Surface Defects on Semicoherent and Incoherent NaCl-Type Carbides Dispersed in Hot-Rolled Ferritic Steel

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The interface structure of semicoherent titanium carbide (TiC) nanoparticles and incoherent micron-sized TiC precipitates in Fe–C–Ti alloy hot-rolled steel sheets was studied by transmission electron microscopy (TEM) and positron annihilation spectrometry (PAS). The TiC nanoparticles were formed by interphase precipitation during the γ-to-α transformation, and the coarse micron-sized TiC precipitates remained in the matrix as undissolved carbides in the slab reheating process before hot rolling. The semicoherent TiC nanoparticles have coherent planes with the Baker–Nutting orientation relationship and incoherent surface almost parallel to {001}α planes. The present investigation revealed that positrons are not annihilated inside TiC particles but rather are trapped at open volume misfit defects located at the incoherent interface between TiC particles and the matrix. The positron lifetime related to misfit defects associated with the semicoherent TiC nanoparticles and incoherent micron-sized TiC precipitates was around 240 ps and 500 ps, respectively. Considering the results of TEM observations and the theoretical positron lifetime, it can be concluded that the positron annihilation site related to TiC nanoparticles is located at the incoherent interface and consists of some vacancies.

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I. INTRODUCTION

PRECIPITATION hardenable steels have been utilized commercially for decades[1] because they can be efficiently strengthened by addition of small concentrations of suitable alloying elements.[2] Carbide particles dispersed in steel are basically designed to be as small as possible because the magnitude of precipitation hardening increases with decreasing size and increasing density of the carbide particles based on the Ashby–Orwian relationship.[3] Nano-sized and NaCl-structure carbides such as TiC, NbC and VC precipitate in the ferrite matrix with the Baker–Nutting orientation relationship[4,5] so that the carbides maintain the minimum surface energy by forming a coherent interface with the matrix.

The coherency of the interface between a carbide particle and the matrix can affect the toughness[6,7] and hydrogen embrittlement of steel. In particular, atom probe tomography has confirmed that NaCl carbides such as TiC,[8] and NbC[9] act as hydrogen trapping sites. However, different hydrogen trapping energies of NaCl carbides have been reported, for instance, about 90 kJ/mol for TiC,[10,11] about 82 kJ/mol for NbC[12] and about 60 kJ/mol for V4C3.[13] Moreover, the hydrogen trapping energy of an incoherent interface is well known to be larger than that of a semicoherent interface,[14,15] and it has also been reported that the highest hydrogen trapping capacity per unit surface area was achieved with a thin plate-shaped carbide with a length of 10 nm,[16] which suggests that hydrogen trapping efficiency is size dependent. Therefore, it is important to evaluate the structure of the interface between carbide particles and the matrix in order to elucidate the hydrogen trapping efficiency of carbide particles and discover the ideal interface structure for maximizing hydrogen trapping efficiency. The problem is that it is almost impossible to quantify the size of open volume defects on the interface related to hydrogen trapping efficiency from previous research showing several models of the carbide–matrix interface based on observation by transmission electron microscopy (TEM)[17,18] or the lattice position and orientation relationship.[19-21]

In the present paper, the term ‘coherent interface’ means an interface between precipitate and matrix which does not show any discontinuous change of inter-atomic distance between the precipitate and the
matrix. Slightly different inter-atomic distances in the precipitate and the matrix are compensated purely by elastic distortion of the precipitate and surrounding matrix. A ‘semi-coherent interface’ retains coherency with the matrix locally and accumulated misfit of inter-atomic distances is released by periodic introduction of misfit dislocations. Finally an ‘incoherent interface’ does not retain coherency with the matrix at all and there is a discontinuous step in the inter-atomic distance in the whole interface.

However, positron annihilation spectroscopy (PAS)\cite{22,23} enables direct detection of open volume defects such as vacancies, vacancy clusters and dislocations in metals, and therefore was used in the present work to gain further insight into the coherency and structure of carbide-matrix interfaces in steels. In this study, several steels containing different volumes or sizes of TiC carbides were investigated by PAS combined with TEM in order to clarify the effect of the coherency of the carbide particles on the physical properties of the steels and obtain information concerning the structure of the carbide-matrix interfaces.

