Coarsening particle of Nb(CN) in Nb-HSLA Steel after deformation at 900°C in austenite phase during thermomechanical treatment

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ABSTRACT

Nb(CN) particle in Nb-HSLA steels plays important role to retard recrystallisation process and to strengthen the mechanical properties by precipitation hardening. The behavior of Nb(CN) particle growth after deformation needs to evaluate in order to optimize the production process. HSLA steel containing 0.03% Nb is used and the thermomechanical treatment including reheating, air cooling, finishing, and relaxation is applied to the test steel. The results obtained in this way shows that the kinetics coarsening of Nb(CN) particle after deformation at 900°is considerably accelerated compared with when the coarsening is controlled by a bulk diffusion process.

INTRODUCTION

The decomposition of a supersaturated solid solution into one or more phases may generally be regarded as taking place in three stages; (i) the formation of nuclei of the new phase, (ii) growth the nuclei to impingement or depletion of the matrix and, (iii) coarsening, the process whereby the larger particles consume the small ones with the volume fraction of particles remaining constant.

After the formation of nuclei of the new phase, the high density of small precipitation will tend to coarsen into a lower density of larger particles with a smaller total interfacial area. The diffusional growth and diminution of precipitated particles in a solid matrix is generally known as Ostwald Ripening. Theoretical treatments of this process have been given, among others, by Greenwood [1], Wegner [2] and Lifshits & Slyozov[3]. Greenwood derived the differential equation governing the process, under several restrictive assumption. Subsequently, Wegner and Lifshitz & Slyozov {LSW] analyzed the the problem more rigorously. A new method of driving fundamental rate equation for oswald ripening has been proposed by Fujii et al[4]. Figure 1 shows the schematic growth of a particle by diffusion.

It has been established that when there is distribution in particle sizes, particles larger than the average size grow and the remainder shrink and eventually dissolve. Assuming the diffusion between the particles to be rate-determining, the basic equation given by [5]],

$$r\frac{dr}{dt} = \frac{2DC_{eq}\gamma\Omega}{kT}\left[\frac{1}{r_e} - \frac{1}{r}\right]$$

Where r is the particle radius, D is the solute diffusion coefficient, C_{eq} the solubility of a very large particle, γ is the interfacial energy particle/matrix, Ω is the volume of an atom in the particle, r_e is a critical radius and kT its usual meaning.

The relationship between the mean radius coarsening particles, r, and time, t, depend on the process which is controlling the rate of particle growth. When an interfacial reaction is controlling, $r \alpha t^{1/2}$, and when the coarsening is controlled by a bulk diffusion process, $r \alpha t^{1/3}$. Similarly, if grain boundary diffusion is controlling then $r \alpha t^{1/4}$, and when pipe diffusion is controlling $r \alpha t^{1/5}$.

For coarsening controlled by volume diffusion of Nb in Micro-alloyed steel, the change in mean particle radius with time is suggested [2] as

$$r^3 - r_0^3 = \frac{8/9\, D_{Nb} C_0 \gamma V_m^2}{kT}[k_r]$$

Waiss and Jonas [6] calculated particle coarsening of Nb(CN) in Nb-steel containing 0.035% Nb, 0.05%C and 0.04% N, during

deformation by using Wagner's diffusion-controlled model [2] as,

$$r_t^3 = r_0^3 + kt$$

$$k = \frac{8 D_{Nb} C_0 \gamma V_m^2}{RT} [9 k_s]$$

r_t is the average particle radius at time t. They show that after deformation at 900°C, the rate of coarsening is increased by about three order magnitude, as indicated by the ratio,

$$\frac{k_{dyn}}{k_{nor}} = 3.68 \times 10^3$$

The effect of the static recrystallisation which occurred during holding on the rate of coarsening of the particles Nb(CN) in 0.07% Nb in HSLA steel was established by Chandra et al[5]. They found that the fifth power of the main radius, r^5, increased linearly with aging time, t, in keeping with a model for coarsening controlled by the rate of pipe diffusion. They also reported that the growth rate of Nb(CN) in about three times as fast in the presence of static recrystallisation as its absence at both temperature.

The coarsening of Nb(CN) in dynamic recrystallisation of Nb microalloyed steel has been examined by Chandra et al[5] in terms of the Kreye

$$r^5 - r_0^5 = kt$$

theory[7] of particle growth which leads to

$$k = \frac{4 D_{Nb} C_0 \gamma V_m^2}{\pi RT}$$

Figure 2 shows dependence of fifth power of mean radius r^5 on time for 0.018% Nb steel during dynamic coarsening at different temperature. The growth rate during dynamic recrystallisation is reported [5] much faster about 10 times than during static recrystallisation.

