Characterization of mechanical properties of S-phase coatings

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S-phase ($\gamma_N$, expanded austenite) is a metastable nitrogen and/or carbon supersaturated solid solution in austenitic stainless steel. The phase shows comparable or better corrosion resistance and higher hardness as well as wear resistance than austenitic stainless steel. The paper presents results of investigation on mechanical properties of S-phase coatings deposited by reactive magnetron sputtering on austenitic stainless steel substrates. Substrate temperature (200–400°C) and nitrogen content in reactive atmosphere (15–50% vol.) were varied. Hardness and Young’s modulus of the coatings were investigated by nanoindentation. Their adhesion was evaluated by scratch test method. Hardness and Young’s modulus depended on nitrogen content in the atmosphere while substrate temperature had a negligible effect. These mechanical parameters depended on the coating microstructure and grain size rather than on nitrogen content in the coating. Results of scratch tests showed a minor effect of deposition parameters on coatings adhesion. It was also observed that for certain parameters of the deposition process a nitrogen diffusion layer in the substrate may form. The presence of the diffusion layer resulted in a decrease of nitrogen content in the coating, but its effect on hardness and adhesion of the coating was not straightforward.

Key words: S-phase, nitrogen diffusion layer, coating adhesion, coating hardness.

1. INTRODUCTION
Modification of austenitic stainless steel surface aiming at improvement of mechanical and functional properties, such as hardness or wear resistance, has been one of the main tasks of surface engineering for several decades. One of the methods to improve these properties is obtaining a nitrogen and/or carbon supersaturated solid solution in austenitic which is called S-phase (also $\gamma_N$ or expanded austenite). The most frequently used method is low-temperature nitriding. S-phase layers have higher hardness and comparable to or sometimes even better corrosion resistance than austenitic stainless steel [1–7]. Low-temperature treatment is a process carried out at temperature below 500°C. It prevents the formation of nitrides (mostly chromium nitrides), the presence of which significantly decreases corrosion resistance of austenitic stainless steel.

It is also possible to obtain S-phase as a coating with magnetron sputtering. Austenitic stainless steel is then sputtered in reactive atmosphere containing nitrogen [1, 2, 8–22]. This method allows the temperature of the preparation of S-phase to be reduced even below 200°C. Moreover, an easy control of nitrogen concentration in the coating is also possible by regulation of the nitrogen content in the reaction chamber. Thanks to the combination of these two basic parameters the deposition of coatings with varying thickness, morphology and mechanical properties is possible.

2. MATERIAL AND METHODS
Coatings were deposited by means of reactive magnetron sputtering method (RMS). Discs of 50 mm in diameter made of austenitic stainless steel (wt %: 18.5 Cr, 9 Ni, 2 Mn, 0.5 Si, 0.4 Cu, Fe in balance) were used as targets. Substrates were made of the same steel grade. Prior to the deposition they were ground using abrasive papers down to 1200 and then with diamond pastes down to 1 μm. After grinding the substrates were vibro-polished with Al$_2$O$_3$ in order to remove the layer of ferrite resulting from plastic deformation occurring during the grinding process. Furthermore, the substrates were ultrasonically cleaned in an acetone bath for 10 min and dried in hot air. After the preparation the substrates were placed in the reaction chamber which was pumped down to a base pressure of about 10$^{-5}$ Pa. Then the chamber was filled back with Ar up to 2.7 Pa, at the flow rate of 10 cm$^3$s$^{-1}$. Then the ion cleaning of substrate proceeded for 30 min with RF negative bias. Voltage of about 200 V was applied. After cleaning the chamber pressure was lowered to the fixed value of 0.8 Pa.

During the deposition the constant total gas flow rate of 13 cm$^3$s$^{-1}$ was maintained but with variable nitrogen ratio from 15 up to 50% vol. The coatings were deposited at various substrate temperature from 200 to 400°C. Other sputtering parameters, such as time (180 min), magnetron power (two magnetrons with 200 W each) and target to substrate distance (110 mm) were kept constant.

The phase composition of the coatings was determined by means of X-ray diffraction (XRD) in Bragg-Brentano geometry (Cu K$_\alpha$ radiation, X’Pert Pro, PANalytical). Nitrogen concentration in coatings was quantitatively measured using X-ray microanalysis with CrN standard (Thermo Scientific, Hitachi SU-70). Thickness of the coating was determined on the micrographs of the coating cross-sections obtained by scanning electron microscopy (SEM).

