Effect of annealing process on the abnormal grain growth behavior during carburizing of 20CrMnTi steel

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Abstract
Abnormal grain growth (AGG) as an important physical metallurgical behavior is to be avoided during carburizing due to its adverse effect on properties such as fatigue, impact toughness and the quenching distortion. In this work, two types of annealing process which produce different morphology of precipitated particles were conducted to investigate its effect on the subsequent austenite grain growth behavior during carburizing of 20CrMnTi steel. Calculation from Humphreys’ model exhibited a good agreement with experimental observations, which indicates the large sized particle from high temperature annealing led to the locally insufficient pinning force for the blockage of grain boundary migration and is therefore responsible for the AGG. The isothermal precipitation kinetics for TiC particles is able to be described by the diffusional growth and LSW coarsening models with reasonable accuracy provided with the transition time from growth to coarsening stage. Design of microalloying and pre-treatment processing to suppress AGG can be assisted with the combinatory application of Humphrey’s model and precipitation kinetics model.

1. Introduction
Abnormal grain growth (AGG) leads to coarse grains which pose adverse effects on properties of manufactured parts such as fatigue, impact toughness and at the same time, increase the quenching distortion. Besides, currently in-use technological measures aimed at the inhibition of AGG give rise to the manufacturing cycle and costs. For example, normalizing or annealing subsequent to cold working is often required to prevent AGG during carburizing. High temperature carburizing, where the processing time can be shortened, is avoided because of the high grain coarsening tendency induced by AGG.

Considering its technological importance, AGG behavior and the counter measures in alloy chemistry and processing design have been investigated in large amount. The theoretical basis for most of the studies is the Gladman equation \[ r_{\text{crit}} = \frac{6Rf}{\pi} \left( \frac{3}{2} - \frac{2}{X} \right)^{-1} \]

where \( r_{\text{crit}} \) is the critical radius of precipitate particle, \( R \) is the average radius of matrix grain, \( f \) is the volume fraction the precipitates, and \( X \) is the size ratio defined as the radius of growing grain divided by \( \bar{R} \).

Using Gladman equation, Kubota and Ochi [2] developed anti-coarsening steels for carburizing with different levels of Al and Nb addition. The optimal alloy design is correlated with manufacturing process in such a way that small initial grain size, large degree of grain size mix and small pinning effect by second phase particles should be avoided. Tanaka et al [3] investigated the grain coarsening behavior of SCM420, ‘SCM420 + Nb’ and ‘SCM420 + Ti’ steel. Smaller particle size and larger volume fraction of TiC in ‘SCM420 + Ti’ steel facilitated the maintained fine grain size even at the simulated carburizing temperature of 1050 °C. Imanami et al [4] redesigned SCM420 steel which allows the removal of annealing prior to cold forging and normalizing before carburizing. The easy grain coarsening of cold forged parts during carburizing was suppressed by sufficient
2. Materials and methods

2.1. Materials and experiments

A commercial steel i.e. 20CrMnTi supplied in Φ38mm hot-rolled bar was employed in the present work. The chemical composition is shown in Table 1. Considering free N is fixed by Ti due to the formation of TiN, the remaining Ti content of 0.05 wt% was employed for thermodynamic calculation by using ThermoCalc with TCFe9 database. With the major elements including the C, Mn, Cr and Ti, the variation of equilibrium weight fraction of phases with respect to temperature was calculated and presented in figure 1.

Samples with a dimension of Φ38 mm × 12 mm was sliced from hot-rolled bar and heat treated following experimental procedure illustrated in figure 2. In order to dissolve the pre-existing TiC precipitates, the steel was first homogenized at 1200 °C for 2 h and water quenched. Then, two types of annealing treatment were carried out, i.e. holding at 650 °C for 1 or 3 h and holding at 1025 °C for 3 or 5 h subsequent to 1 h-holding at 650 °C. Correspondingly, they are designated as ①, ②, ③ and ④ sample, respectively. Finally, quasi-carburizing was conducted at 930 °C for 8 h. Heating rate for every stage of treatment was 2 °C−5 °C s⁻¹.

2.2. Microstructure characterization

Samples for optical metallography (LEICA-DMIRM) were prepared by conventional method, including grinding, polishing. Observation of prior austenite grain boundaries was made by etching with saturated aqueous solution of picric acid containing a wetting agent i.e. sodium dodecyl benzene sulfonate. And at least 1000 grains were counted for each sample to determine the distribution of prior austenite grain size. For TEM (TECNAI G2 20 F) analysis, 400 μm thick slices were cut from the samples followed by mechanical grinding to 50 μm. Next, twin-jet electrolytic thinning was carried out in a mixture of 9% perchloric acid and 91% absolute ethyl alcohol at 248 K and potential of 25 V. More than 150 precipitated particles per sample were collected for TEM. Samples for TEM were prepared by conventional method with twin-jet electrolytic thinning in a mixture of 4% perchloric acid and 96% absolute ethyl alcohol.

