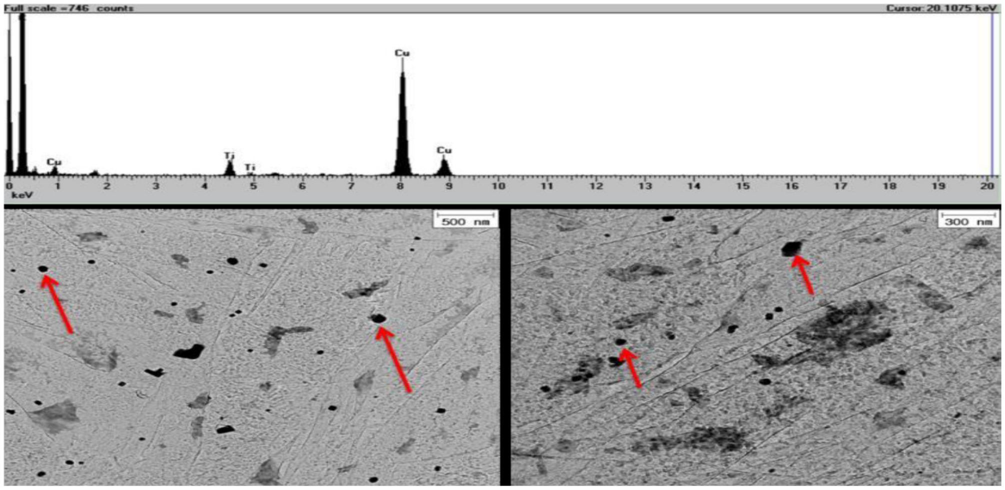

Fig. 8: TEM Micrographics with EDS for sample B

Etching is an important step in this technique, usually etching is performed in the range of 3-5% nital solution because in the steel matrix, precipitates are existing therefore it is necessary to etch the steel matrix with etchant (5% Nital) to drag the particles outside. Care should be taken that the surface should be little over etched. The particles were then kept in the copper grid usually used for TEM analysis. After catching the particles for both Steel-A and Steel-B, samples were then ready for TEM observation. TEM connected with the EDS, is a powerful instrument to reveal the second phase particles as shown in Fig. 8, and the arrows showed in the TEM micrographs are showing the second phase particles. In case of Steel-B, where Nb was not present, precipitates of Ti were only present without any trace of Si, Al and Cr as shown in the EDS peaks. TEM micrographs clearly reveal the Nano sized second phase particles in the matrix of steel. EDS peaks were studied and it was found that the peaks showed the titanium peaks in both the Sample-A and Sample-B but the Nb peaks were found in the Sample-A only and surprisingly there was no any peak found for aluminium. Stoichiometric calculations were carried out as shown in Table 2 and **Figs. 9-10**, it was found that weight percent nitrogen required for forming TiN is 0.0073, however the total nitrogen present in both the steels A and B is 0.0058 and 0.0061 respectively that means all the nitrogen present in the steel matrix was consumed by titanium to form the TiN so there was no nitrogen remain to fulfil the requirement of aluminium to form the aluminium nitride particles.

4. STOICHIOMETRIC ANALYSIS

Solubility of nitrogen in aluminium and titanium to form AlN and TiN respectively, an isotherm curves were plotted at various temperature ranges from 850-1250°C as shown in Fig. 9. By closing look at the Fig. 10, it was found that wt. % nitrogen required to form the nitride nano particle at 850°C is about 0.0073 (area in the circle) and in the similar way observe in Fig. 9. The nitrogen required to form the AlN precipitates at 850°C is less than 0.002 (circled area). By increasing the temperature, the nitride particles become soluble in the matrix.

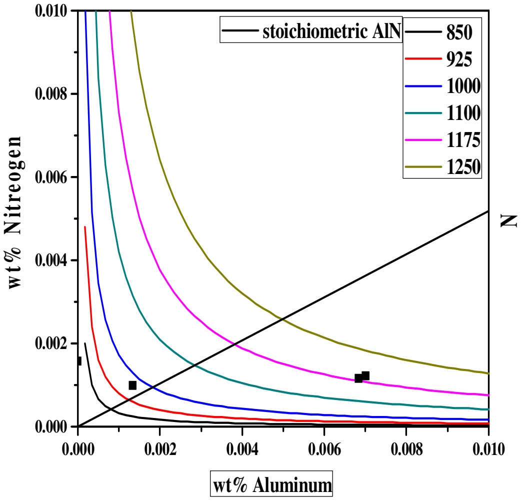

Fig. 9: Stoichiometric Calculations of AL and N

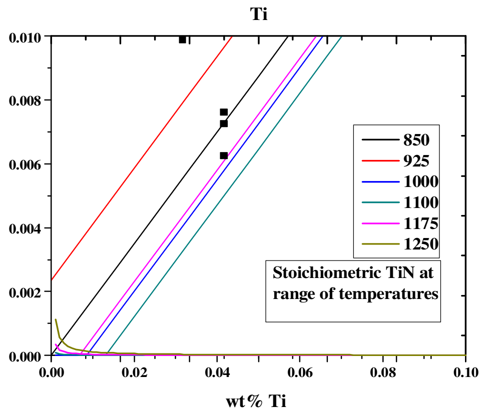

Fig. 10: Stoichiometric Calculations of TI and N

Mathematical calculation was performed to know and verify theoretically the exact amount of nitrogen needed to form the precipitates when nitrogen combines with titanium. The calculation is shown in Table 2. Thermodynamic calculation can also be performed for aluminum with nitrogen (Log ([Al] [N]) = 1.03 - 6770/T) and titanium with nitrogen (Log ([Ti] [N]) = 3.82 - 15020/T).

Table 2: Mathematical Calculation of Ti And N to form ALN

Ti Atomic Mass	48	wt.% Ti in Steel-B = 0.025
N Atomic Mass	14	(0.025 x 14)/48 = 0.0073

5. CONCLUSION

Effect of Niobium and Titanium addition on formation of second phase particles in CHQ steel using TEM was examined and comparison of two steels with different chemical compositions that contain micro-alloying elements i.e. Al, Ti, B, Si and Cr is carried out to study the precipitation behavior of both steels. The Steel-A contains Nb while the Steel-B does not contain Nb. It was found that in Steel-A the precipitates of Nb and Ti were present while in Steel-B only Ti precipitates were present. In both steels none of the alloying elements among Al, B, Si and Cr showed any formation of precipitates. Stoichiometric calculations were carried out and it was found that weight percent nitrogen required for forming TiN is 0.0073, however the total nitrogen present in both the Steel-A and Steel-B is 0.0058 and 0.0061 respectively that means all the nitrogen present in the steel matrix was consumed by titanium to form the TiN so there was no nitrogen remain to fulfill the requirement of aluminum to form the aluminium nitride particles.

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