The Carbide $M_7C_3$

in Low-Temperature-Carburized Austenitic Stainless Steel

Frank Ernst,* Dingqiang Li, Arthur H. Heuer, Harold Kahn, and Gary M. Michal

Department of Materials Science and Engineering,
Case Western Reserve University, Cleveland, Ohio 44106-7204, USA.

Abstract

Prolonged low-temperature gas-phase carburization of AISI 316L-type austenitic stainless steel can cause intragranular precipitation of the carbide $M_7C_3$ ($M$: randomly dispersed Fe, Cr, Ni). Transmission electron microscopy revealed that the carbide particles have the shape of needles. They grow by a ledge-migration mechanism and in a crystallographic orientation relationship to the austenite matrix that enables highly coherent interphase interfaces. A small solubility limit of Ni in the carbide and restricted Ni diffusivity at the processing temperature leads to Ni pileup around the particles and may explain the extreme aspect ratio of the particle shape. These characteristics closely resemble what has been observed earlier for precipitates of $M_5C_2$ under slightly different processing conditions and can be rationalized by considering the particular constraints imposed by carburization at low temperature.

Key words: Metal carbides, carbide precipitation, austenitic stainless steel, Fe–Cr–Ni, surface alloying, low-temperature gas-phase carburization.

*Email address: frank.ernst@cwru.edu (Frank Ernst).

Preprint submitted to Acta Materialia 10 November 2010
1 Introduction

Recent work [1–8] demonstrates that the mechanical properties (including surface hardness, fatigue resistance, and wear resistance) and the corrosion resistance of AISI 316-type austenitic stainless steel (Fe–Cr–Ni alloy) can be significantly improved by a novel, low-temperature gas-phase carburization process developed by the Swagelok Company [9–12].

Details of the Swagelok process, including a $T[t]$ (temperature–time) processing diagram, are described in a previous publication [13]. In short, low-temperature carburization requires an activation step that removes the passivating Cr$_2$O$_3$-rich layer from the steel surface to make it transparent to inward diffusion of carbon [14]. In the Swagelok process, this is accomplished by exposing the material to a gas atmosphere that contains HCl as the active component. Subsequently, the material is exposed to another gas atmosphere that provides carbon at a processing temperature $T_p$ for a processing time $\tau_p$. Recently, it was established that the process works best at $T_p \approx 723$ K (450 °C).

The reason why the Swagelok low-temperature carburization process dramatically improves alloy performance is that it generates a homogeneous, precipitate-free “case” (hard shell) in which the concentration of interstitially dissolved carbon can reach levels of $\approx 15$ at%, corresponding to $\approx 10^5$ the equilibrium solubility of carbon at room temperature [6, 8].

This “colossal” supersaturation with carbon arises for two reasons: (i) The carbon atoms, as they reside in interstitial sites, diffuse much faster than the metal atoms (Fe – iron – and solute atoms substituting for Fe) in the alloy. At $T_p$, the metal atoms are nearly immobile, whereas carbon can diffuse over considerable distances within $\tau_p$. (ii) The Cr (chromium) contained in the alloy and carbon have a high affinity for each other. This
leads to a mutual reduction of the activity coefficients of Cr and carbon (compared to an “ideal” solution), and – absent carbide precipitation because of (i) – enables solid solutions with very high fractions of carbon.

However, prolonged low-temperature carburization (e.g. multiple successive applications of the Swagelok process) eventually does lead to the precipitation of carbides. This is usually undesired because it degrades the corrosion resistance and certain mechanical properties (e.g. the fatigue life). Previous work revealed that colonies of carbide particles precipitate in a zone below the surface in which the average carbon fraction exceeds the non-equilibrium solubility limit $X^*_C \approx 0.12$ for bulk 316L) [7, 8, 15]. We have found two different carbide modifications: $M_5C_2$ (or $\chi$ phase) and $M_7C_3$. “M” stands for random occupancy of the Fe lattice sites with Fe and appropriate fractions of other metal atoms substituting for Fe in the solid solution. For our purpose, $M = \text{Fe, Cr, Ni}$. Previous work of our group revealed that in AISI 316L low-temperature-carburized at $T_p = 748 \text{ K}$, the majority of the carbide particles are $\chi$ phase ($M_5C_2$) [7, 8, 15]. They have the crystal structure of Fe$_5$C$_2$, the “Hägg carbide” [16–18], with very similar lattice parameters [7, 8, 19, 20]. The crystal structure of Fe$_5$C$_2$ is monoclinic and has the space group C2/c (15). This carbide and its interface with $\gamma$ (austenite) was the main subject of two recent publications [7, 15].

