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Поступила в редакцию 30.10.2024
Поступила после доработки 03.12.2024
Принята к публикации 09.12.2024

[https://doi.org/10.53360/2788-7995-2024-4\(16\)-49](https://doi.org/10.53360/2788-7995-2024-4(16)-49)

IRSTI: 55.22.19



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DURABILITY AND CORROSION BEHAVIOR OF Ni-Cr-Al DETONATION COATINGS UNDER Na₂SO₄/NaCl EXPOSURE

Abstract: *This study investigates the durability and corrosion resistance of Ni-Cr-Al detonation-sprayed coatings when exposed to high-temperature environments containing molten Na₂SO₄ and NaCl. Such conditions are highly corrosive and frequently encountered in aerospace, energy, and chemical industries. Gradient and homogeneous Ni-Cr-Al coatings were compared to understand their behavior under aggressive exposure. The reveal of results those gradient coatings exhibit superior corrosion resistance due to their ability to retain protective oxides, such as Cr₂O₃, and mitigate stress-induced damage through compositional grading. In contrast, homogeneous coatings displayed significant degradation, including widespread corrosion, delamination, and the formation of sodium-based phases like NaNiO₂. XRD analysis confirmed the presence of oxidation and sulfidation products, with gradient coatings showing enhanced stability against phase transitions. These findings highlight the potential of gradient Ni-Cr-Al coatings to improve component performance in extreme conditions and provide valuable insights for optimizing coating compositions and processes to enhance operational reliability in harsh environments.*

Key words: *detonation spraying, NiCr-Al coatings, Na₂SO₄/NaCl salts, gradient coatings, aggressive environment.*

Introduction

Nickel-based coatings, particularly Ni-Cr-Al coatings, have become critical in high-temperature environments due to their excellent oxidation and corrosion resistance. These coatings are widely employed in industries such as aerospace, energy, and chemical processing, where components are subjected to aggressive environments containing molten salts like sodium sulfate (Na₂SO₄) and sodium chloride (NaCl) [1]. The combination of chromium and aluminum enhances the formation of protective oxide layers, primarily Cr₂O₃ and Al₂O₃, which act as barriers against further oxidation and corrosion [2-3].

Detonation spraying technique, has proven effective for producing dense and adherent Ni-Cr-Al coatings with superior mechanical and tribological properties [4]. However, the durability of such coatings under simultaneous exposure to Na₂SO₄ and NaCl remains a critical challenge. Molten salts are known to disrupt protective oxide layers through mechanisms such as basic fluxing and acidic dissolution, accelerating the degradation process. This is particularly relevant in environments with fluctuating temperatures, which may lead to the cyclic formation and spallation of oxide scales [5-7].

The synergistic effects of Na₂SO₄ and NaCl in inducing hot corrosion further complicate the material's performance. NaCl introduces chlorine-induced degradation mechanisms, including pitting and intergranular attack, while Na₂SO₄ contributes to the formation of low-melting eutectic phases, exacerbating coating degradation [8-9]. Investigating the corrosion behavior of Ni-Cr-Al detonation

coatings under these conditions is vital to understanding their long-term reliability and optimizing their composition and processing parameters [10].

This study focuses on the durability and corrosion mechanisms of Ni-Cr-Al detonation coatings under Na_2SO_4 and NaCl exposure. The findings aim to provide insights into improving the coatings' resistance to high-temperature corrosive environments.

Materials and methods

To produce homogeneous and gradient coatings based on Ni-Cr-Al, low-alloy heat-resistant boiler steel 12Kh1MF was selected as the substrate material. Samples were prepared in dimensions of 15x15x3 mm. Prior to coating application, the surfaces of the substrates were ground on all six sides using MIRKA sanding paper with a grain size of 1200 to ensure a uniform and flat surface. Subsequently, the samples were sandblasted on all six sides to enhance the adhesion of the sprayed coating. The coatings were prepared using a composite Ni-Cr-Al powder, consisting of 80 wt.% Ni-Cr powder (Ni20Cr80) and 20 wt.% Al (purity 99,99%). The nominal particle size of the powder ranged from 30 to 45 μm . Coatings were deposited using the CCDS 2000 detonation unit. Homogeneous Ni-Cr-Al coatings were obtained with a barrel filling volume of 50% with explosive gas, while gradient coatings were produced by decreasing the barrel filling volume to 25% with explosive gas. Detailed information on the gradient coating process is described in our previous work [4]. Both homogeneous and gradient Ni-Cr-Al coatings were applied to all six sides of the substrates.