Hardness and Young’s modulus of the coatings were evaluated by nanoindentation with Berkovich tip (Nano Indenter XP, Agilent). Adhesion of coatings was tested by scratch test method with the progressive loading of 0–20 N (Revetest Scratch Tester, CMS Instruments).

3. RESULTS AND DISCUSSION
X-ray diffraction patterns show that all coatings were composed of S-phase (Fig. 1). S-phase peaks are seen as a set of peaks which are shifted towards lower 2 theta angles in comparison to austenite peak positions. The higher nitrogen concentration in coatings the higher shift observed. It can be seen that the shift of the peak position increased with an increase of nitrogen content in the atmosphere, which means that nitrogen concentration in the coatings increased as well. It well corresponds to the results of nitrogen concentration measurements presented in Table 1.

Depending on the deposition parameters, coatings with different morphology and texture can be obtained. For the lowest nitrogen content in the atmosphere grains both with (111) and...
these samples the intensity of peaks was again much lower which suggests a small grain size.

These observations were confirmed by SEM studies of the coating cross-sections (Fig. 2). The coatings obtained in 33% nitrogen atmospheres demonstrated strongly columnar microstructure with many pores, while the coatings deposited at the highest and the lowest nitrogen content were compact with small grain structure – much finer for the latter.

Additionally, for coatings deposited with nitrogen content of 33 and 50% vol. at temperature above 350°C, an additional peak was observed between the S-phase and γ (austenite) peaks. This peak corresponded to S-phase originating from the diffusion sub-layer, which was formed during deposition in the substrate below the coating (Fig. 3). The appearance of this sub-layer reduced the nitrogen content in the coating (Tab. 1). This phenomenon was observed as well in previous studies [2, 10]. The formation of S-phase diffusion sub-layer is probably possible thanks to removal of the chromium oxide layer during the ion cleaning step. Once the passive layer is removed the nitrogen diffusion from the coating to the substrate.

Table 1. Influence of deposition parameters on nitrogen content in coatings

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate temperature °C</th>
<th>Nitrogen content in atmosphere % vol.</th>
<th>Nitrogen content in coating wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>200</td>
<td>15</td>
<td>3.7</td>
</tr>
<tr>
<td>C2</td>
<td>250</td>
<td>3.7</td>
<td>3.7</td>
</tr>
<tr>
<td>C3</td>
<td>300</td>
<td>3.3</td>
<td>3.3</td>
</tr>
<tr>
<td>C4</td>
<td>350</td>
<td>3.4</td>
<td>3.4</td>
</tr>
<tr>
<td>C5</td>
<td>400</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>C6</td>
<td>200</td>
<td>33</td>
<td>7.9</td>
</tr>
<tr>
<td>C7</td>
<td>250</td>
<td>7.9</td>
<td>8.1</td>
</tr>
<tr>
<td>C8</td>
<td>300</td>
<td>8.1</td>
<td>8.1</td>
</tr>
<tr>
<td>C9</td>
<td>350</td>
<td>8.1</td>
<td>7.5</td>
</tr>
<tr>
<td>C10</td>
<td>400</td>
<td>50</td>
<td>7.5</td>
</tr>
<tr>
<td>C11</td>
<td>200</td>
<td>50</td>
<td>11.8</td>
</tr>
<tr>
<td>C12</td>
<td>250</td>
<td>50</td>
<td>11.5</td>
</tr>
<tr>
<td>C13</td>
<td>300</td>
<td>50</td>
<td>11.2</td>
</tr>
<tr>
<td>C14</td>
<td>350</td>
<td>10.3</td>
<td>10.3</td>
</tr>
<tr>
<td>C15</td>
<td>400</td>
<td>50</td>
<td>8.6</td>
</tr>
</tbody>
</table>

(200) orientations were present in diffraction patterns (Fig. 1). The intensity of S-phase peaks was very low which can indicate their very fine grain structure.

Increase of nitrogen content in the atmosphere from 15 to 33% vol. at the temperature range from 200 to 300°C resulted in formation of grains with a preferred orientation of (111). For higher temperature (100) grains were also visible. At the same time intensity of the peaks was much higher and narrow indicating a greater grain size. The coatings deposited at the highest nitrogen content in atmosphere (50% vol.) demonstrated a strong (200) texture. This texture was better pronounced at lower deposition temperature. For
Thickness of the coatings decreased as the nitrogen content in the working atmosphere increased. An influence of temperature on the thickness of the coating is ambiguous, although a small downward trend with increasing temperature of the substrate could be observed (Fig. 4). Decrease in deposition rate with an increase of nitrogen flow was observed as well by others [14] and it happens probably due to an increase poisoning of the target with increase nitrogen content in the atmosphere.

