



Article Rapid Alloy Surface Engineering through Closed-Vessel Reagent Pyrolysis

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Abstract: For rapid surface engineering of Cr-containing alloys by low-temperature nitrocarburization, we introduce a process based on pyrolysis of solid reagents, e.g., urea, performed in an evacuated closed vessel. Upon heating to temperatures high enough for rapid diffusion of interstitial solute, but low enough to avoid second-phase precipitation, the reagent is pyrolyzed to a gas atmosphere containing molecules that (i) activate the alloy surface by stripping away the passivating Cr_2O_3 -rich surface film (diffusion barrier) and (ii) rapidly infuse carbon and nitrogen into the alloy. We demonstrate quantitatively that this method can generate a subsurface zone with concentrated carbon and nitrogen comparable to what can be accomplished by established (e.g., gas-phase- or plasma-based) methods, but with significantly reduced processing time. As another important difference to established gas-phase processing, the interaction of gas molecules with the alloy surface can have auto-catalytic effects by altering the gas composition in a way that accelerates solute infusion by providing a high activity of HNCO. The new method lends itself to rapid experimentation with a minimum of laboratory equipment.

Keywords: alloy surface engineering; colossal supersaturation; nitrocarburization; reagent pyrolysis; auto-catalytic effect

1. Introduction

The mechanical behavior and the corrosion resistance of a broad spectrum of Crcontaining structural alloys can be substantially improved by infusing concentrated interstitially dissolved carbon or nitrogen through the alloy surface at *low* temperature [1–9]. "Low temperature," in this context, refers to temperatures at which metal atom diffusion is effectively frozen over the processing time, such that, despite typically low equilibrium solubility limits of carbon and nitrogen, the infused solute atoms cannot precipitate as metal nitrides or carbides. On the other hand, since the diffusivity of interstitially dissolved atoms is comparatively high at low temperatures, the processing temperature can still be high enough to enable the solute to diffuse into considerable depth *z* and form a subsurface zone ("case") of concentrated solute level within a technically feasible processing time. The result is a graded subsurface diffusion profile with maximum nitrogen- or carbon concentrations that can reach $\approx 10^5$ times the equilibrium solubility limits at room temperature, corresponding to a "colossal supersaturation" with interstitial solute.

From a technical point of view, it is desirable to (i) maximize the fraction *X* of interstitial solute at each depth *z* below the surface (while avoiding precipitation), (ii) minimize the processing time τ_p , and (iii) maximize the mean depth \overline{z} of the interstitial solute below the alloy surface. In the literature, the latter is often loosely characterized as "case depth" or "thickness" ζ of the infused layer, which is physically incorrect because a diffusion profile does not have a sharp depth. To design a process with high efficiency, from a fundamental point of view, there are three distinct components to consider:



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- 1. The chemical potential of solute at the alloy surface.
- 2. The "transparency" of the surface for the interstitial solute.
- 3. The mobility of the solute in the alloy.

To provide a driving force for infusion, the process needs to deliver solute into the alloy surface with a chemical potential higher than that directly below the surface. Controlling the chemical potential at the surface is probably the most complex component and can be influenced by the largest variety of processing parameters. For example, solute atoms can be provided by a gas atmosphere, a salt bath, a solid–solid interface, or a plasma. In addition to primary processing parameters, catalytic or reactive responses of the particular alloy surface may influence the gas, salt, or plasma composition at the alloy surface—and thus the chemical potential of the solute and the driving force for infusion.

The transparency of the surface to solute atoms may be limited by microscopic mechanisms required for acquiring solute atoms from the environment, a surface layer of passivating oxide, or a "Beilby" layer [10,11], i.e., a layer of high defect density as generated by surface machining. The process of increasing surface transparency by removing such obstacles is known as "surface activation." This can occur in various ways, e.g., by chemicalor plasma etching, and it can occur just at the beginning or continuously throughout the entire infusion process [7–9,12–14].

The mobility of the solute in the alloy generally depends on the local solute concentration. For a given mobility, the transport rate of interstitial solute increases with the local gradient of the chemical potential. For the usual description of the flux density as the product of the concentration gradient with a diffusion coefficient (Fick's First "Law"), previous experimental work has revealed that the diffusion coefficients D_C , D_N of carbon and nitrogen in austenite strongly increase with the local atom fractions X_N , X_C , respectively [15–17]. For a given alloy composition, the main parameter through which D[X] can be controlled is the specimen temperature T_s .

For technical applications, it is most practical to provide the solute from a gasphase at atmospheric pressure (0.1 MPa). Building on this approach, Christiansen and Somers [18,19] have reported an elegant method where the alloy work piece is placed in the stream of a gas mixture consisting of a carrier gas and gaseous products originating from pyrolysis of a solid reagent while heating from room temperature T_0 to a maximum temperature of e.g., $T_{\text{max}} = 710 \text{ K} (440 \,^{\circ}\text{C})$ within a processing time of e.g., 2.7 ks (45 min). Upon reaching T_{max} , the article is cooled to room temperature in Ar within e.g., 0.6 ks (10 min) [18,19]. It was found that the gas mixture resulting from pyrolysis can effectively both activate the alloy surface and provide carbon and nitrogen to diffuse into the alloy. Although this "open-vessel" process described by Christiansen and Somers produced good results, the exact conditions at the specimen surface are difficult to infer and depend on many parameters. Especially since the reservoir of reagent is changing in time, the composition of the gas and the activities of its components at the specimen surface are not easy to control. Neither is the streaming velocity field at the specimen surface. Moreover, with that method, it is possible that the reagent and the specimen are at different temperatures, i.e., $T_r \neq T_s$. Therefore, the results obtained with a specific setup may be difficult to reproduce with another setup and scientific studies may be compromised by uncontrolled parameters.