Acceleration of pipe diffusion of niobium along the dislocation links, as shown in figure 3, has been proposed by Dutta et al [8]. They reported that coarsening controlled by volume diffusion, see equation 2, is found disagree with the observed rates and suggested that the particle growth has occurred by volume diffusion controlled flux of niobium atoms directly to the particle, or to the dislocation line linking the particle. They suggest changes in particle size by diffusion along the dislocation line between particles as shown in figure 4.

The isothermal precipitation behavior of Nb(CN) in austenite, recently has been investigated by Akamatsu et al[9] using steel of different carbon contents. The observed progress of precipitation in extra low carbon steel is found much faster and the size of the precipitates is apparently larger than those in steels with higher carbon content. They suggested that the acceleration of the growth of Nb(CN) in that steel is caused by the larger concentration gradient of Nb from the γ/Nb(CN) moving interface at the site of austenite phase. A new model has been established and a comparison of the calculated and observed fractions and mean particle diameter of Nb(CN) particles has been presented [10].

In this presence investigation, the coarsening of Nb(CN) particles after reheating and finishing at 900°C are followed by using 0.03% Nb HSLA steel. The rate of Nb(CN) particle coarsening is investigated and the model of coarsening particle is evaluated by collecting rate coarsening data in Nb-HSLA steel.

EXPERIMENTAL PROCEDURE

Steel Used for the experimental work

A low Nb-high C HSLA steels was used in the present investigation. The steel is a conventional hot-rolled plate steel which the chemical compositions of the steel is displayed in table I.

Table I. The chemical composition of the test steel.

Element	wt[%]
C	0.1
Si	0.37
Mn	1.35
P	0.02
S	0.019
Al	0.041
N	0.0042
Nb	0.031

Compression specimens, as illustrated in figure 5, were machined from the as-received plates. In order to prevent oxidation and scaling during reheating, the specimens were chromium plated to 15 μm thickness.

TESTING PROCEDURE

Mechanical method

A mechanical method, which has been developed by Liu and Jonas [10], was used to detect initial precipitation and coarsening precipitation particle isothermally. The samples thus prepared were now ready for testing under plane strain compression by using the servo-hydraulic driven, computer controlled machine know as the SERVOTEST machine as shown in figure 6. Start time for precipitation and growth are calculated by analyzing of isothermal stress relaxation data showing that relaxation is retarded at the start of precipitaton. The stress relaxation curve of Nb-HSLA steel after deformation at 900°C and relaxation has been reported by Siradj[11].

The sample were reheated to dissolve the Nb(CN) precipitates. The dissolution temperature of Nb(CN) precipitation can be calculated from the equation given by Irvine et al[12] as,

$$\text{Log}[Nb][C+{}^{12}/_{14}N]=-6770/T+2.26$$

Where [Nb] and [C + $^{12}/_{14}$N] are the concentrations of Nb, C and N in solution (wt%) at the absolute temperature, T. To ensure that the dissolution is complete, the austenizing temperature used in this investigation is approximately 50 – 100°C above the calculated solution temperature. Therefore, leading to a reheat temperature of 1200°C and held for 15 minutes to stabilize the temperature.

After reheating at a temperature 1200°C, the specimen is air cooled to a finishing temperature of 900°C. Figure 7 shows the thermomechanical cycle applied in this test steel. After finishing, relaxation ware performed for 10, 100 and 200 seconds and then the deformed-specimen were quenched.

Metallography

Both optical metallography and electron microscopy are used to examine microstructure and precipitation growth. Etching to reveal austenite grain boundaries was carried out by using aqueous picric acid containing a small amount of HCL and a wetting agent teepol according to procedure of Baldinger et al [13].

The presence of precipitation Nb(CN) in specimens is observed in this investigation by using carbon replication. In this method the polished specimens are etched with 2 % nital for about 5 seconds and then a thin layer carbon is evaporated onto the etched surface. The samples are immersed in 10 % nital for up to 60 seconds. The carbon film is then floated off by immersion in distilled water, collected on copper grid, and examines in the electron microscope. A Philips 400 and A Joel 200CX transmission electron Microscope (TEM) are used to observe these replicas.