Mechanical properties of the coatings depended mostly on nitrogen content in the reactive atmosphere. The coatings obtained at the lowest nitrogen content had the highest values of Young’s modulus (Fig. 5) and hardness (Fig. 6), while those obtained at the atmospheres containing 33% of nitrogen had the lowest values. Treatment temperature had very little influence on both parameters. Only in case of 50% nitrogen atmosphere a small decrease of these parameters could be observed with increasing temperature, which for highest temperature can be attributed to the reduced nitrogen content due to diffusion to the substrate.

This specific decrease of hardness for 33% nitrogen atmosphere was also observed in previous studies on the total pressure influence on S-phase coating deposition [17]. It was even more pronounced when the total pressure was lower than that in the current experiments. However, no clear explanation of this observation was found.

According to literature data it is expected that the higher nitrogen concentration in the coatings the higher their hardness [2]. Hardness and Young’s modulus drop can be observed for very high nitrogen content due to other phase precipitations, which was not the case for our analysis. One of possible explanations of such behaviour could be texture changes which were observed as nitrogen content was changed. However, there is no clear relation between hardness and texture. Out of coatings with the lowest hardness, only three of those deposited at the lowest temperature have clear (111) texture which is not reflected in hardness or Young’s modulus values (Fig. 5 and 6.). However, there is a clear difference in microstructure of the coatings obtained. Those with the lowest hardness have a clear columnar structure with the biggest grain size. The hardest coatings have the finest microstructure. Similar relation can be observed in results presented by Dahm at al. [2] even though it was not clearly outlined in their work.

The influence of deposition parameters on the brittleness and adhesion of coatings was also studied. The results are presented in Figures 7–9.

For the coatings deposited at the lowest nitrogen content the critical load \( L_{C1} \) (the force related to the first brittle cracks) is the lowest (Fig. 7). It may be related to the highest hardness of these coatings. In contrast to that these coatings demonstrate the biggest values of \( L_{C3} \) critical load which reflects their better adhesion properties. However, in general no major differences between coatings obtained at higher nitrogen content can be observed in this respect.

All coatings showed rather good adhesion. Coating delamination was limited and coatings followed the plastic deformation of the substrate under the load (Fig. 9). The expected positive influence of the diffusion sublayer forming beneath the coating on the improvement or deterioration in the adhesion of the coating to the substrate was not straightforward.
4. CONCLUSIONS

S-phase coatings were successfully deposited by reactive magnetron sputtering from austenitic stainless steel on austenitic stainless steel substrates. The following observations can be concluded:

1. An increase of nitrogen content in the reactive atmosphere led to increase of nitrogen concentration in the coatings and to decrease of deposition rate.

2. Hardness of the coatings varied between 3.14 and 7.89 GPa. It depended on the coating microstructure and grain size rather than on nitrogen content in the coating. Nitrogen diffusion from coating to substrate during deposition at 400°C caused reduction of coating hardness.

3. All coatings demonstrated good adhesion properties. No significant effects of the coating texture on their brittleness and adhesion was observed.

4. Coatings deposited at low nitrogen content in the reactive atmosphere were the most brittle, but those deposited at a temperature above 250°C showed the highest adhesion to the substrate. On the other hand, coatings deposited at higher nitrogen content had higher toughness, but lower adhesion. The adhesion of coatings to substrates decreased slightly with increasing substrate temperature.
REFERENCES


Charakterystyka właściwości mechanicznych powłok zbudowanych z fazy S

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Słowa kluczowe: faza S, warstwa dyfuzyjna azotu, przyczepność powłok, twardość powłok.

1. CEL PRACY

Modyfikacja powierzchni stali nierdzewnej o strukturze austenitycznej w celu poprawienia jej właściwości mechanicznych i użytkowych, takich jak twardość czy odporność na ścieranie, jest od wielu lat jednym z głównych zadań stawianych przed inżynierią powierzchni. Jedną z metód poprawy właściwości tych stali jest wytworzenie na ich powierzchni warstwy przesyconego azotem i/lub węglem roztworu stałego austenitu, nazywanego fazą S (także γ_N lub austenitem ekspandowanym). Jedną z powszechnie wykorzystywanych metod w celu wytworzenia fazy S jest proces niskotemperaturowego azotowania. Warstwy zbudowane z fazy S wykazują większą twardość oraz porównywalną, a czasami lepszą, odporność korozjną niż stal o strukturze austenitycznej [1+5]. Proces nisko-temperaturowy jest prowadzony w temperaturze poniżej 500°C. W ten sposób zapobiega się powstawaniu azotków (najczęściej azotków chromu), których obecność znacznie zmniejsza odporność korozjną tych stali.

