Microstructure and age hardening of C276 alloy coatings

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1. Introduction

Ni-Cr-Mo alloys such as the Hastelloy C series are high-grade corrosion-resistant materials which are considered to be the most corrosion-resistant Ni-based superalloys [1]. C series alloy tubes and components are used in a variety of highly corrosive environments such as those present in nuclear reactors and chemical processing and petrochemical industries [2,3]. However, these alloys are quite expensive and they have reduced machinability and formability when compared to plain carbon steels due to their tendency toward work hardening [4]. Therefore, it is desirable to combine the excellent surface protection properties of these alloys with the excellent bulk properties of plain carbon steels in terms of strength, cost, machinability, and formability. We envision that this can be achieved by depositing a protective C series alloy layer on top of carbon steel components and have already reported that Hastelloy C276 coatings that are deposited on 4140 steel substrates suppress pit formation and reduce the corrosion rate by three orders of magnitude during cyclic polarization and autoclave testing with H2S exposure [5].

In this paper, we present the results of a study of the microstructure, temperature stability, and mechanical properties of C276 films on 4140 steel. Despite the extensive use of this particular alloy in bulk form, the mechanical properties of directly deposited C276 alloy coatings on steel has not been reported, yet. The coatings are deposited by plasma enhanced magnetron sputtering (PEMS) and their microstructure and composition evaluated using a combination of scanning electron microscopy (SEM), x-ray diffraction (XRD), energy-dispersive spectroscopy (EDS), and Auger electron spectroscopy (AES). A Knoop indenter is used to measure the hardness, which was found to be four times larger than the known hardness for bulk C276. Annealing in air at 600 °C leads to an additional hardness increase of 15–40%. The initial high hardness is attributed to Hall–Petch strengthening. Compositional mapping and secondary x-ray peaks suggest that the hardening upon annealing is due to the formation of precipitates rich in Mo and Cr.

2. Experimental procedure

All samples were deposited at a growth temperature of 400 °C on 4140 carbon steel substrates machined to 27.5 × 27.5 × 6.25 mm² (1.5" × 1.5" × 1/4") blocks. The substrate surfaces were milled (non-polished), had a measured roughness of 1.6 µm (64 microinch), and were cleaned with isopropyl alcohol before introduction into the deposition chamber with a base pressure of 4 × 10⁻⁶ Pa. The samples were chained and hung on a two-fold rotation fixture in a 70 cm cubical plasma enhanced magnetron sputter deposition system [5] with two circular magnetrons of which only one was used in this study. During deposition, pure Ar was introduced into the system at a constant flow rate of 190 sccm, yielding a processing pressure of 0.4 Pa. A constant power of 3.6 kW was applied to the magnetron, yielding a bias voltage of −500 V on the 17-cm-diameter C276 alloy target. Under these conditions, a deposition rate of 5 µm/h was achieved, while a coating thickness of 12 µm was deposited for all samples. The second magnetron that was not used was kept at a floating potential. In order to increase the ion current to the substrate, an additional global plasma was created using a tungsten filament that was heated with an AC
power supply and held at a DC potential of −120 V, yielding a discharge current of 5A at the filament and an ion current of 0.9 A at the substrate holder, which was held at a bias of $V_b = -40$ V. As described in detail previously [6–9], this approach yields an up to 25× higher ion current density at the substrate, which is estimated to be 2.5 A/cm² for these deposition parameters. The high ion current density enhances the film density and adhesion, and also results in grain renucleation and, in turn, nanocrystalline microstructures.

Annealing experiments were done in air, using a box furnace with a resistive heater. Specimens were heated and held for 1 h at annealing temperatures of $T_a = 600$ °C, 700 °C, and 800 °C, followed by either a water-quench or a furnace-cool. Water quenching was done by immersing the specimens into room-temperature water within 2–3 s after removal from the furnace which was still at $T_a$. Furnace cooling was done by controlled slow cooling in the furnace at a rate of 20 °C/min.

Cross sections of samples in as-deposited and annealed conditions were mounted and polished for metallographic examination of the coating and interface. Prior to imaging, the metallographic samples are subjected to a 2% Nital etch in order to evaluate the steel substrate after removal from the furnace which was still at $T_a$. The intensity of the 111 reflection is highest, with the intensity of the 200, 220, 311, and 222 peaks being 17, 231, 33, and 73 times weaker. For a perfectly randomly oriented polycrystalline solid, the expected ratio of 111 to 200 would be 3.7:1 [11], indicating a 111 preferred growth orientation in the as-deposited condition.