EXPERIMENTAL RESULTS

After reheating at a temperature of 1200°C, equiaxed austenite grain structure in 50 ± 6 μm grain size were observed, see figure 8. Elongated austenite grain structure are mostly observed after finishing at a temperature of 900°C, the structure might be seen in figure 9.

A study of replicas by transmission electron microscopy was carried out to investigate the strain induced precipitation associated with plane strain compression of high Nb-Low C HSLA steel. A micrograph of a replica after reheating at a temperature of 1150°C for 15 minutes. An undissolved of Nb(CN) particle of about 200 nm size after quenching from 1200°C has observed by previously work[11]. Such large particles were found only occasionally and no fine particles were present. After cooling down to a finishing temperature of 900°C and holding for 60 sec before quenching, no Nb(CN) precipitates were observed. Figure 10 shown the micrograph of replicas. After finishing at a temperature of 900°C and holding for 10 seconds, fine Nb(CN) particles of sizes 2 to 4 nm presumably existed from the evidence of stress relaxation. The micrograph of replica in figure 11a fails to image these fine particles.

The average particles size increased significantly as the delay time was increased. On holding for 100 seconds, the average particle size become approximately 6 nm, while after 200 seconds, the Nb(CN) particles have considerably increased in size to 8 – 10 nm. The micrograph of replicas in figures 11b and 11c respectively show these precipitates.

DISCUSSION

Undissolved Nb(CN) particle in size larger than 40 nm after reheating have also been observed in literature [14]. It has been also reported [15] that Nb(CN) remaining out of solution does not appear to have had a major effect on precipitation kinetics. After finishing at 900°C and holding for 10 seconds, very fine particles precipitates. The stress relaxation curve for this steel has been reported by Siradj[16] shows that precipitation start for 5% fraction precipitation at 8 seconds and fine Nb(CN) after 8 seconds were observed. Yamamoto et al [17] reported that no precipitation is observed after holding time less than 8 seconds. It was assumed that Nb(CN) precipitates in size approximately 2 to 3 nm have been formed and the fraction of precipitation of 2 – 3% has been obtained[5]. However, the extraction technique fails to extract these particles. Weiss and Jonas [6] show that carbon replica technique is no be able to detect Nb(CN) particles in size below 4 nm.

It is of interest to note that the Nb(CN) precipitates as shown in figure 11b are distributed locally in sizes approximately 3 to 4 nm. Kwon and DeArdo[18] reported that the localized distribution of Nb(CN) particles appear to be a characteristic of Nb(CN) precipitation in deformed austenite. They indicated that these localised areas might include prior austenite grain boundaries, deformation bands and subgrain boundaries.

In order to evaluate the coarsening time, the particle coarsening in terms of the mean cube radius and the theory of Ostwald ripening is adopted. According to Wagner's diffusion-controlled model [2], particle size under Ostwald ripening conditions can be described by,

$$r_t^3 = r_o^3 + Kt$$

where

$$K = \frac{8\gamma D C_o V_m}{9R}$$

where r_t is the average radius at time t, r_o is the average radius at time t_o, D is the diffusivity of Nb in austenite, C_o is the concentration of Nb in the matrix, k is Boltzmann's constant, V_m is the particle molar volume, and γ is the surface energy particle and matrix interface. The coarsening time can be evaluated using the following data suggested by [6],

$\gamma = 15 \times 10^{-7}\ J/cm^2$
$D_o = 5.3 \times 10^{2}\ cm^2/s$
$V_m = 2 \times 10^{2}\ nm^3$
$C_o = 5 \times 10^{-5}$
$Q = 293\ kJ/mol$

This leads to a K value for normal Ostwald ripening of 3.8 x 10^{-2} nm^2/sec, and then coarsening time the diameter of particles to increase from 4 nm to 8 nm is about 1250 seconds. However, this coarsening time above is in disagreement with that observed up to 200 seconds. Figure 12 shows comparison of Nb(CN) particle coarsening observed and coarsening model controlled by a bulk diffusion process.

Dutta et al [8] suggested that volume diffusion cannot be the controlling diffusion process and that the accelerated pipe diffusion of niobium
along dislocation links must also take
place, see figures 5 and 6 respectively. They indicated that the increased from 4 πr^2 to 3(2π bl/2). While, Akamatsu et al [9] suggested that the acceleration of the growth of Nb(CN) in extra low carbon steels is caused by the large concentration gradient of Nb from the austenite/Nb(CN) interface at the side of austenite-phase. This would lead to more rapid particle coarsening and may be the reason for the short time observed experimentally.