II. EXPERIMENTAL PROCEDURE

Hot-rolled ferritic steels containing TiC particles were used in this study. The chemical compositions of the steels and the notation of the samples are shown in Table I. The Ti content in the samples was gradually increased from 0.09 to 0.40 wt pct, and the atomic concentration ratio of C to Ti was kept at approximately 1:1 to avoid formation of coarse cementite particles. The size of the interphase precipitates investigated in this study is known to change depending on the γ-to-α transformation temperature.\cite{24} The interface structure of the interphase precipitates may also change depending on its size, considering the size dependence of the hydrogen trapping efficiency of carbides. Hence, the Mn content was set at 2.4 pct to lower the γ-to-α transformation sufficiently.

The samples were vacuum-melted and cast into 50 kg ingots, and were then rough-rolled into 33 mm thick bars. Slabs with a width of 105 mm, length of 120 mm and thickness of 27 mm were cut from rough-rolled bars and subjected to slab reheating at 1250 °C for 1 h, as shown in Figure 2. After reheating, the slabs were hot-rolled to sheets with a thickness of 3 mm in 9 passes (roll-gap: 18.0 mm, 14.0 mm, 10.2 mm, 8.2 mm, 6.8 mm, 4.4 mm, 3.3 mm, 2.5 mm, and 2.0 mm), and the finishing temperature was controlled to around 900 °C. The hot-rolled sheets were immediately water-cooled to a temperature of (620 ± 30) °C. Subsequently, the sheets were held at 620 °C for 15 min to complete the γ-to-α transformation, followed by air-cooling to room temperature.

It is possible to distinguish two kinds of TiC particles in the samples studied: (i) Coarse incoherent TiC precipitates that are formed during slab reheating at 1 250 °C when the Ti concentration is higher than 0.24 wt pct Ti, which is the maximum TiC solubility\cite{25} at this temperature (Figure 1), and (ii) coherent TiC nanoparticles that are formed after hot rolling when the sample is held at 620 °C, as shown in the processing diagram in Figure 2. In the samples containing 0.09, 0.17 and 0.23 wt pct Ti (denoted 0.09Ti, 0.17Ti and 0.23Ti samples, see Table I), coarse TiC particles were not formed in the course of the steel making process since the Ti content was below the Ti solubility limit in the Fe matrix. However, because the 0.40Ti sample contains 0.40 wt pct Ti, which is above the Ti solubility limit in the matrix at the slab reheating temperature of 1250 °C, coarse TiC particles were formed in this sample during slab reheating before hot rolling. Slabs in 105 mm width, 120 mm length and 27 mm thickness for hot-rolling were cut out from rough-rolled bars, and hot-rolled to 3.6 mm thickness. Finishing temperature was controlled around 900 °C.

In this study, TiC powder (provided by Goodfellow) with purity of 99.8 pct and a particle size in the range of 50 to 150 μm was also investigated in order to examine positron annihilation inside the TiC phase. The TiC powder was annealed at 650 °C for 2 h in an Ar atmosphere, then cooled slowly to room temperature in the furnace.

JIS 5 type plate specimens (gauge length: 50 mm, gauge width: 25 mm) for the tensile test were cut out from the hot-rolled sheets so that the tensile direction was parallel to the hot rolling direction, and ground to a thickness of 2 mm to remove the oxidized surface layer. The tensile tests were carried out at room temperature with a cross head speed of 10 mm/min.

Sections parallel to the rolling direction were etched using a 1 pct nital solution and observed by scanning electron microscopy (SEM) using a JEOL JSM-6010LA with an accelerating voltage of 15 kV. Tens of horizontal and vertical lines having a real length of 35 μm were drawn on the SEM photographs, and the points at the intersection of these lines and the ferrite grain boundaries were counted. The mean lineal intercept length was calculated based on the average of each intercept length and the mean ferrite grain diameter as prescribed by ASTM\cite{26}.

The specimens for TEM observation were ground to a thickness of 0.3 mm and prepared by the twin jet electropolishing method. TEM micrographs were obtained using a JEOL JEM-2100F with an accelerating voltage of 200 kV and an incident direction of the electron beam normal to the (001) plane.