The peak positions are at 43.36°, 50.54°, 74.30°, 90.12°, and 95.51° 2θ, yielding an out-of-plane lattice constant of 0.3608 ± 0.0003 nm. This value is 0.2% smaller than 0.3615 nm, the reported lattice constant of the C276 Ni alloy [11]. We attribute this deviation to a biaxial in-plane tensile stress of 0.7 GPa, which is determined from the measured strain of −0.2% in the growth direction and assuming an isotropic elastic modulus $E = 205$ and Poisson’s ratio $\nu = 0.33$ [12] as well as a relaxed

\begin{equation}
\frac{b'}{a'} = \frac{b}{a} = \alpha \cdot \frac{H}{E}
\end{equation}

where $b$ and $b'$ are the short diagonal of the Knoop indentation before and after elastic recovery, $a$ and $a'$ are the long diagonal before and after elastic recovery, and $\alpha$ is an experimentally determined constant of 0.45. The change in $a$ with elastic recovery is negligible, i.e. $a = a'$. Thus, $E$ is directly determined from the difference in $b'/a$ and $b/a$. Stated uncertainties for $H$ and $E$ correspond to ± one standard deviation.

Structural analyses of the coatings by x-ray diffraction were completed using a PANanalytical X’pert Pro MPD system with a Cu Kα source, a divergent beam with a $0.5^\circ$ divergent angle, and a Pixcel array detector with 255 channels in scanning mode. The scans were performed in the 2θ range of 30°–100° with step size of 0.01°.

Coating compositions of as-deposited and annealed specimens were analyzed in cross section using an FEI Helios Nanolab DualBeam scanning electron microscope equipped with an Oxford Instruments X-MaxN 80 Energy-Dispersive Spectroscopy system. Additionally, Auger electron spectroscopy was completed on metallographically prepared cross sections with a Physical Electronics, Inc. PHI 700™ Scanning Auger Nanoprobe.

### 3. Results

The overall composition of the coatings is independent of deposition parameters such as substrate bias voltage or layer thickness and replicates relatively closely the composition of the C276 target, which is used as deposition source. This is verified by comparing EDS results from cross-sectional coating specimens with those from the C276 bulk material from which the sputtering target was made. The following list shows the measured elemental composition in at.%, indicating the range of compositions measured from three samples deposited under identical conditions and (in parenthesis) the measured composition of the target: 58.4–59.0 (61.5) Ni, 20.0–21.2 (18.7) Cr, 9.8–10.5 (9.7) Mo, 6.2–8.4 (5.8) Fe, 1.7–1.8 (1.7) Co, 0.8–0.9 (1.0) W, 0.5–0.8 (1.2) Al, and 0.01 (0.5) Mn. The relatively small sample-to-sample composition variation of −1% indicates that the deposition process is well suited to obtain reproducible coating compositions. The relative deviation from the target composition is also small (<3%) for the primary elements. However, the Al and Mn doping in the coatings is considerably smaller than in the target, which we attribute to scattering in the gas phase and preferential sputtering from the growing coating, due to the low mass of these elements.

Fig. 1(a) shows typical XRD results from a 12 μm thick C276 coating on 4140 steel. The four spectra are from an as-deposited sample and from samples annealed for 1 h at 600 °C, 700 °C, and 800 °C as labeled. The as-deposited spectrum shows all peaks that are expected for an fcc crystal structure, indicating some degree of random orientation. The intensity of the 111 reflection is highest, with the intensity of the 200, 220, 311, and 222 peaks being 17, 231, 33, and 73 times weaker. For a perfectly randomly oriented polycrystalline solid, the expected ratio of 111 to 200 would be 3.7:1 [11], indicating a 111 preferred growth orientation in the as-deposited condition.

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\[ E = 205 \text{ GPa} \]

\[ \nu = 0.33 \]

Fig. 1. XRD (a) overview scans and (b) detailed scans around the 111-reflections, from a C276 alloy coating as-deposited, and annealed at $T_a = 600$ °C, 700 °C, and 800 °C. The vertical lines in (a) correspond to the expected peak positions for a bulk C276 alloy and $d$ indicates the grain size determined from the peak width. The vertical lines in (b) indicate the measured positions of the primary and secondary 111 peaks.
lattice constant of the coating of 0.3615 nm, which is justified by the coating composition being relatively close to the known C276 alloy and the expected relatively weak composition dependence of the lattice constant. This tensile stress is indicative of a slightly columnar microstructure. Increasing ion irradiation through higher bias or increased current density may result in a denser structure and compressive residual stress, which is desirable for optimized corrosion resistance.