The other carbide we have observed is $M_7C_3$ [7, 8, 15]. After our earlier work focused on $M_5C_2$, it was established that the efficacy of the Swagelok process can be considerably improved by (i) lowering $T_p$ to about 723 K (450 °C) [13] and (ii) gradually changing the gas composition during the process in order to continue to decrease the carbon activity, as described in [13]. It appears that under these conditions, prolonged carburization predominantly precipitates $M_7C_3$. In the present paper, therefore, we focus on $M_7C_3$, henceforth denoted as “$\omega$” phase, and the interface it makes with $\gamma$ (austenite).
The crystal structure of $\text{M}_7\text{C}_3$ was first described as trigonal [21] with a hexagonal Bravais lattice and lattice parameters [22, 23]

\begin{equation}
\begin{aligned}
a'_\omega &= 0.6882 \text{ nm}, \\
c'_\omega &= 0.4540 \text{ nm}.
\end{aligned}
\end{equation}

However, later work [24–26] revealed that it is actually orthorhombic. $\text{Fe}_7\text{C}_3$, in particular, has the lattice parameters [25]

\begin{equation}
\begin{aligned}
a_\omega &= 0.4540 \text{ nm}, \\
b_\omega &= 0.6879 \text{ nm}, \\
c_\omega &= 1.1942 \text{ nm}.
\end{aligned}
\end{equation}

TEM (transmission electron microscopy) studies clarified that $\text{M}_7\text{C}_3$ usually contains equivalent volumes of three different, twin-related orientation variants of the orthorhombic unit cell and high densities of anti-phase and twin boundaries [24]. Since $c_\omega/b_\omega \approx \sqrt{3}$, the "average" structure of a volume containing approximately equal fractions of the three variants (e.g. sampled by X-ray diffractometry) appears to be trigonal.

The literature provides crystallographic data for $\text{Fe}_7\text{C}_3$, $\text{Mn}_7\text{C}_3$, and $\text{Cr}_7\text{C}_3$. In all three cases, the space group is Pnma (orthohombic). As expected, the reported lattice parameters differ for all three phases. However, the lattice parameters of $\text{Fe}_7\text{C}_3$ and $\text{Cr}_7\text{C}_3$, the phases relevant to the present work, only differ by $+0.24\%$, $-1.7\%$, and $-1.9\%$ for $a_\omega$, $b_\omega$, and $c_\omega$, respectively. The reported metal and carbon atom positions of $\text{Cr}_7\text{C}_3$ differ somewhat from those reported for $\text{Fe}_7\text{C}_3$ and $\text{Mn}_7\text{C}_3$. It seems possible that exchanging the metal atoms (e.g. replacing Fe with Cr) not only changes the lattice parameters, but also the positions of metal and carbon atoms, e.g. because of different atom radii. However, the fact that Cr, Mn, and Fe are neighbors in the periodic table and the atom positions reported for $\text{Fe}_7\text{C}_3$ and $\text{Mn}_7\text{C}_3$ are identical indicates that atom
size effects on the other positions are rather weak. Accordingly, the discrepancy in the reported atom positions probably arises from uncertainties in the experimental data and data processing. In the following, we assume that the structure of a “mixed” carbide $M_7C_3$ (where $M = \text{Fe, Cr, Ni}$) with a low fraction of nickel has the atom coordinates reported for $\text{Cr}_7\text{C}_3$ [26], since this structure was published three years later than [25] and the latter publication explicitly states that the atom positions are only “approximate.” Figure 1 shows the structure of $\text{Cr}_7\text{C}_3$ in $[\overline{T}00]$ projection, revealing the pseudo-trigonal symmetry.

2 Experimental Methods and Procedures

It is difficult to prepare TEM specimens from low-temperature-carburized stainless steel because both the hardness as well as the corrosion resistance of the carburized layer differ significantly from the corresponding properties of the non-carburized core of the material. For this reason, we chose foils (rather than bulk material) of AISI 316L-type stainless steel as the starting material. We purchased foils compliant with ASTM A240, annealed and with a thickness of 51 $\mu$m (0.002 in). As this thickness corresponds to only twice the typical case depth (i.e. thickness of the carbon-rich shell) observed for low-temperature-carburized bulk material, low-temperature carburization should build up significant carbon levels through the entire thickness of the foil, and preparing plan-view TEM specimens from such foils should always produce electron-transparent area showing carbon-rich regions (case), rather than non-carburized alloy core. The initial surface hardness of the foils was 74…78 on the Rockwell B scale.

The foils were exposed to 2 cycles of low-temperature-carburization, each one carried out at a processing (carburization) temperature $T_p = (723 \pm 10) \ K = (450 \pm 10) \ ^\circ\text{C}$ for
$t_p = 144.0 \text{ ks} = 40 \text{ h (after activation)}$. During the carburization step ($t_p$), the fraction of CO in the gas atmosphere was ramped downward by changing the initial gas composition from $X_{CO} = 0.45$, $X_{H2} = 0.45$, $X_{N2} = 0.10$ to $X_{CO} = 0.10$, $X_{H2} = 0.50$, $X_{N2} = 0.40$. During the entire process, the pressure of the gas atmosphere was kept slightly (a few hPa) above atmospheric pressure.

TEM foils were prepared from the low-temperature-carburized foils by cleaning, mechanical pre-preparation, and Ar$^+$ ion beam milling in a PIPS (precision ion polishing system, Gatan) system, followed by surface cleaning in a Ar$^+$ plasma cleaner (Fischione Model 1020).

