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STUDY OF Ni-20Cr COATINGS FOR HIGH TEMPERATURE APPLICATIONS – A REVIEW

BADANIA POWŁOK Ni-20Cr DO ZASTOSOWAŃ WYSOKOTEMPERATUROWYCH – PRZEGLĄD LITERATURY

Hot corrosion is a serious problem in various high temperature applications. The thermal spray coatings provides possible solution to counter the problem of hot corrosion in high temperature environment and enhances the life of equipment. Ni-20Cr alloy compositions require long initiation time at which the hot corrosion process moves from the initiation stage to the propagation stage. In this review, the performance of Ni-Cr coatings by different investigators has been presented to understand the mechanism of hot corrosion under different environments.

Keywords: hot corrosion, nickel-chromium coatings, surface engineering, boilers

Wysokotemperaturowa korozja jest poważnym problemem w zastosowaniach wysokotemperaturowych. Możliwym rozwiązaniem problemu korozji w warunkach wysokiej temperatury poprzez zwiększenie żywotności urządzeń jest zastosowanie termicznych powłok natryskowych. Stopy o składzie Ni-20Cr wymagają długiego czasu inicjacji, po którym proces korozji wysokotemperaturowej z etapu inicjacji przechodzi do etapu propagacji. W tym przeglądzie zostały zaprezentowane badania zachowania powłok niklowo-chromowych wykonane przez różnych badaczy, żeby zrozumieć mechanizm korozji wysokotemperaturowej w warunkach różnych środowisk.

1. Introduction

Corrosion is a natural occurrence commonly defined as the deterioration of a substance (usually metal) or its properties as a consequence of its reaction with the environment. The direct cost of metallic corrosion in the U.S. is \$276 billion-which is 3.1% of the Nation's Gross Domestic Product (GDP) [1]. So it is important to understand the nature of all types of degradation of metals and alloys so that preventive measures can be economically devised against metal loss to ensure safety and reliability in the use of metallic components. Corrosion draws the attention of researchers in the field of environmental degradation of metals [2]. The power plants suffered major loss due to hot corrosion resulting in substantial economic loss [3]. The temperature of steam produced in boilers depends on corrosion and creep resistance of boiler components, both the factors effects the thermal efficiency of the boilers. Consequently, the thermal efficiency decreases and hence electricity production is reduced [3].

Hot corrosion is a serious problem in high temperature applications such as boilers, gas turbines, waste incinerations, diesel engines, coal gasification plants, chemical plants [4]. It is accelerated oxidation of materials, at elevated temperatures, induced by a thin film of fused salt deposit [5]. The fireside corrosion in a boiler occurs because of the reaction of the sulphur species in the gas phase with metal surfaces [6].

The sulphur present in the coal and fuel oils, especially in low-grade fuels, yield SO₂ on combustion which is partially oxidized to SO₃.

The power plants boiler tubes of coal fires boilers suffers big economic losses due to high rate of corrosion, erosion-corrosion of boiler tubes. To overcome this problem the use of thin anti-wear and anti-erosion-corrosion thermal spray coatings is the perfect choice there is an increasing trend in the deposition of Ni based metallic alloy coatings such as Ni-20 wt.% Cr for protection against hot corrosion using thermal spray processes. This is because of high resistance offered by chromium, nickel-chromium alloys against high-temperature oxidation and corrosion. This makes Ni-Cr coatings widely used as welded and thermally sprayed coatings in fossil fuel-fired boilers, waste incineration boilers, and electric furnaces [7].

Oxidation behavior of Ni-20Cr metallic coatings using high-velocity oxy-fuel (HVOF) and air plasma spray process on 9Cr-1Mo substrate steel was observed in the temperature range of 600-750°C [8]. The kinetics of hot corrosion like formation of protective oxide scale of Cr₂O₃, diffusion of nickel from the coatings to the substrate and the diffusion of iron from the substrate to the coatings for longer exposures to steam oxidation was investigated. The trend of formation of scale initiation with temperature and time duration was also observed at the interface between the coating and the substrate in case of

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the APS coating. In the similar investigation the researchers also investigated the behavior of Mn and Si in the spray powders during steam oxidation of Ni-Cr thermal spray coatings on the 9Cr-1Mo type steel [9]. In the present review the resistance offered by Ni-Cr coatings against hot corrosion is presented.