The spectrum from the 600 °C annealed specimen exhibits the same reflections, with a slight reduction in the 111:002 intensity ratio from 17 to 14, indicating some recrystallization and development of a more random orientation. This trend continues with annealing at 700 °C and 800 °C with a further reduction in the intensity ratio to 10 and 4, respectively, where the latter value is close to the ICDD value of 3.7, indicating recrystallization and nearly perfect random orientation for the coating annealed at 800 °C. The 111 peak width at half maximum of the as-deposited and annealed specimens are nearly identical, 0.232°, 0.195°, 0.184°, and 0.218°, corresponding to average grain sizes of 37, 44, 46, and 39 nm, respectively, as determined using the Scherrer formula after accounting for instrumental broadening. Annealing also causes shifts in all XRD peaks. This is illustrated more clearly in Fig. 1(b) for the 111 reflections. The plot shows the logarithm of the intensity over a narrow 2θ range of 42.2°–44.5°. The 111 peak position shifts from 43.36° for the as-deposited specimen to 43.48°, 43.53°, and 44.02° for the sample annealed at 600 °C, 700 °C, and 800 °C, respectively. This peak shift corresponds to a decrease in the out-of-plane lattice constant from 0.3608 ± 0.0003 to 0.3603 ± 0.0002, 0.3601 ± 0.0002, and 0.3563 ± 0.0002 nm, as determined by analyzing the peak positions for all reflections, that is, the 111, 002, 220, 311, and 222 reflections. The lattice constant decrease could, in principle, be attributed to an increase in the tensile stress. However, spatial composition fluctuations in the annealed coatings (presented below) as well as the asymmetric XRD peak shape for T_a = 700 °C and the formation of a discrete secondary peak for T_a = 800 °C suggest that these shifts are due to compositional segregation. In particular, the 111 peaks of the samples annealed at 700 °C and 800 °C exhibit a shoulder and discrete peak, respectively, labeled as “secondary peak” in Fig. 2. These secondary peaks at 2θ = 43.2° for 700 °C and 42.57° for 800 °C are 5× and 4× less intense than the main peaks at 43.53° and 44.02°, and the corresponding out-of-plane lattice parameters of 0.3626 and 0.3686 nm are 0.7% and 3.4% larger than the values from the main peaks and 0.5% and 2.2% larger than the lattice parameter from the as-deposited sample. We attribute this secondary phase with a larger lattice constant to Cr-, Mo-, and W-rich precipitates, which form within the Ni-based matrix during annealing. This segregation causes the remaining major- ness test indent, which is intentionally located approximately in the middle between coating surface and interface, and was done on this sample after sample annealing and polishing but prior to the Nital etch. The indent exhibits the characteristic elongated parallelogram shape, replicating the Knoop indenter. Fig. 2(b) shows the edge of the same specimen. The gray contrast indicates an oxide scale that has formed during annealing on the right edge of the steel. In contrast, the top surface of the steel that is covered with the C276 coating shows no indication of degradation, illustrating the effectiveness of the coating in protecting the underlying substrate from high-temperature oxidation.

Fig. 3 is a plot of the measured hardness of an as-deposited and annealed C276 coating. All data in the plot are from the same 12-μm-thick coating, which was cut into multiple specimens that were, prior to hardness measurements, exposed to different annealing treatments, including annealing at 600 °C, 700 °C, and 800 °C for 1 h, followed by quenching (q) or slow furnace cooling (fc), as labeled. The error bars in the plot correspond to the standard deviation determined
from 5 to 6 individual indentation measurements taken from each specimen. The hardness of the as-deposited coating is 6.2 ± 0.3 GPa. This is four times higher than the reported range of 1.5–1.9 GPa for annealed bulk C276 [12], and nearly twice as high as H = 3.4 GPa, the value for heavily cold worked bulk C276 [13]. The coating is also two times harder than the typical hardness of 4140 high strength low alloy steel of 2.6–3.7 GPa [14]. The large hardness in the as-deposited condition is attributed to Hall–Petch strengthening, as discussed in the next section. The measured hardness of the annealed specimens ranges from 7.3 to 8.5 GPa, which corresponds to a 15–40% increase over the as-deposited value. Differences in the hardness between different annealing temperatures, times, and cooling procedures are comparable to the experimental uncertainty, so that no clear trends can be detected from the data in Fig. 3 regarding how specimen size affects the experimental uncertainty so that no clear trend can be detected from the data in Fig. 3 regarding how annealing parameters affect the coating hardness. Elastic modulus, E, for the as-deposited, 600 °C(fcc), 700 °C(fcc), and 800 °C(fcc) were measured to be 240 ± 60, 210 ± 40, 250 ± 50, and 250 ± 80 GPa, respectively. The average values are in agreement with the expected E = 205 GPa but as with the hardness of annealed specimens, all values lie within the experimental uncertainty so that no clear trend can be detected with annealing parameters.