Three types of samples were subjected to exposure in a $\text{Na}_2\text{SO}_4/\text{NaCl}$ environment: samples with homogeneous Ni-Cr-Al coatings, samples with gradient Ni-Cr-Al coatings, uncoated heat-resistant low-alloy steel 12Kh1MF. The surface of the samples prior to exposure is presented in Figure 1. The exposure tests were conducted at 700°C in static air under atmospheric pressure. Three samples were tested simultaneously, placed in a heat-resistant crucible capable of withstanding temperatures up to 2500°C. A muffle furnace (SNOL 7,2/1100) with a ceramic chamber and a maximum operating temperature of 1100°C was used for the tests. Prior to testing, the samples were photographed. The samples were held at 700°C for one hour per cycle, followed by 20 minutes of air cooling. The total exposure duration comprised 15 cycles.

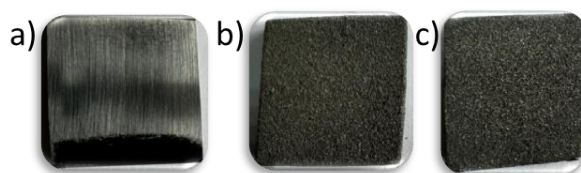


Figure 1 – The surface of the samples prior to exposure:
a) uncoated steel 12Kh1MF, b) homogeneous Ni-Cr-Al coatings, c) gradient Ni-Cr-Al coatings

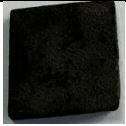
To identify the phases formed in the coatings after high-temperature oxidation tests, X-ray diffraction (XRD) analysis was performed using an X'PertPRO diffractometer with Cu-K α radiation ($\lambda = 1,54 \text{ \AA}$) at 40 kV and 30 mA. Diffractograms were collected in the 2θ range of 20° to 90° with a step size of 0,02° and a counting time of 0.5 seconds per step. The data were analyzed using the HighScore software.

Results and discussion

The surface morphology of gradient and homogeneous Ni-Cr-Al coatings before and after exposure to the $\text{Na}_2\text{SO}_4/\text{NaCl}$ environment demonstrates clear differences in their corrosion resistance (table 1). Initially, gradient coatings exhibit a smoother surface transition, while homogeneous coatings show uniform but slightly rougher textures. After exposure, gradient coatings display localized oxidation and sulfidation with relatively intact structural integrity, whereas homogeneous coatings suffer severe degradation, including widespread corrosion, cracking, and delamination. The observed corrosion products, consistent with XRD results (e.g., Cr_2O_3 and $\text{Ni}_{3-x}\text{S}_2$) in figure 2, indicate that gradient coatings better retain protective oxides and resist stress-induced damage, highlighting their superior durability compared to the uniform composition of homogeneous coatings. The initial steel shows the most significant degradation over time, with visible signs of corrosion and cracking after multiple cycles. The homogeneous Ni-Cr-Al coating provides moderate protection, but its performance diminishes over time as wear and coating detachment occur. The gradient Ni-Cr-Al coating outperforms both the uncoated steel and the

homogeneous coating, exhibiting minimal degradation even after extended cycles, likely due to the gradient structure's enhanced mechanical and chemical stability.

Table 1 – The surface morphology of samples before and after exposure to the Na₂SO₄/NaCl environment: Initial steel 12Kh1MF, homogeneous and gradient Ni-Cr-Al coatings

Cycles	Initial steel 12Kh1MF	Homogenous Ni-Cr-Al coating	Gradient Ni-Cr-Al coating
after 1 cycle			
after 5 cycles			
after 10 cycles			
after 15 cycles			

Prior to testing for high-temperature cyclic oxidation, the homogeneous Ni-Cr-Al coating consisted of the CrNi₃ phase and the Ni-Cr-Al gradient coating consisted of the CrNi₃, Al, and NiAl phases [4]. The XRD results reveal distinct phase transformations in both gradient (Figure 2a) and homogeneous (Figure 2b) Ni-Cr-Al coatings after exposure to the Na₂SO₄/NaCl environment. For the pristine coatings, stable phases such as CrNi₃, NiCrO₃, Cr₂O₃, and Al₂O₃ are observed, contributing to high thermocorrosion resistance. Upon exposure, both coating types exhibit the formation of new phases like Ni_{3-x}S₂, NiCr₂O₄, NaNiO₂, and CrS, indicating oxidation and sulfidation processes, particularly affecting chromium. In gradient coatings, the phase transitions suggest enhanced resistance due to better stress distribution and compositional grading, whereas homogeneous coatings show more pronounced degradation, evidenced by a higher intensity of sodium-based phases such as NaNiO₂.