The primary goal of the work reported here was to establish a new method for performing laboratory-scale low-temperature carburization, nitridation, or nitrocarburization by pyrolysis of solid reagents under simple and flexible, but, at the same time, welldefined and easily reproducible experimental conditions. Building on our earlier work on nitridation of Ti-base alloys [20,21] and nitrocarburization of Co–Cr–Mo alloys [22,23], our approach, illustrated in Figure 1, consists of *encapsulating* the reagent and the alloy workpiece in an inert container—specifically, a fused-silica ampoule. With this new "closedvessel" approach, there is no net gas flow and all components are at the same temperature, which we denote as the processing temperature $T_p = T_r = T_s$. Another important difference is that this process can operate over a broad range of well-defined and adjustable pressure, which can be controlled via the effective reagent concentration c_r in the ampoule, e.g., expressed as number ν of moles per free ampoule volume V, Figure 1.



Figure 1. Concept of low-temperature nitrocarburization of alloys by closed-vessel reagent pyrolysis, the "Encapsulation Method" [22].

Another goal of our work was to analyze the pyrolysis products of the solid reagent (urea) and to understand which molecular species are key for nitrocarburization.

For brevity, in the following, we denote the approach of low-temperature nitrocarburization of alloys by reagent pyrolysis in a closed vessel as the "Encapsulation Method". In this article, we demonstrate the efficacy and potential of this method for exploiting and exploring pyrolysis of solid reagents for the purpose of alloy surface engineering by low-temperature infusion of carbon and nitrogen.

2. Material and Experimental Methods

The specimens for this work were as-machined Swagelok[®] ferrules. Figure 2 depicts the shape and size of a ferrule. The ferrules we used have an outer diameter $\emptyset \approx 10$ mm. These parts are used in gas tubing to enable gas-tight tube connectors ("fittings"). They are made from AISI-316L (austenitic Fe–Cr–Ni stainless steel containing Mo), but with a somewhat (1.05 times) higher Cr atom fraction and a significantly (1.2 times) higher Ni atom fraction than standard AISI-316L—within the allowed compositional range of AISI-316L. More precisely, the specification requires mass fractions $M_{\rm Cr} \geq 0.170$ and $M_{\rm Ni} \geq 0.120$ for Cr and Ni, respectively, while typical values for standard AISI-316L are $M_{\rm Cr} \geq 0.165$ and $M_{\rm Ni} \geq 0.105$. Table 1 shows the composition of the Ni- and Cr-rich AISI-316L by *atom* fractions. These specimens were chosen as they are produced under extremely well controlled conditions. This means that property changes observed after nitrocarburization can uniquely be attributed to the latter, rather than e.g., be caused by unknown changes in the microstructure between different samples from a less-defined material.

Table 1. Composition of the Ni- and Cr-Rich AISI-316L by Atom Fractions X.

Fe	Cr	Ni	Mn	Si
0.643	0.186	0.118	0.020	≤0.015
Мо	Ν	С	Р	S
0.012	≤0.0039	≤ 0.0014	≤ 0.0008	≤ 0.0005



Figure 2. Ferrule, made of a Ni-rich and Cr-rich austenitic stainless steel AISI-316L.

To establish the novel method of low-temperature infusion of interstitial solute, the first goal of our work, the ferrule specimens—after cleaning by ethanol and airdrying—were placed into a half-open fused-silica ampoule together with $CO(NH_2)_2$ (urea) powder as reagent. As urea is hygroscopic, it was prepared by baking at 370 K (97 °C) for 3.6 ks (1 h) and stored in a desiccator prior to usage. The open side of the tube was connected to a rotary pump via a PVC tube and sealed using an acetylene–oxygen torch while being evacuated by the pump to a residual gas pressure within (1..2) Pa (".." denotes a continuous range). After sealing the ampoule, infusion of interstitial solute into the alloy was accomplished by heat-treating the ampoule in a tube furnace. Several heat-treating schemes were tested, all of them with keeping the ampoule ("a"), the reagent ("r"), the gas ("g"), and the specimen ("s") at the same temperature $T = T_a = T_r = T_g = T_s$ (Figure 1).

Initial experiments were carried out at a single specimen/reagent temperature $T_p = 720 \text{ K}$ for a processing time $t_p = 7.2 \text{ ks}$ (2 h). Then, we discovered that better results are obtained by a two-step process with $T_{p_1} = 620 \text{ K}$ (350 °C) for $t_{p_1} = 3.6 \text{ ks}$ (1.0 h) followed by $T_{p_2} = 720 \text{ K}$ (450 °C) for $t_{p_2} = 7.2 \text{ ks}$ (2.0 h). The results presented in this work refer to this particular two-step process.

The amount of urea was chosen such that—for the given volume of the ampoule—the net pressure p_r of decomposition products was 0.5 MPa (5 atm). Typically, in a fused-silica ampoule with a radius of 5.5 mm and a length of ≈ 200 mm, this requires 0.13 g of urea, corresponding to 2.2 mmol.

The pressure that develops under these conditions was *measured*. Specifically for this purpose, we designed an experimental procedure that involves heating an equivalent amount of urea in a cylindrical metal container closed by an initially planar, $\approx 0.5 \,\mu\text{m}$ thick sheet of an Al-alloy, held by a flange. The gas pressure that builds up during urea pyrolysis can then be determined from the plastic bulging of this sheet [24].