Fig. 4 shows Auger electron spectroscopy results from a C276 alloy coating cross-sectional specimen, which was annealed at 800 °C and furnace cooled. The plot in Fig. 4(a) shows the ratio of the measured Ni-to-Cr intensity I_{Ni}/I_{Cr} vs position, and Fig. 4(b) is the corresponding secondary scanning electron micrograph where the red line indicates the position used for the Auger line scan. The contrast in Fig. 4(b) is attributed to the surface topography caused by differential polishing of domains with different hardness. For comparison, the inset in Fig. 4(a) shows the measured I_{Ni}/I_{Cr} for an as-deposited specimen. The Ni and Cr intensities are chosen for this analysis because these two elements have the highest concentration in C276, while the lower concentration elements Mo, Fe, Co, and W do not yield sufficiently intense Auger peaks for accurate quantification. The line scan from the as-deposited sample was obtained from 200 points along a 4 μm line, using a 10 kV, 10 nA electron beam with a 20 nm spot size. As shown in the inset, the composition is essentially uniform across the sample with an average I_{Ni}/I_{Cr} = 1.96. In contrast, the line scan from the annealed specimen, which consists of 256 points along 1.79 μm obtained with a 20 kV, 1 nA electron beam with a spot size of 7 nm, indicates considerable concentration variations. In particular I_{Ni}/I_{Cr} varies from a minimum of 0.39 to a maximum of 2.7. This compositional variation indicates phase segregation during annealing.

Fig. 5 shows results from an EDS line scan analysis, which is done to obtain higher quantitative compositional accuracy than from the Auger analysis, however, at a lower spatial resolution. The plot shows the measured concentration of Ni, Cr, and Mo at 500 points along a 6-μm-long line parallel to the substrate surface in the middle of a C276 coating, which was annealed at 800 °C followed by cross-sectional specimen preparation using a focused ion beam. The measured Fe, Co, and W concentrations do not exhibit significant fluctuations beyond the noise level and are not plotted. All three measured elements, Ni, Cr, and Mo, exhibit considerable spatial fluctuations within the 6 μm plotted in Fig. 5. For example, the Ni concentration varies from 50 to 67 at.%, while the measured noise level, as determined from the intensity variations of neighboring points, is only 2%. The measured Ni:Cr ratio fluctuates from a minimum of 1.7 to a maximum of 4.5, while Ni:Mo ranges from 3.2 to 10.5. In order to do a first-level lateral length scale analysis, we add the Cr and Mo concentrations and determine the Ni:(Cr + Mo) ratio, which fluctuates from a minimum of 1.2 to a maximum of 3.0. We define regions with Ni:(Cr + Mo) ≤ 1.5 or ≥ 2.5 as Ni-poor and Ni-rich regions, respectively. The Ni-poor regions are indicated in Fig. 5 by dashed red vertical lines, which correspond to the positions of the region boundaries where Ni:(Cr + Mo) = 1.5. Similarly, the black vertical lines indicate Ni-rich regions.

### 4. Discussion

The primary focus of this section is to discuss the possible physical origins of the relatively high hardness of the as-deposited C276 coatings and the increase in hardness upon annealing.
4.1. As-deposited coating hardness

The measured hardness of the as-deposited coatings is 6.2 ± 0.3 GPa, which is four times higher than the reported bulk hardness of C276 [12, 13]. Hardness enhancements in thin films in comparison to bulk material of the same composition and phase is most commonly attributed to compressive stress and/or a small grain size [15,16]. We attribute the high hardness of the as-deposited C276 coatings in this study to the relatively small average grain size of 37 nm since the coatings exhibit a tensile (rather than compressive) stress of 0.7 GPa, which renders hardness enhancements due to residual stresses unlikely. The well-established Hall–Petch relation [17,18] predicts an increase in hardness with decreasing grain size, for grains larger than a critical size in the nanocrystalline regime below which an inverse relationship emerges [19,20]. The grain size of 37 nm is significantly higher than the threshold value for the inverse Hall–Petch relation reported for Ni and Ni(W) of 7.7 nm [20]. Thus, a regular Hall–Petch relation can be applied to explain the hardness of the as-deposited coatings. The Hall–Petch hardness enhancement is related to the increase in yield strength $\sigma$, which is described by $\sigma = \sigma_0 + kD^{-1/2}$, where $D$ is the mean grain size and the constants $\sigma_0$ and $k$ are the friction stress and Hall–Petch slope, respectively. For the case of Ni, $\sigma_0 = 37$ MPa and $k = 5538$ nm$^{-1/2}$ [21,22]. These values yield a predicted eight-fold increase in the yield strength from 119 MPa for large grained bulk annealed Ni to 947 MPa for 37-nm-grain refined Ni. That is, the expected Hall–Petch increase in $\sigma$ by a factor of eight is twice as high as the measured hardness enhancement of a factor of four. This difference is attributed to the fact that C276 is a high work hardening alloy, rendering comparisons of $\sigma$ and $H$ non-quantitative.

