metals

Editorial

Advances in Low-Temperature Nitriding and Carburizing of Stainless Steels and Metallic Materials: Formation and Properties

Francesca Borgioli [1,*], Shinichiro Adachi [2] and Thomas Lindner [3]

[1] Department of Industrial Engineering (DIEF), Università di Firenze, via di S. Marta 3, 50139 Firenze, Italy
[2] Osaka Research Institute of Industrial Science and Technology, 2-7-1 Ayumino, Izumi 594-1157, Osaka, Japan; shinadachi@orist.jp
[3] Materials and Surface Engineering, Institute of Materials Science and Engineering, Chemnitz University of Technology, 09107 Chemnitz, Germany; th.lindner@mb.tu-chemnitz.de
* Correspondence: francesca.borgioli@unifi.it; Tel.: +39-055-275-8734

check for updates

Citation: Borgioli, F.; Adachi, S.; Lindner, T. Advances in Low-Temperature Nitriding and Carburizing of Stainless Steels and Metallic Materials: Formation and Properties. *Metals* **2024**, *14*, 1179. https://doi.org/10.3390/met14101179

Received: 1 October 2024
Accepted: 15 October 2024
Published: 17 October 2024

1. Introduction

Surface engineering techniques are currently used to overcome the limitations of metal alloys and improve their surface hardness, tribological properties, fatigue resistance and corrosion resistance in specific environments [1,2]. From this perspective, stainless steels have represented a challenge for many years, since nitriding and carburizing treatments, as carried out on low-alloy steels or tool steel, cannot be directly applied to steel of these grades. In fact, when nitrogen (N) and/or carbon (C) surface alloying is performed through thermochemical processes at temperatures comparable to those used for low-alloy steels and tool steels (500–580 °C for nitriding, 850–950 °C for carburizing), chromium (Cr)-based compounds can form in stainless steels. Thus, the Cr-depleted matrix becomes unable to maintain a protective passive film and corrosion may occur [3].

The drawbacks of "traditional" nitriding and carburizing processes can be overcome by "low-temperature" thermochemical treatments. By using sufficiently low treatment temperatures to allow the diffusion of interstitial atoms (N, C), while Cr (substitutional) diffusion is significantly slowed down, the formation of Cr compounds is hindered. Using these so-called para-equilibrium conditions for the surface treatment of stainless steels, supersaturated solid solutions in austenite, ferrite or martensite are obtained [4]. Forming these "expanded phases", as they are often called, can benefit and prolong the life of stainless steel components. These phases enable an increase in the surface hardness, improvements to the wear and fatigue resistance, and the maintenance of the good corrosion resistance of these alloys, or even enhancements of it, in particular in chloride-ion-containing solutions [4].

The formation of expanded austenite, or S-phase, in austenitic stainless steels was first reported in the mid-1980s, and since then, many studies have investigated this phase, its properties and the treatment conditions usable for its production without Cr and/or Fe compound precipitation in different austenitic stainless steels.

Low-temperature treatments have also proven to be suitable for producing expanded phases in other grades of stainless steels (ferritic, martensitic, duplex and precipitation hardening), and the formation of expanded ferrite and expanded martensite has been reported [4,5].

A further step has been the application of these treatments to non-ferrous alloys. The formation of expanded austenite has been reported in nickel-based [5], cobalt-based [5] and high-entropy alloys [6].

Another area of research has focused on the different process techniques used to produce expanded phases. The suitability of many techniques has been studied, from the more "traditional" gaseous treatments, to ion implantation processes, to plasma-based processes [5]. Recently, the active screen or cathodic cage plasma-based process has gained particular attention, since it avoids the edge effect typical of glow discharge DC plasma processes and may enable the combination of the diffusion treatment with surface film deposition [7,8]. An additional step is represented by low-temperature thermochemical treatment application to additively manufactured parts or to powders used for additive manufacturing techniques.

The purpose of this Special Issue is to gather original research and critical review articles on recent advances in all aspects of low-temperature thermochemical treatments using N and/or C applied to stainless steels and ferrous and non-ferrous alloys.

2. Overview of the Published Articles

A total of thirteen articles have been published, which cover different aspects of low-temperature thermochemical treatments, from microstructure analysis and evaluation of the properties of surface-modified alloys, to new proposals for performing thermochemical processes, to applications in different stainless steel grades and other ferrous and non-ferrous alloys, both in the massive and powder state.