At the end of the two-step process, the ampoule was cooled in air and broken to extract the specimens. The effective diffusion depth of interstitial solute was experimentally determined and compared in three different ways from polished cross-sections: (i) indirectly by observing the *apparent* case depth ζ_{LOM} in light-optical metallographs after etching with a specific reagent, (ii) indirectly as the *apparent* case depth ζ_{HV} apparent in Vickers hardness–depth profiles, recorded at 3 different locations under a load of 25 g with a dwell time of 10 s, and (iii) directly from cross-sectional concentration-depth profiles obtained by AES (Auger electron spectrometry) performed by SAM (scanning Auger microprobe). The results were then calibrated by predetermined relative sensitivity factors for each element to quantify element fractions. In addition to these characterization techniques, we employed XRD (X-ray diffractometry) using a Bruker Discover D8 equipped with a Co-K_{α} source (wavelength $\lambda = 0.1789$ nm) in Bragg–Brentano setting.

To obtain further insight into the chemical reactions that take place during an ampoule process, we conducted complementary STA (simultaneous thermal analysis) measurements. These were performed in a Netzsch STA 449 F3 Jupiter paired with a Perseus system, consisting of a heated transfer pipe to a Bruker Alpha FTIR unit with a gas cell heated to $473 \text{ K} (200 \degree \text{C})$, located directly above the furnace.

The urea reagent powder, 8.2 mg, was contained in crucibles with *venting* lids. To study the pyrolysis products absent an alloy specimen, we employed crucibles of inert

material—Al₂O₃—with a volume of 87 μ L. To study the pyrolysis products in the presence of a AISI-316L specimen and to investigate the nitrocarburization it accomplished by the pyrolysis products, we pyrolyzed the urea, 8.7 mg, in crucibles of AISI-316L stainless steel with a volume of 27 μ L. In other words, the AISI-316L crucibles not only served to contain the reagent powder, but also as an *alloy specimen* to be treated by nitrocarburization.

The lids of both crucibles had central holes to allow gas escape. Both measurements followed a 83 mK/s heating rate during which TGA (thermogravimetric analysis), DSC (differential scanning calirometry), and GP-FTIR (gas-phase Fourier-transform infrared spectrometry) measurements were acquired. The instrument furnace was evacuated and purged three times before the start of each sample run. Dry N₂ gas with a total flow rate of 1.2 mL/s was used to purge the system throughout the testing process. The pressure in the furnace was 0.1 MPa during testing.

The GP-FTIR spectra were extracted at temperatures showing the highest absorbance for each thermal event. Traces following wavenumbers for both NH_3 (at 965 cm⁻¹) and HNCO (at 2283 cm⁻¹) were also extracted for comparison with the TGA and DSC measurements.

3. Results

Figure 3 shows a microhardness–depth profile h[z] of a nitrocarburized AISI-316L ferrule. Hardness values of "case" and "core" regions were evaluated and related to the indentations on a polished cross-section to bring out the differences. Two regions are revealed on the etched indented cross-section, the metallographic image of which shows an etch-resistant bright "case" layer and the microstructure of the "core". On the right side of h[z], at a depth $h \ge 35 \,\mu$ m, to which no significant amounts of interstitial solute could diffuse within the processing time, the diagram displays a hardness range of $h = (350 \pm 50) \,\text{HV0.025}$. This level of hardness agrees well with the gray data points shown at the bottom left of the diagram, which were obtained from a *non-treated* (as-received) ferrule. The gray data points do not indicate any significant slope of h[z], especially no increased hardness near the surface (as it might be expected from machining). Accordingly, the increased hardness after nitrocarburization (red data points) is the sole result of the treatment, not influenced by any (e.g., machining-induced) increased near-surface hardness prior to the treatment.

Compared to the base hardness $h = (350 \pm 50)$ HV0.025 exhibited by the non-treated ferrule and in the core of the nitrocarburized specimen, the hardness near the surface of the nitrocarburized specimen, at $z \approx 5 \,\mu$ m, was measured to be (900 ± 20) HV0.025. With increasing depth *z*, i.e., from the surface deeper into the nitrocarburized specimen, the hardness gradually decreases, as expected from the graded solute-fraction–depth profile shown in Figure 5. Extrapolating the graph displayed within the *z* interval (5..10) μ m to the region directly below the surface (where *h* cannot be reliably measured) yields h[0]within (1100 ± 100) HV0.025. Extrapolating to $h = h_b$ yields an apparent case thickness of $\zeta_{HV} \approx 12 \,\mu$ m. Compared to the symmetrical pyramid indents at the "core" region, the indentations around the "case" region all exhibit asymmetry with regard to the vertical indent diagonal plane. This asymmetry can be explained from the gradation of the solute profile and the related gradation of the hardness profile, implying reduced hardness on the right side of the indents.



Figure 3. Microhardness–depth profile h[z] recorded in the region of the solute-rich "case" and the region of the non-infused "core." Hardness values (red data points) in the two regions of the nitrocarburized AISI-316L are highlighted and related to the indents seen on a light-optical micrograph of the polished cross-section of the alloy specimen. The etched cross-section at the same location displays the "case" and "core" regions. The gray data points at the bottom left were obtained from a non-treated (as-received) AISI-316L ferrule.