Table 1. Chemical composition of investigated steel (wt %).

| Element | C | Si | Mn | P | S | Cr | Ti | N |
|---------|---|----|----|---|---|----|----|---|
| wt %    | 0.18 | 0.28 | 0.93 | 0.010 | 0.007 | 1.12 | 0.065 | 0.0045 |

amount of refined NbC precipitates. Kubota et al [5] investigated the effect of spheroidizing annealing prior to cold forging on AGG and found the coarsening of precipitated particles during annealing was the reason for AGG. In a similar study by Tominaga et al [6], the austenite grain refinement at the initial stage of carburization was held to be responsible for AGG.

Despite the wide application, attentions should be paid to two aspects when using Gladman equation and other similar model for alloy or processing design. Firstly, the employed parameters in Gladman equation are time-dependent. Using parameters which characterize the precipitates and matrix prior to or at the initial stage of carburizing cannot accurately predict the subsequent possible AGG. For example, Okamoto et al [7] presented a classical example for the application of 'critical grain size' model regarding to specific morphology of secondary particle in terms of volume fraction and size. On the carburized surface, the distribution of TiC can be assumed to be unchanged and therefore, the model prediction agreed well with the measured grain size. On the other hand, the unstable smaller TiC precipitates dissolved into the matrix at the sample interior part, leading to the decreasing number density of TiC precipitates and ultimately the AGG. Secondly, AGG is essentially induced by the imbalance between driving force for grain growth and pinning force from precipitates. The usage of parameters, such as the average radius of precipitate particles and average diameter of matrix grains, cannot predict a local AGG behavior. For instance, Murakami et al [8] pre-formed 3 different size distributions of Nb(CN) particles and supplied for quasi-carburization. The one with the average particle size smaller than the critical particle size calculated by Gladman equation, however, also led to the AGG. It was concluded that the fast decrease in number density of Nb(CN) particle brought about the locally insufficient pinning force. Recently, Imanami et al [9] revealed that spheroidized cementite particles which exhibit different dissolution kinetics owing to the varied Cr content and particle size result in the local and non-uniform decrease in pinning force and thus the AGG.

In this work, two types of precipitation morphology as represented by volume fraction and size were obtained in 20CrMnTi steel by isothermal annealing at 650 °C alone or further annealing at 1025 °C. Subsequent quasi-carburizing experiments were carried out to investigate the austenite grain growth behavior. The Humphreys' model for AGG and the diffusional growth and LSW coarsening models for precipitated TiC particles were used to interpret the experimental results.
the substantial low particle density. Measurements for prior austenite size and precipitated particles were both done by using Image-Pro Plus software.

2.3. Modeling calculation
Modeling efforts were made to interpret the results obtained from experimental studies. The Humphrey’s model for AGG and the growth and coarsening model for TiC particles employed in this work are described as follows.

(1) Humphrey’s model for AGG [10]

Considering the pinning pressure $P_z = 3f\gamma/d$ exerted by a volume fraction ($f$) of particles with diameter ($d$), the growth rate of the grain assembly $dR/dt$ and a particular grain $dR/dt$ is determined as

$$\frac{dR}{dt} = \ddot{M} \frac{1}{4R} - \frac{3f}{d}$$

(2)

$$\frac{dR}{dt} = M \left( \frac{\gamma}{R} - \frac{\gamma}{R} - \frac{3f}{d} \right)$$

(3)

where $\ddot{M}$, $\gamma$ and $M$ are the boundary energy and mobility for grain assembly and a particular grain, respectively. Then, the condition for AGG of a particular grain is given as

$$RM\left( \frac{\gamma}{R} - \frac{\gamma}{R} - \frac{\varphi \gamma}{R} \right) - RM\frac{1}{4} - \varphi > 0$$

(4)

where $\varphi$ is the dimensionless pinning parameter which equals $3f\gamma/d$. Using the size ratio $X$ i.e. $R/\ddot{R}$ and other two normalized parameters $Q = M/\ddot{M}$, $G = \gamma/\ddot{\gamma}$, the instability condition becomes
3. Results and discussion

Microstructure of prior austenite grains after quasi-carburizing and the corresponding distribution of grain size is shown in figures 3 and 4, respectively. It is suggested that the distribution similar to lognormal type is seen from both sample © and ®. While, some extremely large prior austenite grains with size ≥ 75 μm can be found in sample © and ® which are delineated by red lines in figures 3(c), (d), and their number fraction is over 10%.