The microscope we employed was a Tecnai F30 S-TWIN (FEI), operating with a field-emission gun at 300 kV and providing an information resolution limit of 0.14 nm. The instrument is equipped with a HAADF (high-angle angular dark-field) detector (Model 3000, Fischione Instruments), a post-column imaging energy filter (“GIF 2001,” Gatan, retrofitted with a $2 \times 2$ k CCD camera), and an X-ray energy-dispersive spectrometer (EDAX) with a Si–Li detector. Employing these attachments, we performed XEDS line scans in STEM (scanning TEM) mode, based on Z-contrast imaging with the aid of the HAADF detector. In these experiments, the full width at half intensity maximum of the electron probe was $\approx 0.5 \text{ nm}$, corresponding to gun lens setting #7 and spot size #6 in nano-probe mode. Specimen drift was compensated by the instrument’s built-in capability of monitoring the position of a characteristic image feature.

3 Results

As expected, the low-temperature-carburized AISI 316L-like foils exhibited significantly increased surface hardness. From the lattice parameter expansion we observed by XRD
(X-ray diffractometry) [6], we conclude that the carbon fraction $X_C$ near the surface is $0.087 \pm 0.02$.

In previous work [7, 15] as well as in the present study, we found that intragranular $M_7C_3$ precipitates in a unique crystallographic orientation relationship with the embedding austenite. Figure 2 presents a SAD (selected-area diffraction pattern) we obtained from an $\omega$ ($M_7C_3$) particle and its austenite matrix [7]. While in earlier work we indexed the carbide component of the pattern based on a hexagonal lattice, Fig. 2 shows indices referring to the - true - orthorhombic structure [27]. The viewing direction of the SAD pattern corresponds to $[100]_\omega$ in the $M_7C_3$ and $⟨111⟩_γ$ in the austenite. The black circles in Fig. 2 highlight the six $\{220\}_γ$ reflections that characterize $⟨111⟩_γ$ diffraction patterns of austenite as well as one reflection from $\omega$ near the $γ$ reflection we indexed as 220. As indicated in the figure, this reflection originates from the $\{019\}_ω$ planes. As the corresponding scattering vectors are parallel to each other, i.e. $\vec{g}_{019}^ω \parallel \vec{g}_{220}^γ$, the OR (orientation relationship) between the carbide and the austenite can be expressed as

$$\left\| \begin{array}{c} (100)_ω \parallel (1\overline{1}1)_γ \\ \wedge (019)_ω \parallel (110)_γ \end{array} \right\| . \quad (3)$$

Significant for what follows, this OR implies that the following lattice directions in $ω$ and $γ$ are parallel to each other:

$$\left\| \begin{array}{c} [001]_ω \parallel ⟨321⟩_γ , \\ [010]_ω \parallel ⟨541⟩_γ , \\ [013]_ω \parallel ⟨110⟩_γ . \end{array} \right\| . \quad (4)$$

Figure 3 illustrates the OR (3) by showing the relative orientation of the unit cells of $ω$ and $γ$ – drawn to scale and in two different perspective views. In addition to the actual unit cells, the figure features a number of lattice planes and directions in $ω$ and $γ$. In particular, it shows the $(1\overline{1}1)_γ$ plane that is parallel to $(100)_ω$ and the $(110)_γ$ plane that
is parallel to \((019)_\omega\).

Figure 4 presents a TEM image of an \(\omega\) \((M_7C_3)\) carbide needle in \(\gamma\) (low-temperature-carburized austenite with a colossal supersaturation of carbon and correspondingly expanded lattice parameter). This image was recorded under high-resolution (multibeam) conditions, but does not reveal lattice fringes at the low magnification view of Fig. 4. The image features part of an \(\omega\) particle with two branches. The branch parallel to the bottom of the image and the upper branch both have diameters of order 20 nm. Their lengths are different and much larger – of order 1 \(\mu\)m. In the interior of both branches, the TEM image reveals characteristic fringes, corresponding to a sinusoidal intensity modulation. In the lower branch, the fringes are oriented in a direction that corresponds to a \(\approx +8^\circ\) rotation relative to the vertical direction. The upper branch also exhibits these fringes, plus an equivalent set of fringes in the direction inclined \(\approx -54^\circ\) against the vertical direction. Another type of fringes appears at the \(\omega-\gamma\) interface where the box-like protrusion that the lower branch exhibits towards the top. These are apparently moiré fringes that arise from an overlap of parallel \(\omega\) and \(\gamma\) planes that are oriented parallel to the viewing direction and have slightly different spacings.

The \(\omega-\gamma\) interface appears to be straight over extended sections at the magnification of Fig. 4, but does not seem to follow particular crystallographic directions in either phase. Interestingly, a dark fringe accompanies the \(\omega\) particle on the \(\gamma\) side, indicating a higher projected scattering density than that of the austenite matrix. The center of Fig. 4 features the pointed end of the upper branch of the particle. This region is of particular interest because the aspect ratio of the \(\omega\) particle suggests that it grows much more rapidly into the axial direction than into the direction normal to the particle axis. Correspondingly, the tip of the particle constitutes the most active growth interface.

The inset at the top left of Fig. 4 shows an SAD pattern of a circular area that includes
part of the carbide particle and the adjacent austenite matrix. The pattern corresponds to a superposition of a single-crystallite austenite pattern in [110]_γ direction and a single-crystallite M_7C_3 pattern in [013]_ω direction.

Figures 5 and 6 zoom into the two regions of the upper branch of the particle in Fig. 4. Figure 5 is from the region labeled “R1” in Fig. 4, whereas Fig. 6 displays region “R2.”