2. Hot corrosion

The concept of hot corrosion or high temperature corrosion came into existence with the failure of boiler tubes and later with the failure of gas turbine air-foil materials [5]. Hot corrosion occurs when salt or ash deposits accumulate on the surfaces of alloys and alter the environment-alloy reactions that would have occurred had the deposit not been present [10].

According to Hancock (1987), Hot corrosion is an accelerated form of oxidation which occurs when metals are heated in the temperature range of 700-900°C in the presence of sulphate deposits formed as a result of the reaction between sodium chloride and sulphur compounds in the gas phase around the metals as shown in Fig. 1.

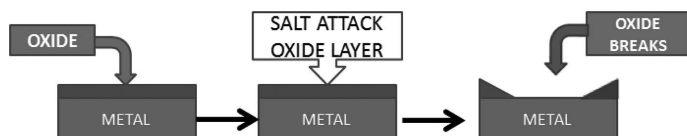


Fig. 1. Mechanism of hot corrosion

According to Rapp and Zhang metals and alloys sometimes experience accelerated oxidation when their surfaces are covered with a thin film of fused salt in an oxidizing gas atmosphere at elevated temperatures this mode of attack is called high temperature corrosion. The nature of hot corrosion attack involves more severe degradation of the alloy compared to that occurring in the same gas environment in the absence of the deposit. The increase in attack often minimal initially, with the alloy shows little effects of deposit. Eventually, the degradation mechanism is modified by the deposit in a way such that the rate of attack is increased by an order of higher magnitude. Finally the deposit is usually liquid. The hot corrosion process is dependent on parameters such as alloy composition, deposit composition, and temperature [10].

2.1. Stages of Hot Corrosion

The phenomenon of hot corrosion occurs in two stages.

a. Initiation stage of Hot Corrosion

During the initiation stage elements in the alloy are oxidized and the electrons are transferred from the metallic atoms to reducible substances in the deposit. A reaction product barrier is formed beneath the deposit on the alloy surface which exhibits the features resulting from the gas-alloy reaction. Eventually the protective barrier formed via selective oxidation is rendered ineffective and the hot corrosion process enters into the propagation stage [10].

b. Propagation modes of hot corrosion

The propagation stage of the hot corrosion sequence is the stage for which the super alloy must be removed from the ser-

vice since this stage always has much larger corrosion rates than for the same super alloy in the initiation stage [10, 11].

2.2. Hot corrosion mechanism

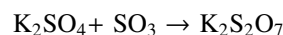
Hot corrosion can occur by two mechanisms termed as type I and type II hot corrosion, also known as high temperature hot corrosion (HTHC) and low temperature hot corrosion (LTHC) respectively [12,13].

Type I Hot Corrosion

Type 1 HTHC is observed in the temperature range of about 825-950°C (melting point of pure Na₂SO₄ is 884°C) [14]. This type of mode is identified by the formation of sulfides and a corresponding depletion of the reactive component in the alloy substrate [15-18].

Type -II Hot Corrosion

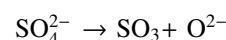
In coal based power plants, fireside corrosion involves hot corrosion of type II. Na₂SO₄ or K₂SO₄ formed from the reaction of SO₂ with NaCl or KCl (present in the coal) is the principal salt deposits in the ash [19]. As the maximum outer wall temperature of steam generating tubes range from 550°C to 650°C, the hot corrosion does not take place till the sulphate deposits react with SO₃ to form pyrosulphates. For the reaction



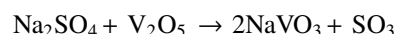
about 150 ppm of SO₃ is required and for a similar reaction with Na₂SO₄, the requirement of SO₃ is about 2500 ppm. Once the pyrosulphates are formed, the complex mixture of the two melts at about 451°C for the potassium salt and 551°C for the sodium salt and severe hot corrosion takes place [19].

Salt Fluxing Reactions

The process by which the reaction product barrier becomes non-protective due to the formation of species that are soluble in the liquid deposit have been called fluxing reactions. In molten salt sulphate deposit the following equation can be used to define acidity and basicity:



With the equilibrium constant, $K = P_{SO_3} \cdot a_{O^{2-}}$, where P_{SO_3} is the pressure of SO₃ and $a_{O^{2-}}$ = activity of oxide ions in the melt. Acidity increases as the P_{SO_3} is increased. Acidity is not controlled by the P_{SO_3} in the gas alone when there are other gradients in the system. For example V₂O₅ can react with Na₂SO₄ to increase the acidity of the melt via reaction given below:



3. Deposition of Ni-20Cr coatings using various thermal spray processes

Ni-20Cr, Ni-50Cr and 100% Cr powders were deposited on Ni base alloys and steels using detonation spraying, HVOF spraying and plasma spraying [20]. The hot corrosion behavior of coated samples was tested in actual refuse incineration

plant. It was inferred that Ni-50Cr sprayed coating by detonation gun remained in excellent condition even after 7 years and thickness lost was 1/37 of carbon steel.