CONCLUSION

1. Coarsening particle Nb(CN) in Nb-HSLA steel after deformation at 900°C is considerably faster compared with the Wagner's diffusion controlled model. Coarsening particle from 2 to 8 nm is achieved by holding time for 200 seconds, while according to the diffusion controlled model needs 12500 seconds.
2. Increasing the coarsening rate of particle Nb(CN) in Nb-HSLA steel is reported by previously work [8] and suggested that volume diffusion cannot be the controlling diffusion process. The accelerated of particle growth is caused by pipe diffusion along dislocation links. The other work [9] reported that large concentration gradian of Nb from interface of austenite and particle Nb(CN) at the site of austenite-phase leads more rapid particle coarsening

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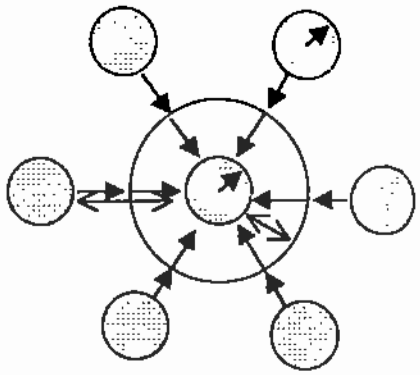

Figure 1. Growth of a particle of radius r by the diffusional flow of solute atoms from the surrounding particles of radius r [4]

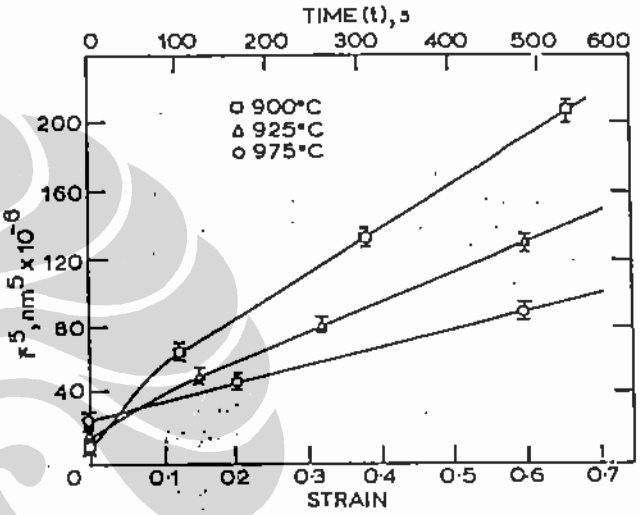

Figure 2. Dependence of the fifth power of the mean particle radius on time for 0.018%Nb steel during dynamic coarsening at 900, 925 and 975°C [5]

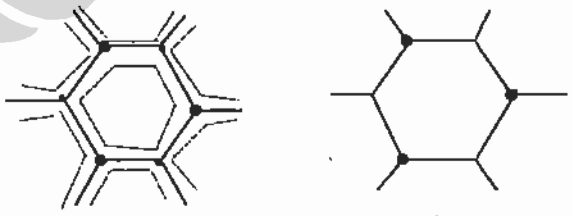

Figure 3. Schematic diagram of particle distribution and solute deplete zones when accelerated diffusion takes place along dislocation (a) after particle growth (b) after further growth [8].

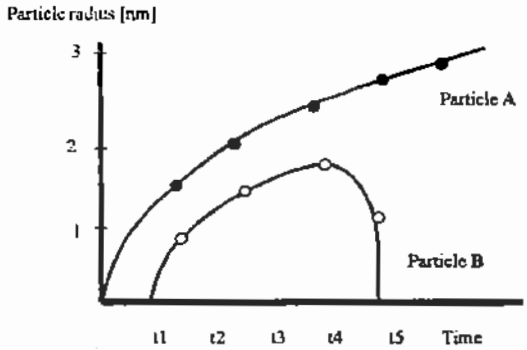

Figure 4. Change in size of particle A and B in figure 3 with time [8]

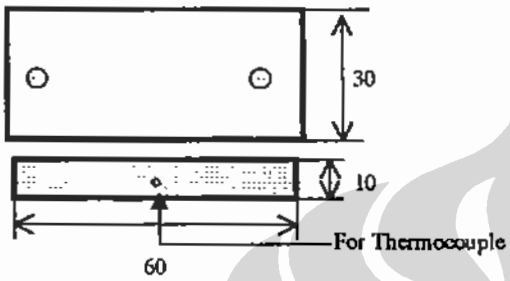

Figure 5. Illustrated the compressive test specimen in mm.