Figure 5 reveals lattice fringes in both ω and γ. The pattern observed in γ corresponds to a ⟨111⟩ viewing direction with one set of {111} planes approximately horizontal. The lattice image of ω features mm symmetry and has one set of fringes parallel to the approximately horizontal {111} planes of γ. These fringes in ω exhibit a superperiodicity: every other fringe has increased intensity. The right inset in Fig. 5 shows an enlargement of the region included in the dashed rectangle for comparison with a simulated HRTEM image in the left inset. This simulation was carried out for imaging ω in [013] direction with a thickness of 45 nm under the experimental imaging conditions of Fig. 5 (Tecnai F30 operating at optimum underfocus ζ = 1.2√Csλ = 58 nm). The excellent match between the image pattern of the simulation and the experimentally observed image pattern suggests that Fig. 5 does indeed show ω in [013] direction. (From the diffraction pattern or HRTEM image, [013] is indistinguishable from [05T], obtained by rotating [013] by +120° about [100]_ω, the pseudo-trigonal axis. However, a different diffraction pattern and HRTEM image would result in [021], the other direction obtained by rotating [013] by −120° about [100]_ω.) As expected, Fig. 5 is consistent with the OR (3) and its implications (4). Figure 3 explicitly shows [013]_ω||[110]_γ. The experimental HRTEM image in Fig. 5 corresponds exactly to the view on the right hand side of Fig. 3, except that the (001)_ω||{(1T1)} planes are not exactly (but close to) horizontal in the experimental image.

This interpretation of Fig. 5 is further supported by comparing the simulated diffraction
pattern at the top left of the inset with the $\omega$ component of the experimental diffraction pattern included in Fig. 4, even though the experimental pattern shows additional reflections corresponding to the sinusoidal intensity modulation; this effect is not included in the simulation. However, the simulated diffraction pattern in Fig. 5 explains the superperiodicity of the fringes parallel to the approximately horizontal $\{111\}$ planes of $\gamma$: These fringes represent the (200) planes, and the superperiodicity arises from the presence of kinematically forbidden $\{100\}$ reflections, shown gray in the simulated diffraction pattern of Fig. 5.

The atomistic structure of the particle tip and the $\omega$-$\gamma$ interface at different inclinations becomes fully apparent in Fig. 6, which includes two further enlargements of the outermost tip area (Fig. 6b and c). The $\omega$-$\gamma$ interface is faceted on $(200)_\omega$ planes, and, according to (3), $(111)_\gamma$ planes. This is most apparent at the top interface of the particle, close to the top of the image, which features a very long atomically flat $(200)_\omega$ facet. The interface at the bottom of the particle is significantly more inclined and therefore features correspondingly shorter $(200)_\omega$ facets. Figure 6a also reveals that the OR (3) is not perfectly fulfilled in this area; the two extended white lines near the bottom of the image indicate a deviation of nearly $1^\circ$ between $\{100\}_\omega$ and $\{1\overline{1}1\}_\gamma$. Figure 6b shows an enlargement of the outermost tip of the $\omega$ particle. Here, the projected $\omega$-$\gamma$ interface is parallel to $\{03\overline{1}\}_\omega$. The lattice image of $\gamma$ in this region is of low quality, presumably because $\gamma$ is strongly distorted in this region. Figure 6c shows the bottom side of the tip, i.e. the region immediately adjacent to the region shown in Fig. 6b on the bottom side of the particle. This section features short $\{200\}_\omega$ facets and a clearer lattice image of $\gamma$ than Fig. 6b, indicating a lower degree of distortion in $\gamma$ in this region.

Figure 7a shows a Z-contrast image we obtained from the region of Fig. 4 by STEM using a HAADF detector. As expected, the carbide particle appears with lower intensity than
the austenite matrix because its mass density is lower. The dark fringe that appears on the γ side of the ω–γ interface in the HRTEM images shows up as a bright fringe in the Z-contrast image, confirming that the γ region next to the ω–γ interface is a region of increased mass density. Dark spots all over the image indicate severe contamination in spite of the plasma cleaning we have applied to the specimen before inserting it into the transmission electron microscope.

Figure 7b presents a composition profile we obtained along the scan line marked in Fig. 7a. This profile was obtained by focusing the electron beam to a diameter of ≈0.5 nm, positioning it at regularly-spaced sample points along the scan line, and recording XEDS spectra at each point. While the line scan was recorded, we intermittently corrected for specimen drift by monitoring the drift of the image features included in the square marked “drift reference.” Unfortunately, the contamination of the specimen was too severe to provide a reliable carbon signal. In Fig. 7b, therefore, we have included only the profiles $Y_m[x]$ ($m = \text{Fe, Cr, Ni}$) of the metal atoms, obtained by re-normalizing the measured fractions $X_m$ to $Y_m := X_m / \sum_m X_m$, implying $\sum_m Y_m = 1$. The data reveal that the Fe and Cr fraction in the ω particle do not differ significantly from those in the γ matrix. For nickel, in contrast, a significant difference is observed. Within the ω particle, the nickel fraction is $Y_{\text{Ni}}^{\omega} \approx 0.05$, compared to $Y_{\text{Ni}}^{\gamma} \approx 0.10$ in γ as indicated by the plateaus in the $Y_{\text{Ni}}^{\gamma}$ profile for $x < 10 \text{ nm}$ and $x > 75 \text{ nm}$. This level of $Y_{\text{Ni}}^{\gamma}$ corresponds exactly to the fraction $Y_{\text{Ni}}^{\gamma}$ one would expect based on the nominal fractions $X_{\text{Fe}}^{\gamma}$, $X_{\text{Cr}}^{\gamma}$, and $X_{\text{Ni}}^{\gamma}$ in the starting material, shown in Table 1, indicating that the experimentally obtained levels of the nickel fraction— and in particular $Y_{\text{Ni}}^{\omega} \approx 0.05$— are trustworthy.