The formation of expanded phases in different stainless steel grades was reviewed by Borgioli (Contribution 1). The formation conditions and the characteristics of expanded austenite, expanded ferrite and expanded martensite were discussed, and their properties were considered, focusing on the microhardness, load-bearing capacity, tribological properties and corrosion resistance of the modified surface layers produced by nitriding, carburizing and nitrocarburizing. Taking into account the most recent studies on this topic, the nature of expanded austenite was also discussed, in particular regarding the ordering of N atoms in the supersaturated lattice.

Experimental contributions have further improved our knowledge of expanded phases and their properties. The characteristics of expanded austenite formed in 316Ti austenitic stainless steel and 904L super-austenitic stainless steel using nitrogen low-energy ion implantation (LEII) were investigated by Mändl and Manova (Contribution 2). Using in situ X-ray diffraction analysis, they studied the expansion of the austenite lattice as N was solubilized, and thus the modified layer growth and N diffusion. Strong variations in lattice expansion were observed as a function of the steel composition, grain orientation, and nitriding conditions, even if N uptake and diffusion were similar for the two steels. The formation of a double layer with two distinct lattice expansions (higher near the surface and lower near the interface with the bulk) was detected for some nitriding conditions. The stability of the expanded austenite was also assessed, highlighting different behaviors regarding CrN precipitate formation for 316Ti and 904L.

Expanded austenite can form not only on massive alloys but also on additively manufactured layers or on powders to be used for thermal spraying.

The effect of low-temperature plasma nitriding on the characteristics of AISI 316L stainless steel-based WC composite layers produced by laser cladding was studied by Adachi et al. (Contribution 3). The WC particles acted as a C source, promoting the formation of mixed carbides and, presumably, C solubilization in the austenite matrix. When low-temperature nitriding was carried out, a N-rich expanded austenite formed at the surface, while a C-rich expanded austenite was present in the inner part, and the modified surface layers were similar to those produced by combining nitriding and carburizing simultaneously (i.e., nitrocarburizing) or in sequence. The Vickers microhardness values at the surface ranged from 1200 to 1400 HV and the hardness profiles were smooth. The nitriding treatment also improved the corrosion resistance in a 3.5 wt.% NaCl solution.

AISI 316L powder surface hardening using low-temperature gas nitrocarburizing and the use of this hardened powder for cold gas spraying were investigated by Lindner et al. (Contribution 4). Expanded austenite was able to form on the particles, even if this was limited to the surface area in most of the powder. Using this hardened powder, a coating was produced successfully using cold gas spraying. The phase fraction of the expanded austenite in the coating depended on the spraying conditions and decreased with the impact velocity of the particles. The spraying conditions also influenced the hardness values, the wear caused by the scratch test and the corrosion resistance.

The influence of different treatment processes on expanded austenite formation and on the properties of the modified surface layers was also explored. Schibicheski Kurelo et al. (Contribution 5) compared two nitriding techniques, glow discharge plasma nitriding (GDPN) and cathodic cage plasma nitriding (CCPN), regarding the mechanical and tribological behavior of the modified surface layers produced on AISI 316 stainless steel. Expanded austenite was obtained with both nitriding techniques, but the process type influenced nitride formation and the thickness of the modified layers. In particular, by using the same treatment temperature, the GDPN technique produced thicker and harder modified layers, having better scratch resistance. However, lower roughness and the absence of Cr depletion were observed in the CCPN-treated samples.

A low-temperature nitrocarburizing process based on the pyrolysis of a solid reagent (urea) was investigated by Illing et al. (Contribution 6). AISI 316L ferrules were used as samples, and they were introduced together with urea powder in a vessel, which was then evacuated and sealed. The heating of the vessel up to 450 °C using a two-step process activated the surface by removing the passive film, and enabled the fast diffusion of interstitial atoms (C, N) into the alloy, so that N- and C-rich expanded austenite was formed. The modified surface layers obtained with this technique were comparable to those produced by a gas- or plasma-based method, but with a significantly reduced processing time. The pyrolysis products of the reagent were also studied and their role in nitrocarburizing was considered, highlighting that the interaction of gas molecules with the alloy surface could have an auto-catalytic effect by altering the gas composition and condensed species.