Table 2. Physical parameters [14] involved in calculation of growth and coarsening kinetics.

| Parameters | Expression or value |
|------------|---------------------|
| $V_m$ (m$^3$ mol$^{-1}$) | $0.712 \times 10^{-5}$ |
| $V_{TiC}$ (m$^3$ mol$^{-1}$) | $1.243 \times 10^{-5}$ |
| $\sigma_{TiC}$ (J m$^{-2}$) | $1.069-0.355 \times 10^{-3}T$ |
| $D_{Ti}$ (m$^2$ s$^{-1}$) | $3.15 \times 10^{-14} \exp(-248000/RT)$ |
| $\log([Ti][C])_{eq}$ | 4.4-9575/T |
| $R$ (J/K mol) | 8.314 |

$^1$[Ti] and [C] is the weight percent of Ti and C, respectively.

\[
Y = (4\varphi - 1)X^2 + 4Q(1 - G\varphi)X - 4QG > 0
\]  

(5)

Then the bounds for normal/abnormal grain growth are defined by two roots

\[
X = \frac{2Q(G\varphi - 1)}{4\varphi - 1} \pm \sqrt{\left(\frac{Q - QG\varphi}{4 \varphi - 1}\right)^2 + \left(4\varphi - 1\right)QG^2/2}
\]  

(6)

Equation (6) can be simplified by considering an ideal grain assembly where all boundary energies and mobilities are equal i.e. $\gamma = \bar{\gamma}$, $M = \bar{M}$. Then, the effect of precipitated particles on austenite grain growth behavior can be formulated as follows.

- For $\varphi < 0.25$, the two roots from equation (6) corresponds to the minimum size ratio for the initiation of AGG and the maximum size ratio to which the grains may eventually grow, respectively.
- For $0.25 < \varphi < 1$, because $dR/dt$ is always zero, AGG will always occur provided that $dR/dt$ is positive.
- For $\varphi > 1$, the growth of even the largest abnormally growing grain becomes impossible as indicated by equation (3).

1. Diffusional growth and LSW coarsening model for TiC particles

According to diffusional growth theory, the evolution of average diameter $d$ of TiC particles with time $t$ follows the parabolic law [11, 12], i.e.

\[
\begin{align*}
\frac{d}{dt} &= k\sqrt{Dt} \\
&= \left(\frac{2X_{Ti}^{eq} - X_{eq}^{Ti}}{X_{eq}^{Ti}}\right)^{1.2} \\
k &= 2\left(\frac{2X_{Ti}^{eq} - X_{eq}^{Ti}}{X_{eq}^{Ti}}\right)^{1.2}
\end{align*}
\]  

(7)

where $X_{Ti}^{eq}$ is the mole fraction of pre-dissolved Ti at solution temperature; $X_{eq}^{Ti}$ is the equilibrium mole fraction of Ti in matrix that can be calculated from solubility product; $X_{eq}^{TiC}$ is mole fraction of Ti in TiC particle which equals 0.5.

For the coarsening of TiC particles, based on LSW (Lifshitz-Slyozov-Wagner) theory [13], the average size $d_i$ after isothermal holding time $t$ is

\[
d_i^3 = d_0^3 + \frac{64\sigma V_{TiC}^2DX_{eq}^{Ti}}{9V_mRT}t = d_0^3 + m^3t
\]  

(8)

where $d_0$ is the original average size of TiC particle; $V_{TiC}$ and $V_m$ is the molar volume of TiC and matrix, respectively; $\sigma$ is the interface energy of TiC with matrix. For simplicity, $V_m$ can be substituted by the molar volume of BCC Fe. R and T have their usual meaning. It should be mentioned that since the molar volume varies negligibly with temperature, the known molar volume of TiC at 1100 °C are employed in the present calculation as a first approximation. Physical parameters involved in calculation were listed in table 2.
indicating an apparent AGG behavior. The resultant size ratio is calculated to be 2.8, 3, 14.9 and 12.7 for sample ①, ②, ③ and ④, respectively.