Ni-20Cr powder using HVOF spraying was deposited on stainless steel samples. XRD revealed that the coating had Ni, Cr₃C₂, Cr-Ni, Fe_{0.9}Ni_{0.056}, Ni-Cr-Fe and Fe-Cr phases in as-sprayed condition. The microhardness of the coatings was found dependent on porosity oxide, un-melted, semi-melted particles and inclusions, which contributed in decreasing the hardness values [21].

NiCrAlY, Ni-20Cr, Ni₃Al and Stellite-6 metallic coatings were deposited on Fe-based super alloy (32Ni-21Cr-0.3Al-0.3Ti-1.5Mn-1.0Si-0.1C-Bal Fe) using plasma spraying [22]. Hot corrosion studies were conducted on uncoated as well as plasma spray coated superalloy specimens after exposure to molten salt at 900°C under cyclic conditions, which revealed the following trend of protection NiCrAlY coating > Ni-20Cr coating > Ni₃Al coating > Stellite-6 coating. The XRD, SEM/EDAX and electron probe microanalysis (EPMA) were used as characterization techniques to analyze the corrosion products. It was concluded that the formation of oxides and spinels of nickel, aluminium, chromium or cobalt contributed to development of hot corrosion resistance in the coatings.

NiCrAlY, Ni-20Cr and Ni₃Al metallic coatings were deposited on Ni based super alloy (superni 718-Inconel 718) by Shrouded Plasma Spray Process. It was found that coatings have lamellar structure with distinctive boundaries along with the presence of some porosity. The microhardness trend of the coatings was found to Ni-20Cr > NiCrAlY > Ni₃Al with the distance from the coating-substrate interface. The XRD characterization of the coatings revealed the formation of solid solutions [23].

Ni-Cr (Ni-45Cr-4Ti) and FeCrAl coatings were deposited on water-wall tubes of boilers using high-velocity electric-arc-sprayed (HVAS). Ni-Cr coatings showed the best anti-corrosion results. It was found that Ni-Cr coatings had slightly lower pores than FeCrAl coatings [24].

Ni-20Cr, Stellite-6 powders were deposited on ASTM-SA210-grade A1, ASTM-SA213-T-11 and ASTM-SA213-T-22 using shrouded plasma spray process. It was found that considerable reduction in the micro-hardness and porosity after laser re-melting of the coatings occurred which contributed to significant dilution of coating due to inter diffusion of atoms [25].

NiCrBSi, Cr₃C₂-NiCr, Ni-20Cr, and Stellite-6 coatings were done on Fe-based super alloy using HVOF thermal spray process. The salt studies were conducted at 900°C under cyclic conditions to study the hot corrosion behavior of the coatings in an aggressive environment of Na₂SO₄-60%V₂O₅. The kinetics of corrosion was studied from the thermo gravimetric technique. The following trend of protection of super alloy was obtained Ni-20Cr > Cr₃C₂-NiCr > NiCrBSi > Stellite-6. It was found that the formation of oxides and spinels of nickel, chromium, or cobalt contributed to the development of hot corrosion resistance in the coatings [26].

Ceramic (Al₂O₃), metallic (Ni-20 wt% Cr), and cermets (WC-12 wt% Co) powders were deposited using detonation spray technique. The effect of particle size and its distribution on the coating properties were studied. The increasing

trend of surface roughness and porosity with increasing powder particle size was observed. The fine and narrow size range WC-Co coating exhibited superior wear resistance. The coarse and narrow size distribution Al₂O₃ coating exhibited better performance under abrasion and sliding wear modes however under erosion wear mode the as-received Al₂O₃ coating exhibited better performance. In the case of metallic (Ni-Cr) coatings, the coatings deposited using coarser powder exhibited marginally lower-wear rate under abrasion and sliding wear modes. However, under erosion wear mode, the coating deposited using finer particle size exhibited considerably lower wear rate [27].