Figure 4 shows a light-optical micrograph from part of a color-etched cross-section of a nitrocarburized AISI-316L ferrule. Parallel to the surface, the image features a bright conformal layer. This layer is the "case", i.e., the solute-rich zone under the alloy surface generated by the infusion process. More precisely, this is the subsurface zone in which nitrocarburization has introduced levels of carbon or nitrogen that made the material resistant to the specific etchant and etching conditions: As diffusion produces *graded* composition–depth profiles, the apparently sharp boundary to the alloy core does not correspond to the end of the diffusion profile. Rather, the *apparent* case thickness ζ_{LOM} depends on details of the metallographic etching. For example, work by Sun [25] indicates that a carbon fraction $X_{\rm C} > 0.015$ is necessary to see the benefits of interstitially dissolved carbon on corrosion resistance in aqueous NaCl solution. In Figure 4, $\zeta_{\rm LOM} = (10.9 \pm 0.4) \,\mu$ m.

Figure 5 presents fraction–depth profiles obtained by SAM from a nitrocarburized, polished, and cross-sectioned AISI-316L specimen. The solid curves are Bézier curves intended to estimate the true nitrogen and carbon fractions in solid solution, accounting for nitride formation (see below) and excessive noise in the SAM data. (Owing to differentiation of the original—noisy—signal, noise in SAM data mainly increases background and scatter in regions of *low* signal [26]). The dashed curve displays their sum, i.e., the total fraction of interstitial solute as a function of depth.



Figure 4. Light-optical micrograph of a color-etched cross-section of a nitrocarburized AISI-316L ferrule.



Figure 5. Fraction–depth profiles of nitrogen and carbon in an AISI-316L ferrule, obtained by SAM. The solid curves are Bézier curves intended to estimate the true fractions of carbon and nitrogen in solid solution, accounting for nitride formation and artifacts of SAM. The dashed curve displays their sum, i.e., the total fraction of interstitial solute as a function of depth.

The SAM data reveal a non-trivial depth-distribution of carbon and nitrogen with the following features:

- 1. A nitrogen-rich outer layer (directly below the surface) with a local thickness $\zeta_{\text{SAM-N}} = 8 \,\mu\text{m}$. In this region, the carbon fraction X_{C} exhibits a positive slope, $dX_{\text{C}}/dz > 0$, corresponding to "uphill" diffusion.
- 2. A carbon-rich inner layer (directly below the outer layer) with a local thickness $\zeta_{SAM-C} = 8 \,\mu\text{m}$. The bottom of this layer corresponds to the bottom of the case, i.e., $\zeta_{SAM} = \zeta_{SAM-C}$.

- 3. Evaluating $\xi_i := \int_0^\infty X_i[z] dz$, i = C, N for the Bézier curves X_i in Figure 5 yields a ratio $X_N/X_C \approx 1.4$, indicating that the specimen assimilated correspondingly more nitrogen than carbon.
- 4. Although high X_N apparently limits the level of X_C , the total interstitial solute fraction $X[z] = X_C[z] + X_N[z]$ (dashed line in Figure 5) decreases monotonously with *z*—although the graph exhibits a small plateau in the transition region where the X_C and X_N cross.

The border between the outer, nitrogen-rich case and the inner, carbon-rich material manifests itself as a dark "line" in the LOM (light-optical microscopy) micrograph of Figure 4 (arrowed). One possible explanation for this observation is that the dark line is a groove caused by preferential attack of the metallographic etchant. As total solute fraction ($X_{\rm C} + X_{\rm N}$) in this region is *higher* than in the carbon-rich region below, this would imply that etch resistance requires either $X_{\rm C}$ or $X_{\rm N}$ —not just their sum—to exceed certain thresholds $X_{\rm C}^*$ and $X_{\rm N}^*$, respectively. This conclusion would also explain why $\zeta_{\rm LOM} < \zeta_{\rm SAM}$. Comparing $\zeta_{\rm SAM}$ in Figure 5 with $\zeta_{\rm LOM}$ in Figure 4 suggests $X_{\rm C}^* > 0.05$. Another potential explanation for the observed dark line between the nitrogen-rich and the carbon-rich region could be grooving or step formation by creation of a local galvanic element.

The case depths ζ we observed in a multitude of experiments exhibits significant variation (e.g., compared a currently used industrial low-temperature carburization process [2]). For ζ_{SAM} , in particular, we observed a (sample) standard variation $s/\sqrt{Z} = 0.2 \,\mu\text{m}$ when measuring various locations in several samples.

In any of its forms (ζ_{HV} , ζ_{LOM} , ζ_{SAM}), the "case depth" sensitively depends on the specific shape of the fraction–depth profile at its tail (where X_N , $X_C \rightarrow 0$. This means that the exact value for the case depth is determined by the spatial distribution of only a small fraction of solute atoms. A more robust measure is the *mean solute depth*

$$\overline{z} := \frac{\int_0^\infty z X[z] \, \mathrm{d}z}{\int_0^\infty X[z] \, \mathrm{d}z} \,. \tag{1}$$

Corresponding evaluation of the Bézier curves in Figure 5 yields the following mean depths of carbon, nitrogen, and both interstitial solutes combined:

$$\overline{z}_{\rm C} = 9.2\,\mu{\rm m},\tag{2}$$

$$\overline{z}_{\rm N} = 3.4\,\mu{\rm m},\tag{3}$$

$$\overline{z} = 5.8\,\mu\text{m.} \tag{4}$$

Figure 6 shows an X-ray diffractogram recorded from a nitrocarburized AISI-316L specimen in Bragg–Brentano setting. For comparison, the plot also shows a corresponding diffractogram of *non*-treated AISI-316L. In the $2\theta_B$ of Figure 6, the A1 (FCC, face-centered-cubic) structure of the austenite generates two peaks, labeled as (111) γ and (200) γ . For the Co-K_{α} radiation employed in this work, the X-ray penetration depth is within (6..16) µm for absorption within the range (80..99) %. This implies that the diffractogram of the nitrocarburized specimen displays significant information from depths *z* within the entire range [0, ζ_{SAM}]. Regions closer to the surface contribute higher intensity than regions deeper below the surface. Based on the SAM fraction–depth profile of the nitrocarburized material in Figure 5, the features of this diffractogram can be interpreted as follows:

- 1. The two peaks of highest intensity, labeled $(111) \gamma_N$ and $(200) \gamma_N$, originate from the outer case, which is rich in nitrogen. Compared to the reference peaks from non-treated material, these peaks exhibit a pronounced shift to smaller $2\theta_B$. This indicates a corresponding increase of the lattice parameter, caused by interstitially dissolved nitrogen expanding the interatomic spacings between the metal atoms.
- 2. The two peaks of third and fourth highest intensity, labeled $(111) \gamma_{\rm C}$ and $(200) \gamma_{\rm C}$, originate from the inner case, which is rich in carbon. Their intensities are lower than those of the corresponding peaks from the outer case because the inner case is deeper

below the surface. The peaks from the inner case also exhibit a shift to lower $2\theta_B$ versus the corresponding values for non-treated material. However, the peak shift is smaller because (i) the maximum carbon fraction in the inner case is smaller than the maximum nitrogen fraction in the outer case and (ii) interstitially dissolved carbon is less effective than nitrogen in increasing interatomic spacings between the metals atoms [27,28].

- 3. The peaks (111) γ_N , (200) γ_N , (111) γ_C , and (200) γ_C are not mirror-symmetric. They exhibit shoulders on the right, i.e., towards higher $2\theta_B$, because in both the outer and the inner case the regions of highest interstitial solute fraction are closest to the surface, i.e., contribute higher diffracted intensity than regions of lower solute fraction in greater depth *z*.
- 4. The diffractogram from the nitrocarburized material also exhibits peaks with low intensity at the positions of the $(111) \gamma$ overlapped with the corresponding peaks from the non-treated material. These peaks originate from the non-infused material at depths $z > \zeta_{SAM}$, proving that diffractogram samples over the entire depth range $[0, \zeta_{SAM}]$ and beyond.
- 5. No additional peaks are observed, indicating that second phases—if formed at all—have a negligibly small volume fraction (<0.05).



Figure 6. X-ray diffractograms of nitrocarburized (red graph) and non-treated (blue graph) AISI-316L ferrules, recorded with Co-K_{α} radiation in Bragg–Brentano setting. *I*: Relative intensity, θ_B : Bragg angle.

To address the second goal of our work, identifying the pyrolysis products of the reagent and their role in nitrocarburizing AISI-316L, we performed GP-FTIR under N₂ at ambient pressure. These experiments were carried out in two different forms: (i) Pyrolyzing urea in an inert (Al₂O₃) crucible. (ii) Pyrolyzing urea in a crucible of AISI-316L. This setup allowed us to study how the resulting solute–depth profiles X[z] correlate with specific processing parameters, but also how the presence of the alloy surface impacts the spectrum of molecular species in the gas atmosphere.

For the two different crucibles, Al₂O₃ and AISI-316L, Figure 7 displays GP-FTIR data for NH₃ (ammonia) and HNCO (cyanic acid), respectively, as well as complementary TGA mass-change and DSC heat-flux data. Regions I, II, III, and IV are similar to those noted by Schaber et al. [29], but with adjustments to encompass the important thermal events observed. Region I, $T_{\rm I} = (406..490)$ K, is above the melting point and includes initial decomposition of CO(NH₂)₂ and the formation of C₂H₅N₃O₂ (biuret). Region II, $T_{\rm II} = (490..523)$ K, includes the decomposition of C₂H₅N₃O₂ and rapid formation of various aromatic compounds. Region III, $T_{\text{III}} = (523..633)$ K, indicates the beginning of primary (CNOH)₃ (cyanuric acid) decomposition. Region IV, $T_{\text{IV}} > 633$ K, is the final decomposition of other aromatic compounds formed earlier in small quantities.



Figure 7. Urea pyorolysis in AISI-316L and Al₂O₃ crucibles heated at 5 K/min under N₂. (**a**) TGA results. (**b**) DSC results; \dot{q} denotes specific heat flow. (**c**) GP-FTIR data; $I_{\rm NH_3}$ is the measured intensity of NH₃ at 965 cm⁻¹. (**d**) GP-FTIR data; $I_{\rm HNCO}$ is the measured intensity of HNCO at 2283 cm⁻¹.

The TGA data reveal that the molecular composition of the gas obtained by urea pyrolysis in the AISI-316L crucible as a function of temperature differs significantly from what is obtained in the Al_2O_3 crucible. The urea in the AISI-316L crucibles lost less mass in Regions I and II than the urea in the Al_2O_3 crucible. In the AISI-316L crucible, the urea also does not have the small, independent mass loss within Region II that accounts for some of the different mass loss in these regions in the Al_2O_3 crucible. Furthermore, the AISI-316L causes the urea to lose more mass in the decomposition observed in Region III/IV.

Like the TGA data, the DSC heat-flux data corroborate these differences. Specifically, the DSC peak for the small mass loss in Region II is not present for the urea sample in AISI-316L crucible and, likewise, the Region III/IV peak (corresponding to the larger mass loss with this sample) is larger and longer in duration in the AISI-316L crucible.