In order to find the cause for AGG behavior in sample ③ and ④, TEM analysis was conducted to reveal the morphology of precipitated particles after annealing. In samples ① and ② (see figure 5), both small sized (<15 nm) and large sized particles (>30 nm) are observed. Figures 5(c) and (d) shows the bright-field and dark-field image of the large sized particles in sample ②, respectively. Corresponding selected area diffraction pattern in inset of figure 5(d) indicates that the large sized particles are cementite. The M₇C₃ carbide, which was calculated to be the equilibrium constituent phase at 650 °C in figure 1, is not present. Figure 6 shows the TEM micrographs for sample ③ and ④. As identified by EDS, the precipitated particles in figure 6(b) are TiC i.e. the only second phase at 1025 °C according to figure 1.
Figure 7 shows the statistics on the size of precipitated particles, where the particle with size larger than 30 nm was excluded in sample ① and ②. Lognormal distribution for sample ① and ② can also be seen. However, due to the limited number of particles as revealed by TEM, no characteristics can be found in the size distribution of sample ③ and ④. The average size of precipitated particles for sample ①, ②, ③ and ④ is 6.1, 8.6, 45.7 and 60.2 nm, respectively.

Considering the successful application of Humphreys’ model in describing the AGG behavior in aluminum alloys [15–19], it was also used in this work to quantify the effect of annealing, in other words, precipitated particles on austenite grain growth behavior at the beginning of quasi-carburizing. In addition to the above known parameters, the size ratio at the time when AGG takes place is to be determined. As a first approximation, by excluding the abnormally grown ones, the austenite grain assembly in figure 3 was employed to calculate the size ratio, which is 2.8, 3, 2.86 and 2.9 for sample ①, ②, ③ and ④ respectively. Figure 8 presents the calculation results in the classical size ratio versus pinning parameter diagram. Sample ① and ② locate in the ’no grain growth region’, while sample ③ and ④ enter into the ’AGG region’. A fairly good agreement has been obtained between the calculation by Humphreys’ model and experimental observations.

As suggested in figure 8, pinning parameter is more critical in determining the austenite grain growth behavior. If one can accurately predict the evolution of diameter and volume fraction of precipitated particles, and therefore the pinning parameter, the design of microalloying and pre-treatment processing to suppress the AGG can be assisted. Therefore, efforts have been made to fit the measured size of TiC particles with the simple and straightforward mean-field diffusional growth and LSW coarsening models.

In figures 5(a), (b), it can be noticed that the number density of precipitated TiC particles decreased when annealing time at 650°C extended from 1 h to 3 h. Therefore, besides the physical parameters listed in table 2, the transition time from growth to coarsening i.e. $t_{tr}$, which was defined as the time when the mean diameter and the critical nucleus diameter become equal [20], is also required and set as the only fitting parameter in this work. In figure 9, as presented by the red curve, a reasonable good agreement between the model calculation and experimental results was achieved when $t_{tr} = 0.5$ h. In comparison, the black curve suggests an overestimation when continuous growth of precipitated TiC particles is assumed i.e. $t_{tr} > 3$ h. Further studies are required to incorporate the nucleation model and then facilitate the calculation of $t_{tr}$.

Following the 1 h annealing at 650 °C, annealing at 1025 °C would result in an overall dissolution of precipitated TiC particles due to the increased solubility of Ti and C. However, complex evolution of average size of precipitated particles during dissolution has been observed by researchers. Lee et al [21] studied the dissolution behavior of NbC during simulated slab reheating process and found the particle coarsening
phenomenon at relatively low heating rate of 0.0013 °C/s. Similar to present annealing treatment, Jones and Ralph [22] investigated the dissolution of NbC in an austenitic stainless steel by annealing at 1100 °C–1300 °C subsequent to isothermal precipitation of NbC at 930 °C. Incomplete solution treatment annealing i.e. at temperatures below solvus resulted in an initial sharp increase of average size of precipitated NbC particles from <10 nm to 70–100 nm. More recently, Gong et al [23] also confirmed the initial coarsening phenomenon during dissolution in Nb steel and even revealed a continuous coarsening behavior in Nb-Ti steel as a result of stabilizing effect from Ti. Apparently, the simple growth and coarsening models would not be able to capture
this complex size evolution of precipitated particles. Besides, the two-step annealing in this work was only
designed for the investigation of AGG and is not a common practice in carburizing heat treatment, the
prediction of size evolution of precipitated TiC particles therein will be left for further investigation.

4. Conclusions

(1) Annealing at 650 °C created finely dispersed TiC which effectively pinned the migration of austenite grain
boundary, while the sparse and large sized TiC for further annealing at 1025 °C led to the abnormal
austenite grain growth.