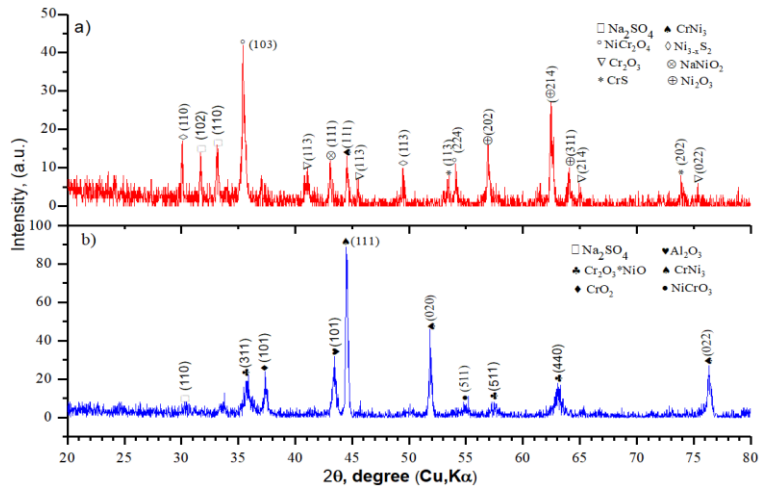


Figure 2 – Diffractogram of Ni-Cr-Al coatings after exposure to the Na₂SO₄/NaCl environment: a) gradient Ni-Cr-Al coating, b) homogenous Ni-Cr-Al coating

Conclusion

The study demonstrates that gradient Ni-Cr-Al coatings outperform homogeneous coatings in resisting high-temperature corrosion caused by molten Na₂SO₄ and NaCl. The superior performance of gradient coatings is attributed to their ability to better retain protective oxides such as Cr₂O₃ and Al₂O₃ and distribute stresses more effectively during thermal cycling. In contrast, homogeneous coatings exhibited significant degradation, including delamination and the formation

of corrosive sodium-based phases. These findings underline the importance of compositional grading in designing Ni-Cr-Al coatings for critical applications in aerospace, energy, and chemical industries where components face aggressive environmental conditions. Future research should focus on further refining gradient coating techniques and exploring their long-term performance in varying operational scenarios.

References

1. A comprehensive study on hot corrosion resistance of NiCoCrAlYTa and NiCrAl thermal-sprayed coatings for CSP applications / A. Daniel et al // Journal of Energy Storage. – 2023. – V. 74. – P. 109346.
2. Comparative hot corrosion performance of APS and Detonation sprayed CoCrAlY, NiCoCrAlY and NiCr coatings on T91 boiler steel / C. Sundersan et al // Corrosion Science. – 2021. – V. 189. – P. 109556.
3. Manjor K. Production of Nanocrystalline Ni-20Cr Coatings for High-Temperature Applications / K. Manjor, S. Harpreet, S. Narinder // Journal of Thermal Spray Technology. – 2014. – V. 23. – P. 692-707.
4. Structure and Tribological Properties of Ni-Cr-Al Based Gradient Coating Prepared by Detonation Spraying / B. Rakhadilov et al // Coatings. – 2021. – Vol. 11(2). – P. 218.
5. Sukhpal S.C. High temperature hot corrosion behaviour of NiCr and Cr3C2-NiCr coatings on T91 boiler steel in an aggressive environment at 750°C / S.C. Sukhpal, S.S. Hazoor, S.S. Buta // Surface and Coatings Technology. – 2012. – V. 206(19). – P. 3839-3850.
6. Madjid S. Corrosion of steel alloys in eutectic NaCl+Na₂CO₃ at 700 °C and Li₂CO₃ + K₂CO₃ + Na₂CO₃ at 450°C for thermal energy storage / S. Madjid, A. Theodore, W. Geoffery // Solar Energy Materials and Solar Cells. – 2017. – Vol. 170. – P. 48-59.
7. Niraj B. Accelerated hot corrosion studies of cold spray Ni-50Cr coating on boiler steels / B. Niraj, S. Harpreet, P. Satya // Materials & Design. – 2010. – Vol. 31(1). – P. 244-253.
8. Lina M. Comparative review of different influence factors on molten salt corrosion characteristics for thermal energy storage / M. Lina, Zh. Cancan, W. Yuting // Solar Energy Materials and Solar Cells. – 2022. – Vol. 235. – P. 111485.
9. Xin R. High-temperature oxidation and hot corrosion behaviors of the NiCr–CrAl coating on a nickel-based superalloy / R. Xin, W. Fuhui, W. Xin // Surface and Coatings Technology. – 2005. – Vol. 198(1). – P. 425-431.
10. Investigation of high-temperature oxidation of homogeneous and gradient Ni-Cr-Al coatings obtained by detonation spraying / B. Rakhadilov et al // Coatings. – 2024. – Vol. 14(11). – P. 1-11.