The mean dislocation density was evaluated by the X-ray diffraction (XRD) method using a Cu X-ray source (wavelength $\lambda = 0.1789$ nm). The full width at the half maximum (FWHM, $\beta$) values of 110, 211 and 220 reflections were measured, and the mean dislocation density ($\rho$) was estimated by Hall-Williamson’s method using the following relationship\cite{27}.

$$\rho = \frac{14.4}{2h^2} \left( \frac{\sum_{i=1}^{3} (\sin \theta_i - \sin \theta)(\beta \cos \theta_i - \beta \cos \theta)}{\sum_{i=1}^{3} (\sin \theta_i - \sin \theta)^2} \right)^2$$

where, $b$ is the Burgers vector (0.248 nm).
The concentration of TiC particles in the hot-rolled steels was obtained by electrolytic dissolution of the samples in a 10 pct acetyl acetone-tetramethyl ammonium chloride-methanol (10 pct AA) solution. Since the solid solution state of Ti in the ferrite matrix is dissolved in the 10 pct AA solution while carbides are adsorbed on the electrodes, the solid state Ti concentration of steels [pct Ti as solid solution] can be determined by analyzing the Ti concentration in the electrolytic solution by inductively coupled plasma ion mass spectrometry (ICP-MS). The concentration of Ti precipitated in TiC particles [pct Ti\textsuperscript{*}] is given by Eq. [2].

\[
\frac{\text{pct Ti}}{\text{C}}^{3/2} = \frac{\text{pct Ti in bulk}}{\text{C}}^{3/2} \cdot \frac{1}{\text{C}}^{4/3} = \frac{32}{\text{pct S}}^{3/2} \cdot \frac{1}{\text{C}}^{4/3}
\]

where, [pct S] and [pct N] denote the amounts of Ti consumed as nitride (TiN) and sulfide (TiS), and the quantities of TiN and TiS were calculated from the total amounts of S and N in the matrix shown in Table I assuming a stoichiometric composition of TiN and TiS. Because the amounts of S and N in the samples were very low, the influence of TiS and TiN on the estimated concentration of TiC was not significant, as the ratios of the amount of TiS and TiN to the amount of Ti as precipitated were no more than 12 pct.

A 22Na radioisotope with activity of about 1 MBq deposited on a Kapton foil with a thickness of 7.0 \( \mu \)m was used as positron source for positron lifetime spectroscopy (PALS) and coincidence Doppler broadening spectroscopy (CDBS) measurements. The positron source was always sandwiched between two pieces of the specimen. A digital spectrometer\[30\] with time resolution of 145 ps (FWHM of the resolution function) was employed for the PALS measurements. At least \( 10^7 \) positron annihilation events were collected in each positron lifetime spectrum. Decomposition of the positron lifetime spectra into exponential components was performed using the PLRF code.\[31\] The source contribution consisting of a component with a lifetime of \( \approx 380 \) ps and intensity of \( \approx 20 \) pct and a very weak contribution of ortho-positronium pick-off annihilation with a lifetime of \( \approx 1.5 \) ns and intensity of \( \approx 0.2 \) pct were always subtracted from the positron lifetime spectra. Decomposition of the PALS spectra was performed in the frame of the simple trapping model (STM),\[31\] i.e., lifetimes \( \tau_i \) and intensities \( I_i \) of exponential components were constrained so that

\[
\tau_B = \left( \sum_{i=1}^{N} \frac{I_i}{\tau_i} \right)^{-1}
\]

where, \( N \) is the number of exponential components and \( \tau_B \) is the bulk positron lifetime (for ferritic steel, \( \tau_B \approx 108 \) ps).\[32\] It should be noted that the PALS spectra of all the samples studied in the present work can be described satisfactorily within the frame of STM.

The CDBS measurements were carried out using a digital spectrometer\[33\] equipped with two high-purity germanium detectors with an energy resolution of 0.9 keV (FWHM) at the energy of 511 keV and a peak-to-background ratio higher than 10\(^5\). At least \( 10^8 \) coincidence events were accumulated in each CDBS

| Steel  | C       | Si | Mn | P     | S | Al | N | Ti |
|--------|---------|----|----|-------|---|----|---|----|
| 0.09Ti | 0.026   | 0.01| 2.44| < 0.002 | 0.0006 | 0.032 | 0.0016 | 0.09 | 0.0022 | 0.0019 |
| 0.17Ti | 0.038   | 0.01| 2.37| < 0.002 | 0.0010 | 0.035 | 0.0046 | 0.17 | 0.0032 | 0.0035 |
| 0.23Ti | 0.062   | < 0.01| 2.45| < 0.002 | 0.0012 | 0.037 | 0.0010 | 0.33 | 0.0071 | 0.0069 |
| 0.33Ti | 0.085   | < 0.01| 2.45| < 0.002 | 0.0012 | 0.036 | 0.0013 | 0.40 | 0.0087 | 0.0083 |
| 0.40Ti | 0.104   | 0.01| 2.45| < 0.002 | 0.0012 | 0.036 | 0.0013 | 0.40 | 0.0087 | 0.0083 |
spectrum. Two-dimensional CDBS spectra were reduced into one-dimensional cuts representing the resolution function of the spectrometer and the Doppler-broadened annihilation peak. The results of the CDB measurements are presented as ratio curves with respect to a well-annealed reference.