The effect of plastic deformation on AISI 316L steel subjected to low-temperature vacuum carburizing without surface activation was studied by Cheon et al. (Contribution 7). Specimens with different deformation states were obtained, starting from cold-worked AISI 316L, on which solution or stress-relieving heat treatments were performed. When carburizing was carried out without surface activation, thinner modified surface layers, with a C-rich expanded austenite exhibiting a smaller lattice expansion, were observed in the specimens with high plastic deformation, while thicker and more uniform modified layers were obtained on the solution-treated specimens. These results could be correlated to the thickness of the oxide layer, which was higher for the plastic-deformed specimens. Therefore, the oxide layer appeared to be the most influential factor for the carburizing efficiency when surface activation was not performed.

The formation of expanded phases was also investigated on ferritic stainless steels. While the formation of expanded ferrite has been assessed by many authors, whether expanded austenite can also form is still a matter of debate. The formation and decomposition of expanded austenite produced by nitrogen plasma immersion ion implantation (PIII) on AISI 444 ferritic stainless steel was studied by Schibicheski Kurelo et al. using in situ synchrotron X-ray diffraction analysis (Contribution 8). It was observed that, even if expanded ferrite was the main phase that formed by nitriding at 300 and 400 °C, when the ion fluences were higher, as occurred when the treatment duration or temperature increased, expanded austenite was also formed. The decomposition of the expanded phases was assessed both during isothermal heating at 450 °C, as well as during the heating period. Nitrogen diffusion caused a reduction in the lattice parameters of the expanded phases. Moreover, in the samples nitrided with the highest fluences, expanded austenite tended to transform into α-ferrite, and CrN and oxides formed.

Low-temperature nitriding treatment has also been performed on non-ferrous alloys and expanded austenite has been successfully produced. De La Rosa et al. (Contribution 9) studied the effects of plasma nitriding on the Inconel 718 Ni-based alloy. Expanded austenite was obtained together with CrN using a 400 °C nitriding temperature. However, when nitriding was carried out at 450 °C, only austenite and CrN were detectable. Surface hardening and a higher scratch resistance were observed in the nitrided specimens. The corrosion behavior of the samples was tested in a 3.56 wt.% NaCl solution using potentiodynamic and potentiostatic tests. Pitting corrosion was detected in all the samples. It was observed that, even with CrN precipitation, the presence of expanded austenite in 440 °C nitrided specimens led to a better performance regarding crevice corrosion.

Thermochemical treatments have been applied to ferrous and non-ferrous alloys using treatment temperatures lower than those usually employed. De Abreu et al. (Contribution 10) investigated the effects of a duplex treatment on the surface properties of AISI M2 tool steel. The authors performed plasma nitriding at 400 °C followed by a cathodic cage deposition (CCPD) at 400 or 450 °C with a titanium cage in a nitrogen-containing atmosphere. As a result, Fe-based nitrides, γ'-Fe_4N and ε-$Fe_{2\text{-}3}N$, and titanium nitride, TiN, were produced. The duplex treatments effectively improved the surface hardness and thicker hardened layers with a smooth hardness gradient were obtained. Moreover, these treatments significantly reduced the wear rate and friction coefficient as evaluated using ball-on-ring tests.

A two-step hollow cathode treatment, which consisted of a nitriding process followed by an oxynitriding treatment in the range of 500–540 °C, was applied by Yan et al. to titanium TC4 (Ti-6Al-4V) (Contribution 11). Modified surface layers consisting of TiO_2, TiN, Ti_2N and a N-rich α-Ti phase were obtained. The two-step process was effective in producing hardened layers, which had a significantly improved corrosion resistance in the artificial saliva solutions.

Other studies have focused on different aspects, which can clarify the properties of modified surface layers in which expanded phases form.

In Fe-N systems, the different phases (solid solutions, expanded phases, nitrides) have different magnetic properties, which may also change as a function of the N content. Kaczmarek et al. (Contribution 12) studied the changes in the phase composition and magnetic properties of AISI 1010 and AISI 1085 steels, which were nitrided and then annealed. The nitriding treatment produced a compound layer consisting of ε-$Fe_{2\text{-}3}N$ and γ'-Fe_4N nitrides. During annealing, ε-nitride decomposed first, and the γ' content significantly increased. The presence of nitrides and their change in composition influenced the magnetic properties of the steels.