On the γ side of the ω–γ interface, Fig. 7b shows regions of strongly enhanced Ni fraction. These regions are $\approx 20 \text{ nm}$ wide and show peaks of $\text{Max}[Y_{\text{Ni}}^{\gamma}] \approx 0.25$, i.e. five times higher than the nickel fraction in the ω particle. The profiles of Fe and Cr feature corresponding
minima Min[$Y_{Fe,min}^Y] \approx 0.60$ and Min[$Y_{Cr,min}^Y] \approx 0.15$, respectively. For both elements, the fractions observed in these minima correspond to 20% less than the fractions observed in $\omega/\gamma$. Accordingly, Ni replaces Fe and Cr with equal probability in the Ni-enriched regions on the $\gamma$ side of the $\omega-\gamma$ interface. The resulting increase in mass density in these regions gives rise to the bright fringes observed in the Z-contrast image of Fig. 7a.

4 Discussion

Different from earlier work, in which we mainly studied $\chi$ ($M_7C_3$) carbide in low-temperature-carburized AISI 316L-type foils of similar composition, the dominant carbide phase in the foils investigated in the present work is $\omega$ ($M_7C_3$). It seems possible that this difference arises because the carburization temperature applied in the present study was significantly lower: $T_p = 723 \, K$ (450°C) versus $T_p = 748 \, K$ (475°C) in earlier work. (However, lower temperatures should actually favor phases of lower crystal symmetry, i.e. $\chi$ with its monoclinic structure over $\omega$ with its orthorhombic structure. Consistent with this rule, $\omega$ is usually observed during conventional – high-temperature – carburization, whereas $\chi$ is not [32]). Further, the dominance of $\omega$ may arise from differences in carbon activity during the optimized low-temperature carburization process or differences in the composition of the starting material, which is slightly deficient in Cr and Ni compared to the material we studied in previous work. In any case, the observation that slight changes in processing parameters or composition cause dominance of one or the other carbide indicates that their free energies are rather similar.

The diffraction pattern of $\omega$ and the HRTEM images are consistent with the established orthorhombic crystal structure (Fig. 1) and lattice parameters (3), except for the sinusoidal intensity modulation that appears in HRTEM images along the $[100]_\omega$ direction and
corresponding satellite reflections in the diffraction pattern. The intensity modulation appears with varying wavelength and varying magnitude across the lattice image of $\omega$. These variations are most obvious in Fig. 6. Accordingly, the modulation is not related to the intrinsic (crystal) structure of $\omega$ or to moiré effects that arise from the beating between two constant spacings, either by overlap of $\omega$ with $\gamma$ or crystal defects in $\omega$ that overlap in the projection of the HRTEM image. Possibly, the modulation arises from planar defects inclined versus the viewing direction (“alpha fringes”). These could e.g. be the anti-phase or twin boundaries on $\{1\overline{1}00\}_\omega$ described by Morniroli et al. [27, 30]. In the orthorhombic lattice, the $\{1\overline{1}00\}_\omega$ planes of the pseudo-trigonal structure correspond to $\{001\}_\omega$. In the HRTEM image of Fig. 5, these planes are inclined by about 10° against the plane of the TEM foil and the $[001]_\omega$ plane normal lies parallel to the $(100)_\omega$ basal plane, consistent with the observed fringe orientation vertical to $(100)_\omega$.

The HRTEM images suggest that the $\omega$ particles grow by adding atoms to ledges on $(200)_\omega$ facets. Accordingly, the fastest growth rate can be accomplished at the tip (at the top right of Fig. 6a and viewed enlarged in Fig. 6b), because here the growth front is approximately normal to the $(200)_\omega$ planes, i.e. parallel to $\{03\overline{1}\}_\omega$. This is also a region of high coherency stress. The spacing of the $(200)_\omega$ planes in Cr$_7$C$_3$ is $\approx$9% larger than that of the corresponding $(111)_\gamma$ planes in non-carburized AISI 316L austenite ($a_0 = 0.359$ nm). The actual mismatch between these planes at the $\omega$-$\gamma$ interface studied here could be quantitatively different owing to (i) the presence of Fe and Ni in $\omega$, (ii) the lattice parameter expansion of $\gamma$ caused by the $\gamma$ region adjacent to the particle-matrix interface not being entirely depleted from interstitial carbon, and (iii) the segregation of Ni to the $\gamma$ side of the $\omega$-$\gamma$ interface (see below). However, calibrating the period of the moiré fringes at the top of the lower branch of the $\omega$ particle in Fig. 4 with the underlying lattice image, we estimate the actual misfit between the $(100)_\omega$ and $(111)_\gamma$ planes to be $\approx$10%, i.e. very similar to the expected misfit between Cr$_7$C$_3$ and non-carburized
AISI 316L. An extended $\omega$-$\gamma$ interface vertical to $(100)_\omega|| (111)_\gamma$, as the interface at the tip at the top right of Fig. 6, should feature corresponding misfit dislocations with a spacing of about 10 $(111)_\gamma$ planes. Interestingly, the tip in Fig. 6 is just narrow enough to avoid misfit dislocations.