III. RESULTS

A. Microstructures of Hot-Rolled Samples

The secondary electron micrographs of the hot-rolled samples are shown in Figure 3. Samples with Ti contents lower than 0.23 wt pct exhibited a fully ferritic microstructure. The mean grain sizes determined by the line-intercept method are listed in Table II. From inspection of the table, it can be concluded that the sizes of the ferrite grains do not change significantly with the Ti content. In contrast, many inclusions were observed in the 0.40Ti sample, as shown in Figure 3(d). The back-scattered electron micrographs of the 0.23Ti and 0.40Ti samples are compared in Figure 4. The black particles in Figure 4(b) are inclusions; here, ten inclusions were analyzed by SEM–EDS as shown Figure 4(c), and all were found to be TiC. Au peak in Figure 4(c) is attributed to the evaporated Au film deposited on the SEM sample to prevent charging. Because the coarse TiC particles in the 0.40Ti sample have a spherical shape and a diameter of a few microns, they are considered to be incoherent with the ferrite matrix. In contrast to the 0.40Ti sample, the 0.23Ti sample contained few inclusions, and those inclusions were expected to be alumina or TiN considering the chemical composition shown in Table I. Thus, in the samples with Ti content ≤ 0.23 wt pct, it can be asserted that almost all coarse TiC particles that formed in the steel-making process were dissolved in the slab reheating process at 1 250 °C (Figure 4(a)).

Figure 5 shows TEM micrographs of the 0.09Ti and 0.23Ti samples, and diffraction pattern in the 0.23Ti sample. The upper and lower panels are bright field and dark field images, respectively. TiC nanoparticles arranged in rows were observed in both samples. Arrangement into rows is a specific feature of interphase precipitates. The TiC nanoparticles have a very narrow size distribution, and their mean size is similar to that of the 0.09Ti and 0.23Ti samples because the size of the interphase precipitates is determined by the γ-to-α transformation temperature, which was 620 °C in this study.

Figure 5(c) suggests that two sets of orientation relationships exist: The (001)_{TiC} plane satisfies the Baker–Nutting orientation relationship with the matrix, while the (111)_{TiC} plane is oriented substantially along with the (011)_{γ} plane. The spots that appeared nearly on (001)_{γ} seemed to be due to the formation of iron oxide although the possibility of double diffraction cannot be ruled out. The lattice coefficient of TiC obtained from Figure 5(c) was 0.431 nm, which is almost identical to the reported value of 0.433 nm, but the C/Ti ratio in the TiC particles may be around 0.6.[39] The period of the coincidence between (001)_{TiC} and (001)_{γ} is 4.22 nm. The TiC nanoparticles in this study are considered to have a misfit dislocation with the Burgers vector of [010]_{γ} or no misfit dislocation on (001)_{γ}. The (001)_{TiC} plane satisfying the Baker–Nutting orientation relationship was regarded as a semi-coherent surface in this study. On the other hand, a misfit dislocation with Burgers vector of [100]_{γ} on (011)_{γ} occurs every 0.86 nm.[39] A (111)_{NbC} plane dispersed in α-Fe was observed to have the Kurdjumov–Sachs orientation relationship and to have two sets of Burgers vectors of [111] on (011)_{γ} and [111] on (110)_{γ}. In addition, (111)_{TiC} was considered to be incoherent because the misfit dislocations are extremely crowded.[17]

Table II shows the mean dislocation density estimated by XRD, the amount of precipitated Ti determined by the electrolytic solution method and the yield strength obtained by the tensile test. The amount of precipitated Ti increases monotonically with increasing Ti content, and the yield strength also increases due to strengthening effect of the semicoherent TiC nanoparticles. However, the yield strength of the 0.40Ti sample is almost the same as that of the 0.23Ti sample in spite of its significantly higher Ti content. This is because the chemical composition of the 0.23Ti sample is already close to the saturated solubility of Ti in the matrix at the slab reheating temperature. Consequently, the amount of nanometer-sized carbides in the 0.23Ti sample is almost identical with that in 0.40Ti sample. Here, it must be mentioned that coarse TiC precipitates do not contribute to strengthening.