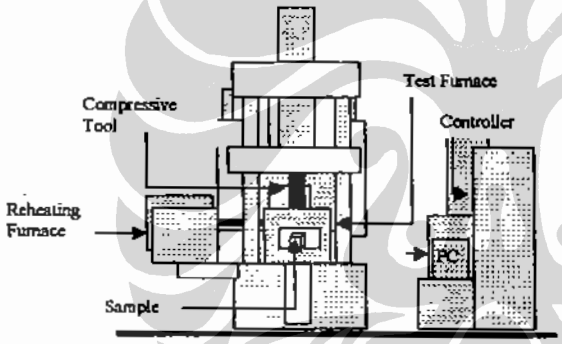

Figure 6. Illustrated Servotest machine

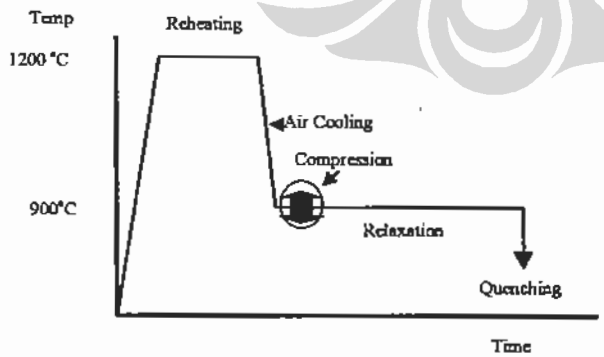

Figure 7. Thermal cycle applied to test steel.

Figure 8. Micrograph of reheated austenite grain structure for test steel reheated at 1200°C for 15 minutes then quenched.

Figure 9. Micrograph of elongated austenite grains for test steel after deformation to a strain of 0.5 at 900°C.

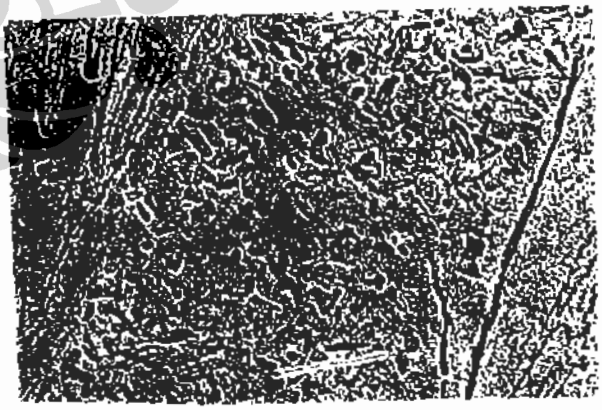

Figure 10. TEM Micrographs from an extraction replica showing no Nb(CN) particles in steel after quenching from 1200°C

Figure 11. TEM Micrographs from an extraction replica showing the presence of Nb(CN) particles in steel after deformation at 900°C and holding it for (A) 10 second (B) 100 seconds and (C) 200 seconds.

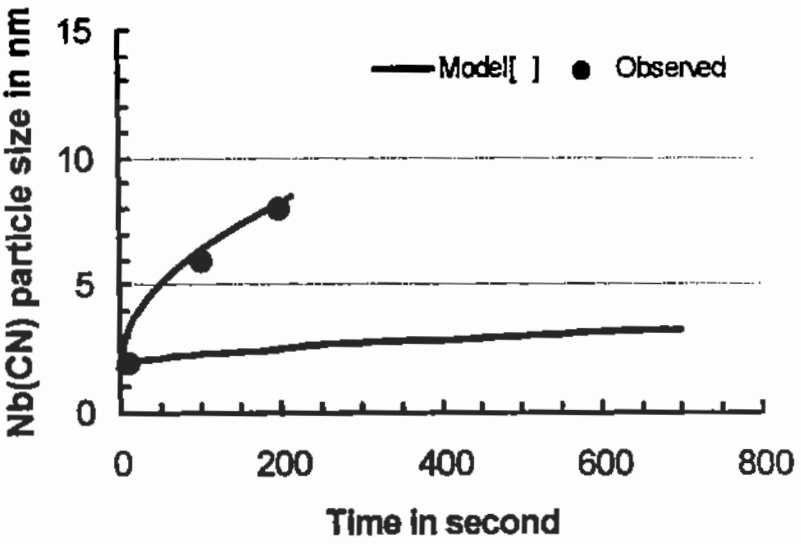

Figure 12. Comparison of particle growth of Nb[CN] observed and the model of a bulk diffusion process [2].