Apart from the crystal structure, the observed features of $\omega$ closely resemble those observed for $\chi$ ($M_5C_2$) carbide in our earlier work [15]. In particular, the elongated shape of the $\omega$ carbide particles is very similar to that of the $\chi$ carbides. Similar to what was discussed in [15], the experimentally observed $\omega$-$\gamma$ OR (3) can be rationalized by considering that $\omega$ precipitates under the constraint of very limited metal ($M = Fe, Cr, Ni$) atom mobility (close to ideal “carbon para-equilibrium” conditions [15]). Figure 8a shows the configuration of the metal atoms in a $(1\overline{1}1)_\gamma$ layer of $\gamma$ (austenite), which has the thickness $t = a_\gamma/\sqrt{3} = 0.21$ nm ($a_\gamma$ denotes the lattice parameter). Figure 8b shows a layer of the same thickness $t$ in $\omega$, oriented according to (3) i.e. with $(100)_\omega|| (1\overline{1}1)_\gamma$ and $(019)_\omega|| (110)_\gamma$. The pattern of the atom positions in the $\omega$ layer closely resembles the close-packed (“honeycomb”) pattern in which the metal atoms are arranged in the $(1\overline{1}1)_\gamma$ layer of $\gamma$, implying that the observed OR (3) enables precipitation of $\omega$ without substantial rearrangement of atom positions. The atom configuration in the $(100)_\omega$ layers not only resembles that in $(111)_\gamma$, but also the atom configuration in corresponding layers of $\chi$ [15]. Therefore, it seems possible that a $\chi$ $\rightarrow$ $\omega$ transformation occurs even under the mobility constraints of near-carbon-para-equilibrium. Accordingly – although we do not have experimental evidence for this – $\omega$ and $\chi$ could actually be subsequent steps in a transformation sequence, as hypothesized earlier [7].

Neglecting the carbon atoms, the metal atom volume in Fe$_7$C$_3$ with lattice parameters (3) is $\Omega_\omega = 0.0133$ nm$^3$. In order to have the same atom volume, the A1 (face-centered cubic) structure of austenite would have to have a lattice parameter of $a_\gamma = 0.376$ nm. In reality,
austenite with about 9 at% interstitial carbon has a lattice parameter of $a_\gamma \approx 0.368$ nm [15], corresponding to $\Omega_\gamma \approx 0.0124$ nm$^3$. As this is 7% smaller than $\Omega_\omega$ and the carbon concentration in $\omega$ is higher than in $\gamma$ (30 at% versus 9 at%), too, the precipitation of $\omega$ generates compressive stress (in addition to the compressive stress induced by the interstitial carbon [6, 8, 15]). However, since the volume misfit is small, this stress could be relaxed by atom transport of correspondingly moderate extent – consistent with near-carbon-para-equilibrium conditions.

However, the data shown in Fig. 7 actually indicates that significant transport of Ni does occur to enable carbide precipitation. Very similar to what has been observed for $\chi$ [15], Fig. 7 indicates that Ni diffuses over a distance of $\approx 20$ nm within the processing time. This requires a diffusion coefficient that is at least three orders of magnitude larger than what would be expected by extrapolating high-temperature diffusion data measured for Fe–15Cr–20Ni to $T_p$ [15, 33]. As speculated in earlier work, the enhanced diffusivity of Ni may originate from and enhance concentration of non-equilibrium structural defects, e.g. excess vacancies. Another explanation arises from the observation that the diffusion coefficient of carbon depends very strongly on the local carbon concentration [13]. This effect has been attributed to a lower saddle point energy (migration energy) owing to the carbon-interstitial-induced expansion of the austenite lattice parameter [13, 34]. For the same reason, the presence of interstitial carbon may enhance the diffusion of substitutional elements, including Ni.

Remarkably, the diameter of the $\omega$ carbide needles is very similar to the diameter of the $\chi$ carbide needles observed in earlier work [15], regardless of the difference in crystal structure. Elongated precipitates with high aspect ratios are known to form because they minimize the energy associated with elastic strain or because of crystallographic anisotropy of the growth rate. However, the example of Fig. 4 shows that the long axis of
ω particles can be aligned to different crystallographic directions in both ω and γ. An alternative explanation for the observed particle shape characteristics arises from the data in Fig. 7: As in χ, the solubility of Ni in ω is limited to about 5 at%. In order for ω particles to form, Ni must be transported outward to reduce the concentration from the initial level of about 10 at% in γ to this solubility limit. Under the near-carbon-para-equilibrium conditions of low-temperature carburization, where the diffusivity of metal atoms is very low, this requirement constitutes a major hindrance for carbide precipitation. The observed particle diameter and aspect ratio appear to optimize the precipitate volume under the given constraints of limited (even if enhanced) Ni diffusion: While ω particles grow rapidly in the direction parallel to their long axis, their small extension in the direction orthogonal to the axis enables the required distance of Ni transport to be small enough to be realized under near-carbon-para-equilibrium conditions.

