Surface modification of austenitic thermal-spray coatings by low-temperature nitrocarburizing

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Abstract. Thermal-spray coatings of austenitic materials are mainly used under corrosive conditions. The relatively poor wear resistance strongly limits their use. In comparative studies between nitrocarburized and untreated thermal-spray coatings, the influence of the nitrogen and carbon enrichment on the properties of the coatings and the microstructure was investigated. The cross-section micrograph of the nitrocarburized coating shows the S-phase formation in the surface layer region. The depth profile of the nitrogen and carbon concentration was determined by glow discharge optical emission spectroscopy (GDOS) analysis. A selective enrichment of the surface layer region with nitrogen and carbon by means of thermochemical heat treatment increases the wear resistance. The interstitially dissolved nitrogen and carbon causes the formation of strong compressive residual stresses and high surface hardness. Increases in the service life of existing applications or new material combinations with face-centred cubic friction partners are possible. In the absence of dimensional change, uniform as well as partial nitrogen enrichment of the thermal spray coating is possible. Nitrocarburized coatings demonstrate a significant improvement in adhesive wear resistance and extremely high surface hardness.

1. Introduction
The properties of thermal spray coatings are mainly determined by the coating material and the spraying process. An influence on the properties of the coatings by variation of the process parameters is only possible within narrow limits. To deliver a combined wear and corrosion resistance, it is usually necessary to apply expensive coating materials. In recent years, there have been increasing efforts to develop low-cost alternatives, mainly materials based on iron. Successes could be achieved by further development of recent alloy compositions [1, 2]. In addition, improvements by mechanical finishing of manganese steel coatings are described [3, 4].

Iron-based bulk parts can be treated by means of thermal, thermochemical or mechanical treatment. This will change the surface properties to achieve the desired wear resistance. Stainless and acid-resistant iron-based materials with face-centred cubic lattice structure are mainly used under corrosive conditions. Due to the wear behavior, pairings and tight fits are so far limited. Particularly critical are metal combinations with similar face-centred cubic lattice structure, where adhesion wear behavior restricts a further practical use. The low-temperature thermochemical treatment of face-centred cubic materials provides the opportunity to extend the applicability by a nitrogen enrichment of the surface layer region. It is necessary to ensure the sufficiently low operation temperature to prevent the precipitation of chromium phases that will lower the corrosion resistance. Promising results for bulk material parts show a significant raise in hardness combined with improved adhesion-wear resistance [5, 6]. Due to the improvement of the properties, a successful treatment provides a high innovation potential with certain new applications.

This article describes exemplarily how a low-temperature thermochemical treatment influences and changes the microstructure as well as the functional properties of thermal-spray coatings with face-centred cubic structure.
2. Experimental
Due to promising results for bulk parts [7, 8], the alloy AISI316L was investigated. The thermal-spray coatings were produced with the HVOF system GTV-K2 with the parameters shown in Tab. 1.

Table 1. Process parameters HVOF GTV-K2

| Parameter                        | Value          |
|----------------------------------|----------------|
| Kerosine                         | 24 l/h         |
| Oxygen                           | 900 l/min      |
| \( \lambda \)                    | 1.09           |
| Combustion chamber pressure      | 7.1 bar        |
| Spraying distance                | 350 mm         |
| Nozzle                           | 150/14 mm      |
| Transverse speed                 | 1 m/s          |
| Offset                           | 5 mm           |
| Powder feed rate                 | 70 g/min       |
| Gas feed                         | \( 2 \times 8 \) l/min (argon) |
| Wiper                            | NL             |

The alloy powder was used in fraction of \(-53+20\) µm. The coating layer was polished followed by nitrocarburization with the industrial process called HARD-INOX\textsuperscript{®}-S by Gerster.

The chemical, mechanical, microstructural, and tribological properties were investigated for the untreated and carburized coatings. The nitrogen and carbon concentration as a function of the surface distance was measured by GDOS (SPECTRUMA GDA750) with a diameter of 4 mm. Furthermore, the microhardness was measured on the surface and on the cross-section using a FISCHERSCOPE HM2000 XYm. XRD measurements (diffractometer D8 DISCOVER) on the surface of the coating were used to identify phases and to determine the lattice parameters. The microstructure was characterized on the cross-section micrograph.

The tribological properties of the coating were investigated with the reciprocating ball-on-plane test leaned on ASTM G 133 as dry couple and the ball-on-disc test leaned on ASTM G 99 as a dry sliding system, both with a spherical counterface.

Table 2. Testing parameters of wear test

| Parameter                        | Value          |
|----------------------------------|----------------|
| Force                            | 26 N           |
| Frequency                        | 40 Hz          |
| Time                             | 900 s          |
| Amplitude                        | 0.5 mm         |
| Ø Al\textsubscript{2}O\textsubscript{3} | 10 mm          |
| Force                            | 10 & 20 N      |
| Radius                           | 5 mm           |
| Speed                            | 96 U/min       |
| Cycles                           | 15916          |
| Ø Al\textsubscript{2}O\textsubscript{3} | 6 mm           |

The test parameters as well as the counterbody material and diameter are shown in Tab. 2. The wear death was profilometrically determined with the 3D profilometer MikroCAD. The benchmarks for all testings were the determined values for the untreated samples.