The precipitation of Mn nitrides may occur in the nitriding of Mn-rich stainless steels, such as AISI 200 series or Ni-free austenitic stainless steel, affecting the properties of the modified surface layers. The electronic structure and hardness of Mn_3N_2 was investigated by Zhang et al. (Contribution 13). Bulk Mn_3N_2 samples were synthesized and their Vickers hardness was measured as 9.9 GPa. This experimental result was useful for revising the theoretical predictions. By combining first-principle simulations and experimental analyses, the authors highlighted the importance of metal bonds in determining the hardness of this nitride.

3. Conclusions and Outlook

Low-temperature thermochemical treatment with N and/or C represents a lively research field, and it allows for increasingly tailored surface modifications to be achieved. The studies collected in this Special Issue report the latest scientific achievements on expanded phases, the characteristics of modified surfaces, and process techniques, and they are valuable for scientists and engineers engaged in the research and development of surface engineering processes for application to stainless steels and other metallic materials.

Acknowledgments: The Guest Editors wish to thank all the authors for their contributions, as well as all the reviewers for their work and efforts to improve the quality of the articles. The Editors appreciate the support from the *Metals* Editorial Office throughout the publication process.

Conflicts of Interest: The authors declare no conflicts of interest.

List of Contributions:

1. Borgioli, F. The "Expanded" Phases in the Low-Temperature Treated Stainless Steels: A Review. *Metals* **2022**, *12*, 331. https://doi.org/10.3390/met12020331
2. Mändl, S.; Manova, D. Comparison of Nitriding Behavior for Austenitic Stainless Steel 316Ti and Super Austenitic Stainless Steel 904L. *Metals* **2024**, *14*, 659. https://doi.org/10.3390/met14060659

3. Adachi, S.; Yamaguchi, T.; Ueda, N. Formation and Properties of Nitrocarburizing S-Phase on AISI 316L Stainless Steel-Based WC Composite Layers by Low-Temperature Plasma Nitriding. *Metals* **2021**, *11*, 1538. https://doi.org/10.3390/met11101538
4. Lindner, T.; Löbel, M.; Grimm, M.; Fiebig, J. Cold Gas Spraying of Solution-Hardened 316L Grade Stainless Steel Powder. *Metals* **2022**, *12*, 30. https://doi.org/10.3390/met12010030
5. Schibicheski Kurelo, B.C.E.; De Souza, G.B.; Da Silva, S.L.R.; Lepienski, C.M.; Alves Júnior, C.; Chuproski, R.F.; Pintaúde, G. Tribo-Mechanical Behavior of Films and Modified Layers Produced by Cathodic Cage and Glow Discharge Plasma Nitriding Techniques. *Metals* **2023**, *13*, 430. https://doi.org/10.3390/met13020430
6. Illing, C.; Ren, Z.; Agaponova, A.; Heuer, A.; Ernst, F. Rapid Alloy Surface Engineering through Closed-Vessel Reagent Pyrolysis. *Metals* **2021**, *11*, 1764. https://doi.org/10.3390/met11111764
7. Cheon, H.; Kim, K.-S.; Kim, S.; Heo, S.-B.; Lim, J.-H.; Kim, J.-H.; Yoon, S.-Y. Effect of Deformation Structure of AISI 316L in Low-Temperature Vacuum Carburizing. *Metals* **2021**, *11*, 1762. https://doi.org/10.3390/met11111762
8. Schibicheski Kurelo, B.C.E.; Lepienski, C.M.; de Oliveira, W.R.; de Souza, G.B.; Serbena, F.C.; Cardoso, R.P.; das Neves, J.C.K.; Borges, P.C. Identification of Expanded Austenite in Nitrogen-Implanted Ferritic Steel through In Situ Synchrotron X-ray Diffraction Analyses. *Metals* **2023**, *13*, 1744. https://doi.org/10.3390/met13101744
9. Nuñez de la Rosa, Y.; Palma Calabokis, O.; Ballesteros-Ballesteros, V.; Tafur, C.L.; Borges, P.C. Assessment of the Pitting, Crevice Corrosion, and Mechanical Properties of Low-Temperature Plasma-Nitrided Inconel Alloy 718. *Metals* **2023**, *13*, 1172. https://doi.org/10.3390/met13071172
10. de Abreu, L.H.P.; Naeem, M.; Monção, R.M.; Costa, T.H.C.; Díaz-Guillén, J.C.; Iqbal, J.; Sousa, R.R.M. The Effect of Cathodic Cage Plasma TiN Deposition on Surface Properties of Conventional Plasma Nitrided AISI-M2 Steel. *Metals* **2022**, *12*, 961. https://doi.org/10.3390/met12060961
11. Yan, J.; Shao, M.; Zhou, Z.; Zhang, Z.; Yi, X.;Wang, M.;Wang, C.; Fang, D.; Wang, M.; Xie, B.; He, Y.; Li, Y. Electrochemical Corrosion Behavior of Ti-N-O Modified Layer on the TC4 Titanium Alloy Prepared by Hollow Cathodic Plasma Source Oxynitriding. *Metals* **2023**, *13*, 1083. https://doi.org/10.3390/met13061083
12. Kaczmarek, S.M.; Michalski, J.; Frączek, T.; Dudek, A.; Fuks, H.; Leniec, G. Mechanical and Magnetic Investigations of Balls Made of AISI 1010 and AISI 1085 Steels after Nitriding and Annealing. *Metals* **2023**, *13*, 1060. https://doi.org/10.3390/met13061060
13. Zhang, S.; Zhou, C.; Sun, G.; Wang, X.; Bao, K.; Zhu, P.; Zhu, J.; Wang, Z.; Zhao, X.; Tao, Q.; Ge, Y.; Cui, T. Electronic Structure and Hardness of Mn_3N_2 Synthesized under High Temperature and High Pressure. *Metals* **2022**, *12*, 2164. https://doi.org/10.3390/met12122164