The GP-FTIR data for NH_3 and HNCO clarify the differences between these samples in different crucibles. Both samples have similar trends in the GP-FTIR traces for NH_3 and HNCO in Region I. However, in Region II, the one in AISI-316L crucible shows a larger NH_3 release and no subsequent emission like the small mass loss seen in that in Al_2O_3 crucible. The Region II in AISI-316L crucible also has a smaller HNCO emission and likewise does not have an emission for the missing mass-loss event. Region III/IV has minimal signal intensity for NH_3 in both samples. However, the urea sample in AISI-316L crucible in Regions III and IV shows a higher intensity of HNCO and longer duration than the same trace for the Al_2O_3 crucible.

4. Discussion

4.1. Efficacy of the Encapsulation Method

For the low rate at which the temperature was changed to obtain the data of Figure 7, it can be assumed that the gas atmosphere is equilibrated at each temperature, i.e., there is no retardation. The results of Figure 7 suggest that already in Step 1 of the new two-step closed-vessel low-temperature nitrocarburization process, the reagent (urea) is pyrolyzed into gas molecules that activate the alloy surface. However, the temperature $T_{p_1} = 620$ K is too low for significant diffusion of interstitial solute within t_{p_1} . Significant diffusion can only occur at $T_{p_2} = 720$ K.

Carbon- and nitrogen-fraction–depth profiles $X_{\rm C}[z]$, $X_{\rm N}[z]$ with the characteristic features of those in Figure 5 have already been observed in earlier work on nitrocarburization [18,19,30]. As seen in Figure 5, the presence of nitrogen in the austenite reduces the carbon fraction near the surface. This has been explained by nitrogen locally elevating the activity coefficient of carbon [22,31]. Therefore, although the chemical potential of carbon globally fulfills the requirement $\partial_z \mu_{\rm C} < 0$ for inward diffusion, ($\partial_z X_{\rm C} > 0$) below the nitrogen-rich near-surface zone, corresponding to an apparent "uphill" diffusion of carbon. Furthermore, as discussed in earlier work [16], the concave shape of $X_{\rm C}[z]$, $X_{\rm N}[z]$ reflects a positive concentration dependence of the respective diffusion coefficients: $\partial_{X_{\rm C}} D_{\rm C} > 0$, $\partial_{X_{\rm N}} D_{\rm N} > 0$.

To investigate the efficacy of the new two-step closed-vessel low-temperature nitrocarburization process, we compare the mean depths (2)–(4) of interstitial solute to the mean depth of carbon accomplished by an industrial low-temperature gas-phase carburization process [16].

Figure 8 presents a carbon-fraction–depth profile of AISI-316L generated by that industrial process, measured by SAM. The processing temperature of $T_p = 726$ K was practically the same as $T_{p_2} = 720$ K in the second step of the new two-step closed-vessel nitrocarburization process introduced in this article. The processing time, however, was much longer: $t_p = 137$ ks (38 h). The continuous line marked "SIM" in Figure 8 is a corresponding *simulated* profile, based on a concentration-dependent carbon diffusion coefficient obtained by Boltzmann–Matano analysis [16].

Based on the simulation shown in Figure 8 and the intermediate carbon-fractiondepth profiles $X_c[t_i]$ at intermediate time steps (not shown), Figure 9 shows how the mean carbon depth \overline{z}_C evolves during the industrial process (data marked by hollow circles and connected by a continuous line). The solid symbols in Figure 9 indicate the corresponding data (2)–(4) for the Encapsulation Method, using the two-step process. The mean depth \overline{z}_N of nitrogen is comparable to the mean depth \overline{z}_C accomplished by the industrial process in the same amount of time (7.2 ks). However, the mean depth \overline{z}_C of carbon is about 4 times the corresponding value accomplished by the industrial process. Conversely, the industrial process takes about 15 times longer to accomplish the same mean depth of carbon (dashed marker lines in Figure 9). The mean depth \overline{z}_I of both interstitial solutes combined is more than 2 times larger than \overline{z}_C after the industrial process, in which carbon reaches this mean depth only after 5 times longer processing.



Figure 8. Carbon-fraction–depth profile of an industrial low-temperature gas-phase carburization process, measured by SAM, and corresponding simulated profile, based on concentration-dependent diffusion [16].



Figure 9. Mean depth of interstitial solute versus processing time t_p . The solid data points marked by \bar{z}_N , \bar{z}_C , and \bar{z}_I refer to the Encapsulation Method, indicating the mean depth of nitrogen, carbon, and both interstitial solutes (nitrogen and carbon combined), respectively. The hollow circular data points, connected by a continuous line, show *simulated* \bar{z}_C data for the industrial process [16].

The definition (1) of the mean solute depth does not include information about the actual level (fraction, concentration) of interstitial solute. As a figure of merit that equivalently reflects solute level as well as solute depth, we define the "penetration"

$$P := \int_{0}^{\infty} z X[z] \,\mathrm{d}z \,. \tag{5}$$

Figure 10 shows *P* as a function of processing time t_p . Data points referring to the Encapsulation Method are marked by solid symbols. *P*_N, *P*_C, and *P*_I indicate *P* for nitrogen, carbon, and both interstitial solutes (nitrogen and carbon combined), respectively, after the processing time of 7.2 ks (2 h, Step 2 of the process). (No significant interstitial solute diffusion will occur during Step 1 owing to insufficient temperature). Data points marked by hollow circles, connected by a continuous line, show corresponding *P*_C data for the established industrial low-temperature gas-phase carburization process [16]. These data (shown only up to 80 ks) were obtained by simulation, evaluating (5) for the intermediate steps that lead to the simulated carbon-fraction–depth profile labeled as "Sim" in Figure 8. Comparing the data in Figure 10 confirms that the Encapsulation Method is *very* effective. The industrial process needs 4 times longer (28 ks) to accomplish the same penetration of carbon—and 6 times longer to accomplish the same total integration of interstitial solute (dashed marker lines in Figure 10).