The high-velocity air-fuel (HVOF) and HVOF coatings were heat treated for up to 30 days at 900°C to generate a range of coating microstructures up to a steady state. Erosion was performed under the same conditions. Heat treatment increased the ductility of the NiCr phase, enabling ductile erosion deformation to occur. Intersplat sintering reduced the significance of splat based erosion mechanisms and forced mass loss to become dictated by the phase microstructure. Such developments improved the quantified erosion resistance of both coating systems relative to the as-sprayed conditions. The coating microhardness was shown to be a poor indicator of erosion response across the range of coating microstructures investigated [28].

Bala 2009 et al. [29] studied the high-temperature oxidation behavior of cold-sprayed Ni-20Cr and Ni-50Cr coatings on SAE 213-T22 boiler steel at 900°C in air under cyclic heating and cooling conditions for 50 cycles. The kinetics of oxidation of coated and bare boiler steel was established with the help of weight change measurements and it was found that all the coated and bare steels obeyed parabolic rate law of oxidation. The uncoated steel suffered corrosion in the form of intense spalling and peeling of its oxide scale, which was perhaps due to the formation of un-protective Fe₂O₃ oxide scale. The trend of protection of coatings against hot corrosion is Ni-50Cr > Ni-20Cr.

Deposition of Ni-20Cr coating on molybdenum substrate by laser cladding was studied. The coating was found free of cracks and pores, and strongly bonded to the substrate. The oxidation behavior of the coating indicates that the laser clad Ni-20Cr coating can effectively prevent oxidation of molybdenum at 600°C in air. The oxide scale formed on the coating surface by oxidation in air is composed of NiO, Cr₂O₃ and NiMoO₄ [30].

Ni-20Cr coatings on boiler steel ASTM A213, 347H using HVOF technique were studied in actual boiler environment at 700°C and 900°C under cyclic conditions to ascertain their erosion-corrosion (E-C) behavior. The kinetics of the hot corrosion was studied using mass change and thickness loss data. It was observed that overall mass loss was reduced by 31% and thickness loss by 44% after the application of the coating. During air oxidation exposures, the coating was found to be intact with only marginal spallation of its oxide scales, which is an indicator of good adhesion between the coating and substrate steel. The air oxidation mass change data revealed that the coating enhanced the oxidation resistance of the steel by 85% [31].

NiCrAlY + CeO₂ alloy coatings on three different super alloys using detonation gun spraying were studied [32].

Average porosity on three substrates was less than 0.58% and surface roughness of the coatings was in the range of 6.17-6.94 μm . Average bond strength and microhardness of the coatings were found to be 58 MPa and 697-920 HV, respectively.

Ni-20Cr coatings on ASTM-SAE 213-T22 using HVOF spray and detonation-gun (D-gun) spray techniques were deposited and studied. The salt ($\text{Na}_2\text{SO}_4\text{-}60\%\text{V}_2\text{O}_5$) studies were carried out at 900°C for bare and coated samples to access the kinetics of hot corrosion. Specimens were also exposed to the superheater zone of a thermal power plant boiler at an average temperature of 700°C under cyclic conditions to ascertain their erosion-corrosion (E-C) behavior. The micro structural study revealed HVOF-sprayed coating intact during exposure to both given environments; whereas the D-gun coating showed spallation of its oxide scale during exposure to the molten salt

environments. HVOF-sprayed Ni-20Cr coating offered better hot corrosion resistance in comparison to D-gun sprayed coatings in boiler applications [33].

Bala et al. [34] investigated the deposition of Ni-20Cr powder on T-22 boiler steel using HVOF and cold spray processes. To evaluate the performance of the coatings in actual conditions the bare as well as the coated steels were subjected to cyclic exposures in the super heater zone of a coal fired boiler for 15 cycles. It was found that the HVOF sprayed coating performed better than its cold sprayed counterpart in actual boiler environment.

Table 1 gives the summary of the investigations by various researchers on Ni-Cr coatings for high temperature applications using thermal spray processes.