References

1. Czerwinski, F. Thermochemical Treatment of Metals. In *Heat Treatment–Conventional and Novel Applications*; Czerwinski, F., Ed.; IntechOpen: Rijeka, Croatia, 2012; pp. 73–112. [CrossRef]
2. Ramezani, M.; Mohd Ripin, Z.; Pasang, T.; Jiang, C.-P. Surface Engineering of Metals: Techniques, Characterizations and Applications. *Metals* **2023**, *13*, 1299. [CrossRef]
3. Lo, K.H.; Shek, C.H.; Lai, J.K.L. Recent developments in stainless steels. *Mater. Sci. Eng. R Rep.* **2009**, *65*, 39–104. [CrossRef]
4. Cardoso, R.P.; Mafra, M.; Brunatto, S.F. Low-temperature Thermochemical Treatments of Stainless Steels—An Introduction. In *Plasma Science and Technology-Progress in Physical States and Chemical Reactions*; Mieso, T., Ed.; InTech: Rijeka, Croatia, 2016; pp. 107–130, ISBN 978-953-51-2280-7. [CrossRef]
5. Dong, H. S-phase surface engineering of Fe-Cr, Co-Cr and Ni-Cr alloys. *Int. Mater. Rev.* **2010**, *55*, 65–98. [CrossRef]
6. Peng, Y.; Duan, H.; Feng, Y.; Gong, J.; Somers, M.A.J. Surface hardening of $Al_{0.1}$CoCrFeNi and $Al_{0.5}$CoCrFeNi high-entropy alloys by low-temperature gaseous carburization. *Intermetallics* **2023**, *160*, 107943. [CrossRef]
7. Borowski, T. Enhancing the Corrosion Resistance of Austenitic Steel Using Active Screen Plasma Nitriding and Nitrocarburising. *Materials* **2021**, *14*, 3320. [CrossRef]
8. Sampaio, W.R.V.; Serra, P.L.C.; Monção, R.M.; de Sousa, E.M.; Silva, L.G.L.; da Silva, F.L.F.; Rossino, L.S.; Bandeira, R.M.; Feitor, M.C.; de Sousa, R.R.M.; et al. Influence of using different titanium cathodic cage plasma deposition configurations on the mechanical, tribological, and corrosion properties of AISI 304 stainless steel. *Surf. Coat. Technol.* **2023**, *475*, 130149. [CrossRef]