B. Results of PALS and CDBS Investigation

The results of the PALS measurements are shown in Figure 6. The lifetime of the exponential components resolved in the PALS spectra are plotted in Figure 6(a), while Figure 6(b) shows the development of the
Table II. Results of Characterization of Hot-Rolled Samples: Diameter of Ferrite Grains ($D_f$), Mean Dislocation Density Estimated by XRD ($\rho$), Amount of Precipitated Ti ($Ti^*$) and Yield Strength (YS)

| Samples  | $D_f$ (µm) | $\rho$ ($10^{14}$ m$^{-2}$) | $Ti^*$ (Mass Pct) | YS (MPa) | TS (MPa) | El (Pct) |
|----------|------------|-------------------------------|------------------|---------|---------|---------|
| 0.09Ti   | 7.6 ± 0.6  | 5.7 ± 1.2                     | 0.07             | 554     | 667     | 23.5    |
| 0.17Ti   | 9.0 ± 1.2  | 0.8 ± 4.0 x 10$^{-2}$         | 0.14             | 609 ± 10| 746 ± 1 | 21.5 ± 0.1|
| 0.23Ti   | 8.4 ± 1.0  | 2.0 ± 1.7                     | 0.19             | 690     | 828     | 19.4    |
| 0.40Ti   | 8.3 ± 1.7  | 0.9 ± 7.5 x 10$^{-4}$         | 0.38             | 698     | 829     | 16.9    |

Fig. 4—Back-scattered electron micrographs of (a) 0.23Ti and (b) 0.40Ti samples, and (c) SEM–EDS of 0.40Ti sample.

Fig. 5—TEM micrographs of (a) 0.09Ti and (b) 0.23Ti samples; bright and dark field images are shown in the upper and lower panels, respectively.

(c) Diffraction pattern in 0.23Ti steel
The intensities of these components. The PALS spectra of the 0.09Ti, 0.17Ti and 0.23Ti samples can be described accurately by three exponential components (except the source contribution). The shortest component with the lifetime $\tau_1$ originates from free positrons not trapped at defects, while the component with a lifetime of $\tau_2 \approx 150$ ps represents a contribution of positrons trapped at dislocations. The longer component with a lifetime of $\tau_3 \approx 240$ ps can be attributed to positrons trapped at larger point defects with an open volume comparable to a few vacancies. In the following, it will be shown that this component originates from positrons trapped at misfit defects located at interfaces between TiC nanoparticles and the matrix. In the case of the 0.40Ti sample, the PALS spectrum also contains a very weak long-lived component with a lifetime of $\tau_4 \approx 500$ ps, which originates from positrons trapped at large vacancy clusters. The latter component is present only in the sample containing coarse TiC precipitates and therefore can be attributed to positrons trapped at voids associated with interfaces of the incoherent coarse TiC precipitates. The relative intensity of this component is very low ($I_4$ = 1 pct) because the surface area of the micron-sized TiC precipitates is much smaller than that of the TiC nanoparticles.

Lifetimes $\tau_2$ and $\tau_3$ do not change with the Ti content, supporting the conclusion that the nature of the corresponding defects remains unchanged. The intensity $I_2$ increases slightly, indicating a moderate increase of the dislocation density. This is accompanied by a slight decrease of $I_3$, since dislocations and misfit defects are competitive trapping sites for positrons.

The mean dislocation density $\rho_D$ was calculated from the PALS data using STM:[31]

$$\rho_D = \frac{I_2}{v_D} \left( \frac{1}{\tau_1} - \frac{1}{\tau_2} \right)$$

where, $v_D = 0.6 \times 10^{-4}$ s$^{-1}$ m$^2$ is the specific positron trapping rate at dislocations in Fe. The mean dislocation densities determined using Eq. [4] are plotted in Figure 7, together with the values determined by XRD. From these results, it can be understood that the dislocation densities determined by PALS and XRD agree in the order of magnitude.

The concentration $c_m$ of vacancy-like misfit defects can also be calculated within STM.[31]