TABLE 1

Summary of the investigations on Ni-Cr coatings using thermal spray process

Author name	Coating material	Substrate	Thermal Spray Process	Testing Environment	Important Findings
1	2	3	4	5	6
Yamada et al. [20]	Ni-20Cr, Ni-50Cr and 100%Cr	Ni base alloys and steels	Detonation spraying, HVOF spraying and Plasma spraying	Actual refuse incineration plant	Ni-50Cr sprayed coating by detonation gun found to have longer sustainability, 1/37 of thickness is lost after 7 years.
Ak et al. [21]	Ni-20Cr	Stainless steel	HVOF spraying		The formation porosity oxide, un-melted and semi-melted particles and inclusions decreased the hardness values.
H Singh et al. [22]	NiCrAlY, Ni-20Cr, Ni ₃ Al and Stellite-6	Fe-based Super alloy (32Ni-21Cr-0.3Al-0.3Ti-1.5Mn-1.0Si-0.1C-Bal Fe)	Plasma sprayed	Na ₂ SO ₄ -60%V ₂ O ₅ under laboratory conditions	Resistance to hot corrosion follows the trend NiCrAlY coating >Ni-20Cr coating >Ni ₃ Al coating >Stellite-6 coating
S B Mishra et al. [23]	NiCrAlY, Ni-20Cr and Ni ₃ Al metallic coatings	Superni 718-Inconel 718	Shrouded plasma sprayed	Power plant boilers	Ni-20Cr >NiCrAlY >Ni ₃ Al
Lianyong et al. [24]	Ni-Cr (Ni-45Cr-4Ti) and FeCrAl coatings		HVAS sprayed	Power plant boilers	Ni-Cr coatings had slightly lower pores than FeCrAl coatings
B S Sidhu et al. [25]	Ni-20Cr, Stellite-6 powders	ASTM-SA213-T-11 and ASTM-SA213-T-22	Shrouded plasma sprayed	Power plant boilers	Considerable reduction in microhardness and porosity.
T S Sidhu et al. [26]	NiCrBSi, Cr ₃ C ₂ -NiCr, Ni-20Cr, and Stellite-6	Fe-based super alloy	HVOF	Na ₂ SO ₄ -60%V ₂ O ₅ at 900°C	Ni-20Cr >Cr ₃ C ₂ -NiCr >NiCrBSi >Stellite-6
P Suresh Babu et al. [27]	Ceramic (Al ₂ O ₃), metallic (Ni-20 wt% Cr), and cermets (WC-12 wt% Co)	Mild steel specimens	Detonation spraying	Power plant boilers	The marginal influence of powder particle size on coating properties and performance.

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1	2	3	4	5	6
S Matthews et al. [28]	Ni-20Cr		HVOF	Air oxidation studies at 900°C	Heat treatment increased the ductility of the NiCr matrix phase.
N Bala et al. [29]	Ni-20Cr, Ni-50Cr	SAE 213- T22	Cold Spray	Air oxidation studies at 900°C	Ni-50Cr >Ni-20Cr
Can Huang et al. [30]	Ni-20Cr	Mo	Laser cladding	Air oxidation studies at 600°C	The oxide scale on the coating after a high temperature exposure is composed of NiO, Cr ₂ O ₃ and NiMoO ₄ , the presence of molybdenum in the oxidation layer resulting from partial coating/substrate dilution.
G Kaushal et al. [31]	Ni-20Cr	A213 347H	HVOF	Actual boiler at 700°C	Coatings enhanced the oxidation resistance of the steel by 85%.
S Kamal et al. [32]	NiCrAlY + 0.4 wt% CeO ₂	Super alloys	Detonation gun		Average porosity was less than 0.58% and surface roughness 6.17-6.94 μm, bond strength 58MPa and microhardness 697-920Hv.
G Kaushal et al. [33]	Ni-20Cr	ASTM-SAE 213-T22	HVOF and D-Gun	Actual boiler at 700°C	HVOF-sprayed Ni-20Cr coating a better choice for the given boiler applications.
N. Bala et al. [34]	Ni-20Cr	SAE 213-T22	HVOF and Cold sprayed	Actual boiler at 700°C	HVOF sprayed coating performed better than its cold sprayed counterpart in actual boiler environment.

4. Summary and Conclusion

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Hot corrosion poses a serious problem in high temperature applications like power plant boilers, gas turbines, waste incinerations, aircraft, and in other energy conversion and chemical process systems. Severity of this problem rises further when fuel of low grades is used in the power plant boilers because of the non-availability of high grade fuel and cost involved in procurement. The only solution to enhance the life of boiler tubes is to use the thermal spray coatings to counter the problem of hot corrosion. It has been concluded after reviewing the literature that Ni-20Cr coatings can be successfully deposited on different boiler steels using various thermal spray processes. Further it is observed nickel alloyed with chromium (Ni-20Cr) oxidizes to Cr₂O₃, and other protective spinel phases such as NiCr₂O₄, which makes it suitable for use up to 950°C to counter hot corrosion in different environments.

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