5 Conclusions

Carbide precipitation imposes fundamental limits on surface engineering of austenitic stainless steel by low-temperature carburization – e.g. the maximum case depth that can be achieved without compromising fatigue and corrosion resistance. Therefore, advances in understanding the details of carbide particle formation under the mobility constraints of low-temperature carburization are important not only under scientific aspects, but also for further optimizing the processing conditions.

Despite the difference in crystal structure and composition, precipitates of M₇C₃ and M₅C₂ exhibit remarkably similar characteristic features: Both carbides have a crystal structure and an orientation relationship to the austenite matrix that enables highly coherent interphase interfaces and phase transformation mechanisms that require only
minor displacement and transport of metal atoms. Both carbides precipitate as elongated needles with an extremely high aspect ratio. Both carbides have a similarly low solubility for Ni – only about 5 at%. Therefore, in order to enable carbide particles to form, Ni needs to be expunged into the austenite matrix. This requirement may be significant for further optimizing the processing conditions and alloy compositions e.g. to obtain larger case depths without carbide precipitation.

The reason why one or the other carbide dominates under slightly different but very similar experiment the conditions is not well understood. Apparently, the free energy of formation of these two carbides is not too different under the conditions of low-temperature carburization. The reason for the dominance of either modification is most likely related to slight differences in alloy composition, processing temperature, or the (time-dependent) carbon activity in the gas phase.

**Acknowledgment**

We acknowledge financial support from the Ohio Department of Development through its Third Frontier program. We thank S. Collins, S. Marx, and P. Williams (Swagelok) for numerous inspiring discussions.
References


Tables

Table 1

Nominal atom fractions of main atom species in AISI 316L-like foil.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>Fe (balance)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.001</td>
<td>0.174</td>
<td>0.096</td>
<td>0.012</td>
<td>0.009</td>
<td>0.012</td>
<td>0.690</td>
</tr>
</tbody>
</table>
Figure Legends

1. Four unit cells of the Cr$_7$C$_3$ crystal structure, viewed in $\overline{1}00$$_\omega$. One unit cell is marked at the bottom left. The atom coordinates (Wyckoff positions) are those given by Rouault [26].

2. Diffraction pattern from a region of low-temperature-carburized $\gamma$ (austenite) containing an $\omega$ ($M_7C_3$) needle, as shown in [7], but indexed according to an orthorhombic unit cell.

3. Crystallographic orientation relationship (3) between the units cells of austenite ($\gamma$) and $M_7C_3$ ($\omega$), shown by the relative orientation of the corresponding cubic and orthorhombic unit cells – drawn to scale and in two different perspective views.

4. HRTEM image of $\omega$ ($M_7C_3$) needles in low-temperature-carburized austenite, shown at low magnification.

5. (a) HRTEM image of an $\omega$ needle (top) and the adjacent $\gamma$ matrix (bottom). (b) Enlargement of the region included in the white dashed rectangle on the middle right of (a). (c) Simulation of $\omega$ in $[013]_\omega$ projection under the conditions of the experimental HRTEM image. (d) Simulated diffraction pattern, including $\{100\}$ reflections excited by double reflection.

6. (a) Magnified view of the $\omega$ needle tip in the HRTEM image of Fig. 4. (b) and (c) Further magnified views of Fig. 6a.

7. Z-contrast imaging and composition profiles across a $\omega$ particle. (a) HAADF STEM image of the region shown in Fig. 4. (b) Fraction–line profiles $Y_m[x]$ ($m =$ Fe, Cr, Ni)
of the metal atoms *only*, obtained by re-normalizing the fractions $X_m$ obtained by XEDS to $Y_m := X_m / \sum_m X_m$, implying $\sum_m Y_m = 1$. The shaded area indicates the position of the carbide particle.

8. Comparison between the spatial arrangement of the metal atoms (Fe, Cr, Ni) in (a) a $(1\overline{1}1)_{\gamma}$ layer of $\gamma$ (austenite), which has the thickness $t = a_{\gamma}/\sqrt{3} = 0.21$ nm ($a_{\gamma}$ denotes the lattice parameter), and (b) a layer of the same thickness $t$ in $\omega$ (carbide $M_7C_3$) oriented in the experimentally observed orientation relationship (3) to $\gamma$, i.e. with $(100)_{\omega} \parallel (1\overline{1}1)_{\gamma}$ and $(019)_{\omega} \parallel (110)_{\gamma}$. The rectangular frame indicates one unit cell of $\omega$. 
Fig. 1. Four unit cells of the Cr$_7$C$_3$ crystal structure, viewed in [100]. One unit cell is marked at the bottom left. The atom coordinates (Wyckoff positions) are those given by Rouault [26].

\[
\begin{align*}
    a_\omega &= 0.4540 \text{ nm} \\
    b_\omega &= 0.6879 \text{ nm} \\
    c_\omega &= 1.1942 \text{ nm}
\end{align*}
\]