3. Results and Discussion
The aim of the nitrocarburization was the saturation and interstitial deposition of nitrogen and carbon in the surface layer region of the thermal spray coating. This was supposed to create high compressive residual stresses and to increase the wear performance.
Figure 1. Nitrogen and carbon GDOS intensities as well as microhardness of nitrocarburized AISI316L HVOF coatings as a function of the surface distance

The determined nitrogen and carbon intensities by GDOS analysis show a decrease with increasing surface distance, Fig. 1. The microhardness varies deeply in dependence of local saturation depth. The shown values are the minimum microhardness values. In the surface-layer region the microhardness increases by about factor of 2 compared with the untreated zone.

Figure 2. XRD diffraction diagrams of the nitrocarburized and untreated AISI316L HVOF coating with the Miller indices of the austenite peaks

The XRD studies show that the lattice parameter of the measured austenite phase strongly expands after nitrocarburization, Fig. 2. In comparison with the untreated sample, a clear shift of the characteristic peaks of austenite to lower angles was determined, which can be explained by the increase of lattice spacing due to the interstitial deposition of nitrogen and carbon atoms. In addition to the main austenitic phase, a small amount of iron chromium carbid phase was determined with a good accordance in the nitrocarburated sample.

The measurement of the residual stress state was not possible because of the broadening of the peaks due to microstrains. With assumption of a constant stress state the qualitative shift of the austenite peaks can be explained by an interstitial solvation of nitrogen or carbon, Tab. 3.
Table 3. Lattice parameters of the austenite phase for the untreated and nitrocarburized AISI316L HVOF coatings

| lattice plane | Young’s modulus $E$ [9] | lattice parameter $a$ |
|---------------|------------------------|----------------------|
|              | untreated              | nitrocarburized      |
| {111}        | 250 GPa                | 3.59 Å               | 3.77 Å               |
| {200}        | 140 GPa                | 3.59 Å               | 3.92 Å               |

Table 3 reveals the lattice spacing of the samples determined by XRD. The nitrocarburized sample shows a great expansion in lattice parameter that follows the anisotropic elastic behavior of austenitic steel. Due to the different Young’s moduli, the expansion of the lattice planes {111} and {200} is expected as a consequence of the residual stress. This can be proven by the following relation:

$$\frac{E_{200}}{E_{111}} \approx \frac{a_{(111)\text{nitrocarb.}} - a_{\text{untreated}}}{a_{(200)\text{nitrocarb.}} - a_{\text{untreated}}}$$

Figure 3. Cross-section of the nitrocarburized AISI316L HVOF coating (etched)

After the etching of the cross-section, two regions are identifiable. The topmost layer (white area in Fig. 3) surface layer region is the so-called expanded austenite phase or S-phase that shows a strong resistance to the etchant. The depth of the S-phase varies between 20 µm and 100 µm.

The marked increase of hardness and compressive stress causes a significant increase in wear resistance. This is particularly applicable for the studied sliding and reciprocating testing methods. For the untreated and nitrocarburized samples, the values of wear are shown in Tab. 4.

Table 4. Wear testing of nitrocarburized and untreated AISI316L HVOF coatings

|                 | untreated | nitrocarburized |
|-----------------|-----------|-----------------|
| reciprocating   |           |                 |
| ball-on-Plane   |           |                 |
| wear volume [mm³] | 0.176    | 0.056           |
| wear depth [µm]  | 92        | 51              |
| ball-on-disc    |           |                 |
| 10 N            |           |                 |
| wear volume [mm³] | 4.975    | < 0.005         |
| wear depth [µm]  | 101       | 3               |
| 20 N            |           |                 |
| wear volume [mm³] | 12.329   | < 0.05          |
| wear depth [µm]  | 175       | 7               |

After the wear testing, the wear depth was profilometrically determined and the volume loss was calculated. The wear volume is determined in the whole trace of wear. For depth of wear, the deepest point in the trace of wear was measured. The comparison of untreated and nitrocarburized samples shows a reduction of the wear volume in reciprocating wear of about 68%. For the nitrocarburized samples in ball-on-disc test, almost no wear could be measured.
4. Conclusion
The great potential of low-temperature thermochemical treatment of thermal-spray coatings has been demonstrated in this paper. Exemplarily for AISI316L HVOF coatings, it is possible to build up a carbon rich surface layer with improved tribological and wear properties without forming chromium carbides. With the enhanced residual stress state, significant improvements in fatigue strength and abrasive wear resistance are possible.

5. Literature

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