Figure 10. Interstitial solute penetration *P*, defined in (5), as a function of processing time t_p . The solid data points marked by P_N , P_C , and P_I refer to the Encapsulation Method, indicating *P* for nitrogen, carbon, and both interstitial solutes (nitrogen and carbon combined), respectively. The hollow circular data points, connected by a continuous line, show *simulated* P_C data for the industrial process [16].

4.2. Auto-Catalytic Effect of the Alloy Surface

Earlier work of our group and others demonstrated the efficacy of NH₃ for both surface activation and infusion of nitrogen [20,21,32–34]. In addition, surface infusion of nitrogen and carbon is provided by decomposition of HNCO, (CNOH)₃, $C_3H_4N_4O_2$ (ammelide), or $C_3H_5N_5O$ (ammeline). We expect small shifts in decomposition and evaporation temperatures as well as changes in gas composition because the Encapsulation Method operates

at 0.5 MPa, while STA testing occurs at 0.1 MPa. As labeled in Figure 7, the pyrolysis of urea occurs in four major reaction regions, which have been adjusted here for clarity based on previous work [29]. Chemical equations for the following reactions can be found in Appendix A. Region I encompasses urea pyrolysis into NH_3 and HNCO according to (A1), $C_2H_5N_3O_2$ formation according to (A2), and small amounts of aromatic compound formation according to (A3)–(A6). In Region II, $C_2H_5N_3O_2$ decomposes by the reverse of (A2) into HNCO and urea (which decomposes as above or further reacts). Reactions producing the aromatic compounds occur at higher rates in this region. Furthermore, NH₃, HNCO and H_2O evolve according to (A3)–(A12). A smaller subsequent thermal event follows with the evolution of HNCO and NH_3 from the solid residue matrix. Only (CNOH)₃, $C_3H_4N_4O_2$ (ammelide), and $C_3H_5N_5O$ are noted as solids present at the start of reaction Region III. As these aromatic compounds (primarily (CNOH)₃) begin to pyrolyze, HNCO forms according to (A13). Region IV covers the conclusion of (CNOH)₃ decomposition and later melt with decomposition of $C_3H_4N_4O_2$ and $C_3H_5N_5O$ with the emission of HNCO and small amounts of NH₃, CO₂ (carbon dioxide), and H₂O. The presently reported results of urea pyrolysis in Al₂O₃ track closely with these reaction schemes from [29].

However, our data reveal significant differences between urea pyrolyzed in an *inert* Al₂O₃- and in a AISI-316L crucibles. The AISI-316L presence caused a more complete conversion of urea to (CNOH)₃ as demonstrated by the AISI-316L sample exhibiting the following features:

- A lower total mass loss in Regions I and II.
- Absence of a small mass-loss event and corresponding DSC peak in Region II.
- A larger mass loss in Region III, continuing into Region IV.
- A higher emission of NH₃ in Region II before the missing event.
- Lower HNCO emission in Region II.
- A larger HNCO emission in Regions III and IV.

Through catalytic or direct reaction with the alloy surface, more HNCO was converted to (primarily) (CNOH)₃ and less HNCO mass was lost in Regions I and II. The missing mass-loss emission event in Region II would normally be from NH₃ and HNCO leaving the solid residue. The absence of this event suggests that there was significantly less HNCO trapped in the solid residue or the reactions that would have released it did not occur in this range. The larger mass-loss event of Regions III/IV for the AISI-316L sample as well as the related HNCO emission during this stage suggests that the larger mass was primarily the (CNOH)₃ that formed in larger quantity because of the alloy surface effects.

The differences in the STA and GP-FTIR data for urea pyrolyzed in AISI-316L vs in Al_2O_3 indicate an auto-catalytic effect of the alloy surface on the spectrum pyrolysis products—or even a direct participation of surface atoms in chemical reactions. These differences in the condensed and gas phases caused by the presence of an alloy surface with the pyrolyzing reagent may provide substantial opportunities for low-temperature alloy surface engineering by solid-reagent pyrolysis. It is not yet known whether liquid phases on the alloy surface or molecular species in the gas phase contributes more to surface activation and infusion of carbon and nitrogen. In an open system, the delayed evolution of active gas species (NH₃ and HNCO) may be beneficial for both the overall treatment effectiveness and efficient reagent use because these species would be present at higher temperatures necessary for treatment instead of exhausting too early to be effective. However, the ampoule process we introduce here and analogous constant volume, closed-vessel processes largely bypass the effect of reagent decomposing too early because all pyrolysis products remain in close proximity to the alloy surface.