Cr in 4c  
(0.0579, 0.2500, 0.6261)  
Cr in 4c  
(0.2501, 0.2500, 0.2063)  
Cr in 4c  
(0.2619, 0.2500, 0.4165)  
Cr in 8d  
(0.0565, 0.0642, 0.8119)  
Cr in 8d  
(0.2509, 0.0657, 0.0218)  
C in 4c  
(0.4594, 0.0025, 0.5629)  
C in 8d  
(0.0288, 0.0291, 0.3428)
Fig. 2. Diffraction pattern from a region of low-temperature-carburized γ (austenite) containing an ω (M₇C₃) needle, as shown in [7], but indexed according to an orthorhombic unit cell.
Fig. 3. Crystallographic orientation relationship (3) between the units cells of austenite (γ) and M₇C₃ (ω), shown by the relative orientation of the corresponding cubic and orthorhombic unit cells – drawn to scale and in two different perspective views.
Fig. 4. HRTEM image of $\omega$ ($M_7C_3$) needles in low-temperature-carburized austenite, shown at low magnification.
Fig. 5. (a) HRTEM image of an $\omega$ needle (top) and the adjacent $\gamma$ matrix (bottom). (b) Enlargement of the region included in the white dashed rectangle on the middle right of (a). (c) Simulation of $\omega$ in $[013]_{\omega}$ projection under the conditions of the experimental HRTEM image. (d) Simulated diffraction pattern, including $\{100\}$ reflections excited by double reflection.
Fig. 6. (a) Magnified view of the ω needle tip in the HRTEM image of Fig. 4. (b) and (c) Further magnified views of Fig. 6a.
Fig. 7. Z-contrast imaging and composition profiles across a $\omega$ particle. (a) HAADF STEM image of the region shown in Fig. 4. (b) Fraction–line profiles $Y_m[x]$ ($m = \text{Fe}, \text{Cr}, \text{Ni}$) of the metal atoms only, obtained by re-normalizing the fractions $X_m$ obtained by XEDS to $Y_m := X_m / \sum_m X_m$, implying $\sum_m Y_m = 1$. The shaded area indicates the position of the carbide particle.
Fig. 8. Comparison between the spatial arrangement of the metal atoms (Fe, Cr, Ni) in (a) a $(1\overline{1}1)_\gamma$ layer of $\gamma$ (austenite), which has the thickness $t = a_\gamma/\sqrt{3} = 0.21$ nm ($a_\gamma$ denotes the lattice parameter), and (b) a layer of the same thickness $t$ in $\omega$ (carbide $M_7C_3$) oriented in the experimentally observed orientation relationship (3) to $\gamma$, i.e. with $(100)_\omega|| (1\overline{1}1)_\gamma$ and $(01\overline{9})_\omega|| (110)_\gamma$. The rectangular frame indicates one unit cell of $\omega$. 
Fig. 1. Four unit cells of the Cr$_7$C$_3$ crystal structure, viewed in [T00]$_{\omega}$. One unit cell is marked at the bottom left. The atom coordinates (Wyckoff positions) are those given by Rouault [26].
Fig. 2. Diffraction pattern from a region of low-temperature-carburized γ (austenite) containing an ω (M₇C₃) needle, as shown in [7], but indexed according to an orthorhombic unit cell.
Fig. 3. Crystallographic orientation relationship (3) between the units cells of austenite (γ) and M₇C₃ (ω), shown by the relative orientation of the corresponding cubic and orthorhombic unit cells – drawn to scale and in two different perspective views.
Fig. 4. HRTEM image of $\omega$ (M$_7$C$_3$) needles in low-temperature-carburized austenite, shown at low magnification.
Fig. 5. (a) HRTEM image of an $\omega$ needle (top) and the adjacent $\gamma$ matrix (bottom). (b) Enlargement of the region included in the white dashed rectangle on the middle right of (a). (c) Simulation of $\omega$ in $[013]_\omega$ projection under the conditions of the experimental HRTEM image. (d) Simulated diffraction pattern, including $\{100\}$ reflections excited by double reflection.
Fig. 6. (a) Magnified view of the ω needle tip in the HRTEM image of Fig. 4. (b) and (c) Further magnified views of Fig. 6a.
Fig. 7. Z-contrast imaging and composition profiles across a ω particle. (a) HAADF STEM image of the region shown in Fig. 4. (b) Fraction–line profiles $Y_m[x]$ ($m = \text{Fe, Cr, Ni}$) of the metal atoms only, obtained by re-normalizing the fractions $X_m$ obtained by XEDS to $Y_m := X_m / \sum_m X_m$, implying $\sum_m Y_m = 1$. The shaded area indicates the position of the carbide particle.
Fig. 8. Comparison between the spatial arrangement of the metal atoms (Fe, Cr, Ni) in (a) a \((1\bar{1}1)_{\gamma}\) layer of \(\gamma\) (austenite), which has the thickness \(t = a_{\gamma}/\sqrt{3} = 0.21\) nm \((a_{\gamma}\) denotes the lattice parameter), and (b) a layer of the same thickness \(t\) in \(\omega\) (carbide \(M_7C_3\)) oriented in the experimentally observed orientation relationship (3) to \(\gamma\), i.e. with \((100)_{\omega}||\,(1\bar{1}1)_{\gamma}\) and \((019)_{\omega}||\,(110)_{\gamma}\). The rectangular frame indicates one unit cell of \(\omega\).