$$c_m = \frac{I_3}{v_m} \left( \frac{1}{\tau_1} - \frac{1}{\tau_3} \right)$$

In the equation shown above, $v_m$ denotes the specific positron trapping rate for misfit defects. From the comparison of the lifetime of $\tau_3 \approx 240$ ps with the results of theoretical calculations of the lifetimes of positrons trapped in vacancy clusters of various sizes in Fe, it can be concluded that the open volume of misfit defects is approximately comparable to 3.4 vacancies. Hence, the specific positron trapping rate $v_m$ can be approximated as $v_m \approx 3.4 v_v$, where $v_v \approx 10^{14}$ s$^{-1}$ is the specific positron trapping rate for monovacancies.[45] Figure 8 shows the development of the concentration of misfit defects related to the nanoparticles determined by Eq. [5] as a function of the Ti content. The misfit defect concentration of TiC nanoparticles remains...
approximately constant in the 0.09Ti, 0.17Ti and 0.23Ti samples and increases slightly in the 0.40Ti sample, while the amount of TiC nanoparticles increases up to 0.23 wt pct. The amount in the 0.23Ti sample is almost as large as that in the 0.40Ti sample since the amount of Ti precipitated [pct Ti*] increases monotonically with the Ti content and the yield strength of the 0.23Ti sample is almost identical with that of the 0.40Ti sample (Table II), suggesting that the misfit defect concentrations of the 0.09Ti and 0.40Ti samples are overestimated. A low magnification TEM micrograph of the 0.09Ti sample is shown in Figure 9. Many of the nanoparticles have pinned dislocations, so diffusion of positrons is affected by pipe diffusion on the dislocations. Therefore, the misfit defect concentrations in the 0.09Ti and 0.40Ti samples with an enhanced dislocation density can be relatively higher than the true density of nanoparticles because positrons are trapped by nanoparticles on dislocations more easily due to pipe diffusion.

The results of the CDBS measurements of the 0.09Ti and 0.40Ti samples are shown in Figure 10. Since there is almost no difference between the CDB curves of the 0.09Ti and 0.40Ti samples, the chemical environments of defects in these two samples is comparable. Note that the micron-sized TiC precipitates did not affect the CDB results significantly due to their low density, which was demonstrated by the weak intensity $I_4$ in Figure 10(b). The CDB ratio curve (related to the defect-free pure Fe reference) for a sample containing TiC particles can be in the high-momentum region ($p_L > 10 \times 10^{-3} m_e c$) expressed as

$$n(p_L) = X_T n_T(p_L) + X_C n_C(p_L) + 1 - X_{Ti} - X_C$$

where, $n_T (p_L)$ and $n_C (p_L)$ represent the ratio curves of pure Ti (a-Ti metal) and C (graphite), respectively. The quantities $X_T$, $X_C$ and $X_{Fe} = 1 - X_{Ti} - X_C$ denote the fractions of positrons annihilated in the vicinity of Ti, C and Fe ions, respectively.

Figure 10(b) shows the result of fitting the CDB ratio curves of the 0.09Ti and 0.40Ti samples using Eq. [6]. From this figure, it can be understood that the CDB ratio curves for 0.09Ti and 0.40Ti are described accurately by Eq. [6]. The fractions $X_i$ which result in the

![Fig. 8—Concentration of misfit defects estimated from PALS data.](image)

![Fig. 9—Low magnification TEM micrograph of 0.09Ti sample.](image)

![Fig. 10—Results of CDBS measurements of hot-rolled samples; (a) CDB ratio curves (ratio to pure Fe) for 0.09Ti and 0.40Ti samples and pure Ti and graphite references, (b) CDB ratio curves for 0.09Ti and 0.40Ti samples with results of fitting using Eq. [6]) with $X_{Ti} = X_C = 0.25$ and $X_{Fe} = 1 - X_{Ti} - X_C = 0.50$.](image)
best agreement of the model function with the experiment are \( X_{Ti} = X_C \approx 0.25 \). These fractions are much higher than the concentration of Ti (and also C) in the sample (Table II), indicating that positrons are preferentially annihilated in the vicinity of TiC particles.

IV. DISCUSSION

A. Annihilation Site Related to TiC in Hot-Rolled Steel

The CDBS results shown in Figure 10 give clear evidence of Ti and C enrichment at the positron annihilation sites in these samples. This indicates that positrons are trapped in misfit defects located at the interfaces between TiC particles and the matrix. Alternatively, positrons can also be annihilated in some defects located inside TiC particles. To examine this possibility, the positron lifetimes for a perfect TiC lattice (NaCl-type structure with lattice parameter \( a = 4.328 \text{ Å} \)) and various point defects in TiC were calculated, and the results are listed in Table III. Positrons in TiC can be trapped either in C or Ti monovacancies. The corresponding lifetimes are 140 and 180 ps, respectively, reflecting the fact that a C monovacancy has a lower open volume than a Ti monovacancy. A Ti + C divacancy is characterized by a longer lifetime of 196 ps.