(2) Humphreys’ model which describes the austenite grain growth behavior agrees well with the experimental
observations, i.e. annealing at 650 °C and further at 1025 °C respectively corresponds to the no growth
region and AGG region.
(3) Provided with the transition time from growth to coarsening stage, the evolution of average size of precipitated TiC particles during annealing at 650 °C can be described by the diffusional growth and LSW coarsening models with reasonable accuracy.

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References

[1] Gladman T 1966 On the theory of the effect of precipitate particles on grain growth in metals Proc. R. Soc. Lond. A: Math. Phy. Sci. 294 298–309
[2] Kubota M and Ochi T 2007 Development of anti-coarsening steel for carburizing Mater. Sci. Forum 539-543 4855–60
[3] Tanaka T, Fujimatsu T, Hashimoto K and Hiraoka K 2006 Austenite grain stability of titanium-modified carburizing steel Solid State Phenom. 118 3–8
[4] Imanami Y, Tomita K and Nishimura K 2018 Development of carburizing steel for innovation in parts manufacturing Process JFE Tech. Rep. 23 36–42
[5] Kubota M and Ochi T 2003 Development of anti-coarsening extra-fine steel for carburizing Shinnittetsu Gihō 378 72–6
[6] Tominaga T, Chiba K and Sato N 1995 Influence of heat treatment on grain coarsening of austenite in cold worked steels Sanyo Tech. Rep. 2 28
[7] Okamoto N, Shindo Y and Nagahama M 2011 Influence of Ti precipitation in carburizing steel containing boron Kobe Steel Eng. Rep. 61 66–9
[8] Murakami T, Hatano H, Shindo Y and Nagahama M 2007 The effects of Nb carbo-nitride precipitation conditions on abnormal grain growth in Nb added steels Mater. Sci. Forum 539-543 4167–72
[9] Imanami Y, Yamashita T, Tomita K and Hase K 2017 Effect of annealing before cold forging on the behavior of abnormal grain growth during carburizing ISIJ Inter. 57 2220–8
[10] Humphreys F J and Hatherly M Recrystallization and Related Annealing Phenomenon (Second Edition) (London: Pergamon Publishing Ltd) 333–78
[11] Bhadeshia H K D H 2003 Advances in the kinetic theory of carbide precipitation Mater. Sci. Forum 426-432 35–42
[12] Wang Z Q, Mao X P, Yang Z G, Sun X J, Yong Q L, Li Z D and Weng Y Q 2011 Strain-induced precipitation in a Ti micro-alloyed HSLA steel Mater. Sci. Eng. A 529 459–67
[13] Jang J H, Lee C H, Han H N, Bhadeshia H K D H and Suh D W 2014 Modelling coarsening behavior of TiC precipitates in high strength, low alloy steels Mater. Sci. Technol. 29 1074–9
[14] Yong Q L 2006 Secondary Phases in Steels (Beijing: Metallurgical Industry Press)
[15] Jana S, Mishra R S, Baumann J A and Grant G 2010 Effect of process parameters on abnormal grain growth during friction stir processing of a cast Al alloy Mater. Sci. Eng. A 528 189–99
[16] Ferry M, Hamilton N E and Humphreys F J 2005 Continuous and discontinuous grain coarsening in a fine-grained particle-containing Al-Sc alloy Acta Mater. 53 1097–109
[17] Hassan K A A, Norman A F, Price D A and Prangnell P B 2003 Stability of nugget zone grain structures in high strength Al-alloy friction stir welds during solution treatment Acta Mater. 51 1923–36
[18] Charit I and Mishra R S 2005 Low temperature superplasticity in a friction-stir-processed ultrafine grained Al–Zn– Mg–Sc alloy Acta Mater. 53 4211–23
[19] Chen K, Gan W, Okamoto K, Chung K and Wagoner R H 2011 The mechanism of grain coarsening in friction-stir welded AA5083 after heat treatment Metall. Trans. A 42 488–507
[20] Dutta B, Palmiere E J and Sellars C M 2001 Modelling the kinetics of strain induced precipitation in Nb microalloyed steels Acta Mater. 49 785–94
[21] Lee H, Park K S, Lee J H, Heo Y U, Suh D W and Bhadeshia H K D H 2014 Dissolution behavior of NbC during slab reheating ISIJ Int. 54 1677–81
[22] Jones A R and Ralph B 1977 Growth and dissolution of NbC particles in an austenitic stainless steel Metallography 10 469–80
[23] Gong P, Palmiere E J and Rainforth W M 2015 Dissolution and precipitation behavior in steels microalloyed with niobium during thermomechanical processing Acta Mater. 97 392–403