4.3. Model of Interstitial Infusion via the Encapsulation Method

Figure 11 shows a model of the micromechanisms underlying the rapid surface engineering of Cr-bearing alloys through closed-vessel reagent pyrolysis. Under the well-defined process parameters within the vessel, particularly a uniform temperature distribution, a controlled reagent quantity per volume of vessel, and a controlled reagent quantity per alloy surface area, ramping up the temperature initiates urea pyrolysis and the evolution of gaseous HNCO and NH₃. The pressure of in the vessel gradually increases as these species evolve. For a sufficiently slow temperature ramp, it can be assumed that the partial pressure of each species corresponds to its equilibrium value for the given temperature and solid-reagent ingot. By decomposing or modifying the passivating Cr-rich oxide film on the alloy surface, accompanied by the release of CO_2 and/or H_2O , HNCO and NH₃ activate the alloy surface (AISI-316L) for infusion of interstitial solute (carbon and nitrogen). Even though we separate the surface activation as a prerequisite step of the whole treatment in this model, the reactions may occur throughout the remainder of the process if chromium oxide should reform, keeping the surface transparent to the interstitial solute. Interaction of the pyrolysis products with the active alloy surface catalyze the formation of $(CNOH)_3$ and other aromatic species according to (A3) and (A4). These species remain present until they decompose at higher temperature. Depending on reagent content and composition, an organic film may form on the alloy surface [13]. Future work needs to show whether this film can directly provide carbon and nitrogen to diffuse into the alloy surface or first needs to decompose to gas species (e.g., HNCO), which then feed the surface with carbon and nitrogen. At the treatment temperature ($T_{p_2} = 720 \text{ K} = 450 \text{ °C}$), the HNCO and NH₃ produced by the pyrolysis reactions may adsorb at the surface and further decompose to produce atomic carbon and nitrogen that diffuse into the surface. Breakdown byproducts include CO₂, H₂O, and H₂. This model can be generalized and applied to a wide array of reagents (e.g., guanidine, GuHCl and biguanide HCl) and alloys (e.g., Al6XN, Inconel 625, Hastelloy C-22).



Figure 11. Model for surface engineering of Cr-bearing alloys by solid-reagent pyrolysis in a closed-vessel. (For clarity, minor reactions and species not shown).

5. Conclusions

The new "Encapsulation Method" introduced in this article, i.e., low-temperature nitrocarburization of alloys by closed-vessel reagent pyrolysis, is highly effective for surface engineering of structural alloys by infusing high concentrations of interstitial solute. The method allows for rapid experimentation at low cost and with a minimum of required laboratory equipment. Furthermore, it has the conceptual advantage of working with a closed-vessel system (ampoule) under well-defined conditions, which, in principle, are easy to control. This should facilitate the reproduction of experimental results. If variations in apparent case depth are observed, these may originate from the fact that the apparent case depth measured by different methods depends on rather insignificant details of the "tail" of the solute-fraction-depth profile. More robust figures of merit have been introduced in this paper, which also provide more meaningful quality parameters than "the" case depth for the success of surface engineering by infusion of interstitial solute.

For laboratory-scale experimentation, a great conceptual advantage of a closed system is the superior control of the gas composition (which can be analyzed as a function of numerous parameters in a suitable open system). Using sophisticated experimental methods we developed for this purpose, we succeeded in measuring (i) the total pressure that the products of pyrolysis build up inside the ampoule and (ii) the major constituents of the gas mixture that forms by pyrolysis of urea. The experimental results indicate that interaction of gas molecules with the alloy surface can have an auto-catalytic effect by altering the surrounding gas composition and condensed species in a way that accelerates solute infusion, especially by providing a higher activity of HNCO at high temperature.

The Encapsulation Method is substantially more effective in driving interstitial solute into the alloy than other low-temperature gas-phase diffusion processes currently used in the industry. As the latter are not limited by the availability of carbon from the gas atmosphere, the higher efficacy of the Encapsulation Method must result from better surface activation, the effect of nitrogen on the chemical potential of carbon, or enhanced mobility of the solute, particularly carbon.

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Appendix A

CO(NH ₂) ₂ (m)	\rightarrow	HNCO (g) + NH_3 (g),	(A1)
$CO(NH_2)_2 (m) + HNCO (g)$	\rightarrow	$C_2H_5N_3O_2$ (g),	(A2)
$C_{2}H_{5}N_{3}O_{2}(m) + HNCO(g)$	\rightarrow	$(CNOH)_3 (s) + NH_3 (g),$	(A3)
3 HNCO (g)	\rightarrow	(CNOH) ₃ (s),	(A4)
$CO(NH_2)_2 (m) + 2 HNCO (g)$	\rightarrow	$C_{3}H_{4}N_{4}O_{2}\ (s)+2\ H_{2}O\ (g)\text{,}$	(A5)
$C_{2}H_{5}N_{3}O_{2}(m) + HNCO(g)$	\rightarrow	$C_{3}H_{4}N_{4}O_{2}(s) + H_{2}O_{7}(s) + H_$	(A6)
$2 C_2 H_5 N_3 O_2 (m)$	\rightarrow	$(\text{CNOH})_3$ (s) + HNCO (g) + 2 NH ₃ (g),	(A7)
$2 C_2 H_5 N_3 O_2 (m)$	\rightarrow	$C_{3}H_{4}N_{4}O_{2}(s) + HNCO(g) + 2 NH_{3}(g) + 2$	H ₂ O (g),(A8)
$C_{2}H_{5}N_{3}O_{2}(m) + HCNO(g)$	\rightarrow	$C_{3}H_{5}N_{5}O(s) + H_{2}O,$	(A9)
$C_{3}H_{4}N_{4}O_{2}(s) + NH_{3}(g)$	\rightarrow	$C_{3}H_{5}N_{5}O(s) + H_{2}O(g)$,	(A10)
$2 \text{ HNCO } (g) + \text{CO}(\text{NH}_2)_2 (m)$	\rightarrow	$C_{3}H_{5}N_{5}O(s) + 2 H_{2}O(g)$,	(A11)
HNCO (g) + $C_2H_5N_3O_2$ (m)	\rightarrow	$C_{3}H_{5}N_{5}O(s) + 2 H_{2}O(g)$,	(A12)
(CNOH) ₃ (s)	\rightarrow	3 HNCO (g).	(A13)

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