Investigation of the annealed TiC powder sample revealed that it exhibits a single component spectrum with a positron lifetime of \((160 \pm 1) \text{ ps}\). This lifetime is significantly longer than the positron bulk lifetime of TiC (110 ps) and represents, therefore, the contribution of positrons trapped at open volume defects. Comparing the experimental lifetime of 160 ps with the results of theoretical calculations, it can be concluded that the annealed TiC powder most probably contains a mixture of C and Ti monovacancies. The CDB ratio curve (ratio to pure Al) of the TiC powder is plotted in Figure 11 and exhibits a dip and a peak at around \( 25 \times 10^{-3} \text{ m}\_e \) and \( 35 \times 10^{-3} \text{ m}_e \), respectively. When the dip and the peak are taken into account, the fitting of the CDB ratio curve showed the best agreement with the experiment with the fraction of \( X_{Ti} = X_C = 0.5 \). Therefore, the constituent of the open volume in the annealed TiC powder is almost the same concentration of C and Ti monovacancies. Note that the CDB ratio curve of the graphite sample differs from that for TiC at low momenta \((p_L < 10 \times 10^{-3} \text{ m}_e)\). This is due to the difference in the electron band structures of TiC, \( \alpha \)-Ti metal and graphite, which leads to different momentum distributions of positrons annihilated by low momentum valence electrons.

The positron lifetime of \( \tau_3 \approx 240 \text{ ps} \) observed in the hot-rolled steel is significantly longer than that measured in the TiC powder, confirming that the annihilation sites of positrons related to TiC nanoparticles in the hot-rolled steel are located at the interfaces between TiC nanoparticles and the Fe matrix.

Note that positron trapping at grain boundaries can be neglected since the samples consist of coarse grains. The mean grain size 7.6 to 9.0 \( \text{μm} \) (see Table II) is more than an order of magnitude higher than the positron diffusion length in Fe. In addition it should also be noted that previous PAS investigations\(^{[47]}\) of severely deformed steel did not revealed any component with the lifetime of \( \approx 240 \text{ ps} \). This indicates that the lifetime \( \tau_3 \approx 240 \text{ ps} \) is specific to the steel containing TiC nanoparticles.

| State                  | \( \tau \) (ps) | \( E_B \) (eV) |
|-----------------------|----------------|---------------|
| Bulk                  | 110            | —             |
| C Monovacancy         | 140            | 0.66          |
| Ti monovacancy        | 180            | 4.40          |
| Ti + C Divacancy      | 196            | 4.92          |

Table III. Calculated Positron Lifetimes \( \tau \) and Positron Binding Energies \( E_B \) for Various States in TiC

![Figure 11](image-url)
B. Interface Structure of TiC Nanoparticles

The TiC nanoparticles have coherent interfaces with the Fe matrix which satisfy the Baker–Nutting orientation relationship and incoherent interface oriented almost parallel to the (001)ₐ planes, as shown in Figure 5(c). The interface with the Baker-Nutting orientation relationship is considered to have a misfit dislocation or to be completely coherent, as mentioned above. At an interface satisfying the Baker-Nutting orientation relationship, the coherent plane is expected to contain monovacancies at most. However, the lifetime of positrons trapped in a Fe monovacancy is 175 ps, which is significantly shorter than the value of τ₃ ≈ 240 ps measured in the samples containing TiC particles. This indicates that the interface contains defects which are larger than monovacancies; that is, positrons are annihilated on the incoherent interface.

Ab-initio calculations were employed in order to identify the atomic configuration of defects located on the incoherent surface of the TiC nanoparticles that are responsible for the positron lifetime τ₃ ≈ 240 ps. Because it is known from TEM observations that TiC nanoparticles obey the Baker-Nutting orientation relationship with the matrix, various point defects located on the surface of a TiC nanoparticle with the Baker–Nutting orientation were considered in these calculations. The proper defect configuration must satisfy two conditions: (i) The lifetime of positrons trapped at such defects must be close to the 240 ps measured in the experiment, and (ii) the fraction of positrons annihilated in the vicinity of Fe must be close to 0.5 while the fraction of positrons annihilated in the vicinity of both Ti and C must be close to 0.25 as determined by CDBS. The calculated lifetimes of positrons trapped in various vacancies and vacancy clusters on the interface between the matrix and a TiC particle which satisfies the Baker-Nutting orientation relationship are plotted in Figure 12. Comparing the experimental lifetime of 240 ps with the calculated results, the open volume of misfit defects present in the sample seems to have an open volume comparable to that of a 4Fe + 2Ti + 2C vacancy cluster. Since vacancy clusters consisting of a smaller number of vacancies are characterized by a too short positron lifetime. Hence, it is clear from the calculations that the proper defect configuration must involve multiple Fe and Ti vacancies. Although there are some other configurations (e.g., 8Fe + 2Ti) which are characterized by similar positron lifetimes, only the 4Fe + 2Ti + 2C vacancy cluster satisfies the condition that the fraction of positrons annihilated in the vicinity of Fe is approximately 0.5 and the fraction of positrons annihilated in the vicinity of Ti and C is compatible with approximately 0.25. Figure 13 shows a schematic image of a 4Fe + 2Ti + 2C vacancy cluster on a TiC nanoparticle. Hence, a comparison of the experimental results with the theoretical modeling suggests that positrons are trapped at 4Fe + 2Ti + 2C vacancy clusters located on the incoherent surface of TiC nanoparticles. In this case, a positron trapped in a 4Fe + 2Ti + 2C vacancy cluster is annihilated with a probability of approximately 0.5 in the vicinity of Fe and 0.25 in the vicinity of Ti and C. Although this is in accordance with the CDBS results, further investigation is called for, for instance, high-resolution TEM observation of the carbide surface from various angles.