4.2. Annealed coating hardness

High hardness is a positive attribute for many applications in which wear or abrasion are prevalent. However, in many material systems, including bulk [23,24] and PVD coatings [25], the hardness associated with the nanocrystalline structure is reduced with exposure to elevated temperatures, which reduce crystalline defect densities and facilitate recrystallization and grain growth. Correspondingly, based purely on the Hall–Petch relation, annealing of the C276 coatings would lead to a reduction in hardness, consistent with the measured grain size which increases slightly from 37 to 46 nm during annealing at 700 °C for 1 h. However, the measured hardness actually increases to 7.6 GPa. The residual stress in the annealed coatings cannot account for this trend since the stress after annealing is slightly more tensile than for the as-deposited coating. Also, indentation measurements on slowly furnace-cooled coatings show comparable hardness values as quenched samples, indicating that the increased hardness after annealing is not due to the development of a super-saturated solid solution during rapid cooling. Third, the C276 alloy cannot form Ni$_3$M strengthening precipitates as common in conventional Ni-based superalloys because the C276 does not contain sufficient Ti and/or Al for precipitate formation.

We attribute the increase in the hardness during annealing of the C276 coatings to the formation of precipitates rich in Mo and Cr. This is supported by the XRD data which shows a splitting of the peaks for annealed specimen. The formation of zones significantly enriched or depleted in Cr and Mo result in larger and smaller lattice parameters, and therefore XRD peak shifts to the left and right, respectively. The Auger results from annealed samples clearly show compositional variations with alternating Ni- and Cr-rich regions, and the EDS results support the formation of alternating regions both depleted and enriched in Cr and Mo in comparison to the base C276 alloy.

Although C276 is not a typical precipitation strengthening alloy, several studies have been conducted on both C276 and the similar C-22 alloy with respect to the age hardening behavior undergoing a variety of heat treatments [26–28]. In Ref. [26], researchers report a ~15% hardness increase during heat treatment. In addition, they find that the hardness plateaus after a certain time period with no further hardening effect with continued aging. This general trend is in good agreement with the results in our study. However, Ref. [26] uses a higher annealing temperature of 850 °C, and annealing for up to 250 h, with a high hardness being reached after ~100 h. In contrast, our study indicates an increase in $H$ already for $T_a = 600$ °C, and that precipitation of secondary phases occurs at grain boundaries in as little as 1 h. The much faster hardness increase for our coatings is attributed to the 2,500 × finer grain size, on the order of 40 nm versus 100 μm for the bulk alloy studied in Ref. [26]. Similarly, Ref. [27] reports a 15–20% increase in strength during aging of bulk C276 for 100–1000 h at 500 °C. The strengthening has been attributed to a short range ordering reaction from a disordered fcc lattice into an ordered Ni$_3$(Cr, Mo) superlattice. Thus, similar to Ref. [26], the aging time is much larger for these bulk samples than for our coatings. We attribute the accelerated age hardening behavior of the coatings in this study to the much finer grain size and associated shorter diffusion length to grain boundaries as well as the larger volume fraction consisting of grain boundaries, resulting in a rapid hardening response during annealing for PVD deposited C276. This unforeseen age hardening effect has positive implications on the utility of these coatings since maintaining mechanical strength at elevated temperatures is of vital importance for many applications.

5. Conclusions

C276 coatings were deposited by plasma enhanced magnetron sputtering on 4140 carbon steel and subsequently annealed for 1 h at temperatures of 600 °C, 700 °C, and 800 °C. The coatings exhibit a face centered cubic nanocrystalline structure with grain size ranging from 37 to 46 nm. The as-deposited coatings are 4 × harder than the bulk C276 alloy, while annealing causes an additional 15%–40% increase in $H$. The high as-deposited hardness is attributed to the small grain size while the hardening during annealing is due to the formation of finely dispersed phases significantly enriched in Cr and Mo. The age hardening behavior is much accelerated compared to bulk C276 due to the fine grain size. The coatings have potential for use as a low-cost, higher strength replacement for bulk C276 alloy components when used in conjunction with plain carbon steel alloys.

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References