Możliwe jest także wytworzenie fazy S w postaci powłok z wykorzystaniem metody reaktywnego rozpylania magnetronowego [1, 2, 6÷17]. Metoda ta pozwala znacząco obniżyć temperaturę procesu wytwarzania fazy S (nawet poniżej 200°C). Jednocześnie daje ona możliwość łatwego sterowania stężeniem azotu w powłoce oraz porównywalną, a czasami lepszą, odporność korozjną tych stali.

2. MATERIAŁ I METODYKA BADAN

Powłoki wytworzone metodą reaktywnego rozpylania magnetronowego (RMS). Do wytworzenia powłok została użyta stal o strukturze austenitowej typu X2CrNi18–9. Z tego samego materiału wykonano podłoża, na które były nanoszone powłoki.

Podczas osadzania powłok utrzymywany był stały przepływ gazów roboczych w komorze reakcyjnej, jednak z różnym udziałem azotu od 15 do 50% obj. Temperatura podłoża, na które nanoszono powłokę zmieniała się i wynosiła od 200 do 400°C. Pozostałe parametry procesu, takie jak ciśnienie robocze, moc rozpylania, czas procesu czy odległość target–podłoże były stałe.


3. WYNIKI I ICH Dyskusja

Analiza otrzymanych dyfraktogramów wykazała, że wszystkie wykonane powłoki zbudowane były z fazy S (rys. 1).

Faza S jest widoczna w postaci refleksów przesuniętych w stronę mniejszych kątów 29 od refleksów dla austenitu. Im większa zawartość azotu w powłoce, tym większe obserwowane przesunięcie refleksów. Zwiększenie zawartości azotu w powłoce wynika ze wzrostu jego udziału w atmosferze roboczej. Zmiany zawartości azotu w powłokach w zależności od zawartości azotu w atmosferze przedstawiono w tabeli 1.

W zależności od parametrów osadzania otrzymano powłoki o zróżnicowanej morfologii i teksturze. Dla najmniejszej zawartości azotu w atmosferze otrzymano powłoki o tekście budowane z fazy austenitycznej typu X2CrNi18–9. Z tego samego materiału zbudowane w atmosferze do 50% obj. spowodowało wytwarzanie powłok o tekście [200]. Powłoki osadzone przy większej zawartości azotu charakteryzowały się większymi ziarnami. Oszacowanie te potwierdziły badania wykonane metodą mikroskopii elektronowej skanującej (rys. 2).

Największy moduł Younga oraz twardość wykazywały powłoki osadzone przy najmniejszej zawartości azotu (rys. 5 i 6). Na to mogą być spowodowane zmianami morfologii i tekstury powłok. Lepszymi właściwościami charakteryzowały się powłoki o zawartościach azotu w atmosferze zawierającej 33% azotu. Zmiany te mogą być spowodowane zmianami morfologii i tekstury powłok. Lepszymi właściwościami charakteryzowały się powłoki o mniejszych zawartościach azotu.

Wszystkie powłoki wykazywały dobrą przyczepność do podłoża. Powłoki osadzone przy największej zawartości azotu w atmosferze wykazywały najlepszą odporność na kruche pękanie (rys. 7). Może to wynikać z większej twardości tych powłok. Jednocześnie powłoki te wykazywały najlepszą przyczepność do podłoża (rys. 8).

4. PODSUMOWANIE

Twardość powłok z fazy S zmienia się od 3,14 do 7,89 GPa i zależy w większym stopniu od wielkości ziaren w powłoce i ich tekstury, niż od zawartości azotu w powłoce. Dyfuzyjna azotu z powłok do podłoża zachodząca w trakcie osadzania powłok w temperaturze powyżej 200°C powoduje zmniejszenie ich twardości. Powłoki osadzone przy najmniejszej zawartości azotu w atmosferze były najbardziej kruche, a jednocześnie w temperaturze powyżej 250°C wykazywały największą przyczepność do podłoża. Przyczepność powłok nieznacznie zmniejszała się wraz ze wzrostem temperatury osadzania.


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