Funding

This paper was performed within the grant financing of scientific research of the Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan. Grant AP22688426.

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Na₂SO₄/NaCl ӘСЕРІНДЕГІ Ni-Cr-Al ДЕТОНАЦИЯЛЫҚ ЖАБЫНДАРЫНЫҢ БЕРІКТІГІ МЕН КОРРОЗИЯЛЫҚ ҚАСИЕТТЕРІ

Бұл зерттеуде жоғары температуралық Na₂SO₄ және NaCl тұзды орталарда Ni-Cr-Al детонациялық бүрікпемен жабылған қабаттардың беріктігі мен коррозияға төзімділігі зерттелді. Мұндай агрессивті жағдайлар жиі авиация, энергетика және химия өнеркәсібінде кездеседі. Агрессивті ортадағы Ni-Cr-Al градиентті және біртекті жабындарының қасиеттері салыстырылды. Зерттеу нәтижелері көрсеткендей, градиентті жабындар жоғары коррозияға төзімділікті көрсетеді. Ал біртекті жабындар елеулі деградацияға, оның ішінде кеңінен таралған коррозияға, қабыршақтануға және NaNiO₂ сияқты натрий негізіндегі фазалардың түзілуіне ұшырады. Рентгендік фазалық талдау нәтижесінде тотығу және сульфидтелу өнімдерінің пайда болғаны расталды, ал градиентті жабындар фазалық ауысымдарға жоғары тұрақтылық көрсетті. Бұл нәтижелер градиентті Ni-Cr-Al жабындарының төтенше жағдайларда қолдану тиімділігін

арттырып, жабын құрамы мен технологиясын оңтайландыру бойынша маңызды ақпарат беретінін дәлелдейді.

Түйін сөздер: детонациялық бүрку, Ni-Cr-Al жабындары, $\text{Na}_2\text{SO}_4/\text{NaCl}$ тұздары, градиентті жабындар, агрессивті орта.

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ДОЛГОВЕЧНОСТЬ И КОРРОЗИОННОЕ ПОВЕДЕНИЕ ДЕТОНАЦИОННЫХ ПОКРЫТИЙ Ni-Cr-Al ПРИ ВОЗДЕЙСТВИИ $\text{Na}_2\text{SO}_4/\text{NaCl}$

В данном исследовании изучается долговечность и коррозионная стойкость покрытий Ni-Cr-Al, нанесённых методом детонационного напыления, при воздействии высокотемпературных сред, содержащих расплавленные Na_2SO_4 и NaCl . Эти условия высокоагрессивны и часто встречаются в аэрокосмической, энергетической и химической промышленности. Проведен сравнительный анализ градиентных и однородных покрытий Ni-Cr-Al для понимания их поведения в агрессивных средах. Результаты показывают, что градиентные покрытия демонстрируют превосходную коррозионную стойкость. В отличие от этого, однородные покрытия подвергались значительной деградации, включая обширную коррозию, деламинацию и образование фаз, содержащих натрий, таких как NaNiO_2 . Рентгенофазовый анализ подтвердил наличие продуктов окисления и сульфидации, при этом градиентные покрытия продемонстрировали повышенную стабильность к фазовым переходам. Эти результаты подчеркивают потенциал градиентных покрытий Ni-Cr-Al для улучшения работы компонентов в экстремальных условиях и предоставляют ценные данные для оптимизации состава и технологий нанесения покрытий.

Ключевые слова: детонационное напыление, покрытия Ni-Cr-Al, соли $\text{Na}_2\text{SO}_4/\text{NaCl}$, градиентные покрытия, агрессивная среда.

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Received 06.12.2024

Revised 10.12.2024

Accepted 11.12.2024