In conclusion, it is possible that the interface structure of industrially valuable TiC nanoparticles can be determined by PAS. However, hydrogen trapping efficiency is size dependent, as mentioned above, and it is likely that the shape and interface structure of NaCl nanoparticles would change by a precipitation mechanism such as interphase precipitation and aging precipitation, or the precipitation temperature. Therefore, all of TiC nanoparticles may not always have the interface structure examined in this study. Further research on the relationship between hydrogen trapping efficiency and the interface structure is expected to clarify the ideal interface structure of NaCl structure nanoparticles.

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Fig. 12—Calculated lifetimes of positrons trapped in monovacancies and various vacancy clusters on the interface between the iron matrix and a TiC particle which satisfies the Baker-Nutting relationship. Positron lifetimes are plotted as a function of the open volume of defects (V_{defect}).

Fig. 13—Configuration of a 4Fe + 2Ti + 2C vacancy cluster on the interface between a TiC nanoparticle and the matrix.
V. CONCLUSION

In this study, the interface structure of semicoherent TiC nanoparticles and incoherent micron-sized TiC precipitates dispersed in hot-rolled ferritic steels was investigated by TEM observation and PAS investigation. The main results obtained in this study can be summarized as follows:

(1) Steels with a Ti content not exceeding 0.23 wt pct contain semicoherent TiC nanoparticles and include virtually no micron-sized inclusions. The interface of the TiC nanoparticles has a coherent surface satisfying the Backer-Nutting orientation relationship and incoherent interfaces which are almost parallel to \(\{001\}_x\) planes. The 0.40Ti sample contained approximately the same amount of TiC nanoparticles as the 0.23Ti sample, and in addition, also contained incoherent micron-sized TiC precipitates.

(2) The positron lifetime related to the semicoherent TiC nanoparticles and incoherent TiC precipitates was about 240 ps and 500 ps, respectively. There was little difference between the 0.09Ti and 0.40Ti samples in the CDBS results because the surface area of the micron-sized TiC precipitates is much smaller than that of the TiC nanoparticles, which resulted in a very low relative intensity related to the micron-sized TiC precipitates in the PALS results. The CDBS results also indicated that the local concentrations of Fe, C and Ti around misfit defects associated with TiC nanoparticles were 0.5, 0.25 and 0.25, respectively.

(3) The positron lifetime of the annealed TiC powder was 160 ps, and the CDB ratio curve indicated that an equal concentration of C and Ti atoms was located in the chemical environment of positron traps. Therefore, it is likely that the annealed TiC powder contains comparable concentrations of C and Ti monovacancies. The positron lifetime measured in the annealed TiC powder was significantly shorter than that measured in the hot-rolled steel, indicating that the positrons in the hot-rolled steel were trapped on interfaces between the iron matrix and TiC nanoparticles, and not inside the nanoparticles.

(4) The coherent interface of TiC nanoparticles satisfying the Baker-Nutting orientation relationship with the matrix does not contain vacancy clusters, but contains monovacancies. Considering the fact that the positron lifetime of 240 ps measured in the experiment is significantly longer than the lifetime of a Fe monovacancy (175 ps), it can be inferred that positrons are trapped at misfit defects on incoherent parts of the TiC nanoparticle interfaces. Comparison with theoretical modeling suggested that the open volume of misfit defects is comparable to that of a 4Fe + 2Ti + 2C vacancy cluster.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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