

THE ROLE OF CHLORIDE SALTS ON HIGH TEMPERATURE CORROSION OF 321 STAINLESS STEEL

VLOGA KLORIDNIH SOLI PRI VISOKOTEMPERATURNI KOROZIJI NERJAVNEGA JEKLA 321

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The effect of CaCl_2 and BaCl_2 salt coatings on the high temperature corrosion of 321 stainless steel at $950\text{ }^\circ\text{C}$ in a slow current of air for the period of 72 hours were studied. The 321 alloy was severely attacked by calcium- and barium-chlorides due to formation of volatile chlorides. The data have been complemented by oxidation kinetics measurements and morphological structures were analyzed using scanning electron microscope (SEM). The elemental distribution on the alloy surface deposits were characterized by using energy dispersive X-ray (EDAX) analysis. The alkaline earth metal chloride salts have deleterious effect on the protectivity of the scale and rapid degradation of the alloy is noted.

Key words: 321 stainless steel, Hot Corrosion, CaCl_2 , BaCl_2 , Scale

Raziskan je bil vpliv prekritij s solmi CaCl_2 in BaCl_2 na visokotemperaturno oksidacijo nerjavnega jekla 321 v počasnem toku zraka pri $950\text{ }^\circ\text{C}$ v trajanju do 72 h. Zaradi nastanka volatilnih kloridov sta oba klorida zlitino močno napadla. Določena je bila kinetika oksidacije, morfologija pa je bila določena z opazovanjem v vrstičnem mikroskopu. Porazdelitev elementov v depozitu na površini je bila določena z energijsko disperzivno spektrometrijo (EDAX). Kloridi alkalnih kovin močno zmanjšajo varovalnost škaje in povzročijo hitro degradacijo zlitine.

Ključne besede: nerjavno jeklo 321, vroča korozija, CaCl_2 , BaCl_2 , škaja

1 INTRODUCTION

The intensification of process engineering in almost every branch of modern technology, and development of new technologies make increasingly higher requirements for metallic construction materials, especially for their heat and scaling resistance. The increase in operating efficiency of certain installations or plants is generally achieved by the application of higher temperatures and pressures and higher flow velocities of gases and vapours which creates gas corrosion hazard for the construction materials¹⁻⁷.

The corrosion process under hot gases or vapours being a mixture of many aggressive components, proceeds usually many times faster and is characteristic by a non-uniform attack of metal surface⁸⁻¹². It became obvious that chloride, always present in such industrial gases, is one of the most dangerous aggressive components of the above mentioned atmospheres^{13,14}.

In this study, the 321 stainless specimens were subjected to treatments of CaCl_2 and BaCl_2 , oxidised at $950\text{ }^\circ\text{C}$ for times ranging 12 h to 72 h was chosen in order to highlight the corrosion phenomena.

Finally the results of morphologies were carried out by using SEM (model Jeol 6460-LA) as well as energy-dispersed X-ray spectroscopy profiles of elements of deposits on the surface of corroded 321 alloy were presented.

2 EXPERIMENTAL

The present study has been carried out using commercially available 321 stainless steel. Its chemical composition was as follows: C-0.08 %, Mn-2 %, Si-1 %, Cr-17.5 %, Ni-10.5 %, P-0.045 %, S-0.03 % and Fe-balance. The 321 stainless steel sheets were cut into small pieces of size (20 × 12 × 3) mm. The surface of each specimens was polished mechanically with (180, 320, 600) grades of silicon carbide paper. The specimens were coated with CaCl_2 and BaCl_2 in a preheated condition to obtain a layer of salt deposition¹³. The coated specimens were dried and weighed, followed transferred into a crucible. The salt coated alloy were oxidised at $950\text{ }^\circ\text{C}$ for the periods of 72 h in slow current of air and mass changes were recorded at every 12 h of interval. For each condition, two series of specimens were corroded in accordance with reference¹⁴.

The microstructural and microchemical characterization were performed using Jeol 6460-LA scanning electron microscope equipped with a energy dispersive X-ray spectrometer and analyzer.

3 RESULTS

Figure 1 shows the curve of mass change versus exposure time of 321 stainless steel coated with CaCl_2 and BaCl_2 , oxidized at $950\text{ }^\circ\text{C}$ in slow blowing air. The

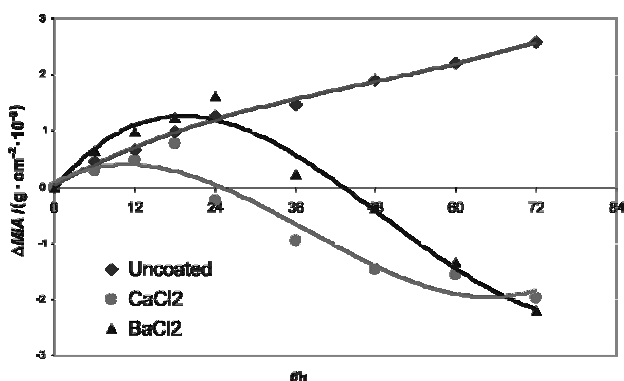


Figure 1: Oxidation behavior of 321 stainless steel without coated, coated with CaCl₂ & BaCl₂ as shown by a plot of mass change vs time, oxidized at 950 °C for 72 h

Slika 1: Oksidacija nerjavnega jekla 321 brez prekritja in z njim s CaCl₂ in BaCl₂. Sprememba mase v odvisnosti od časa pri oksidaciji do 72 hr pri 950 °C

graph of the mass change increases by increasing the exposure times shows for the uncoated alloy, a parabolic curve. The specimens coated with calcium and barium chloride exhibited the weight gain upto 24 h and mass loss with further increase of annealing time. The conclusion is that chlorides are more reactive in presence of metal because of the formation of volatile metallic chloride. The greater activity of calcium chloride is

explained by the weaker bonding of calcium chloride than that of barium chloride.

Morphological Studies of 321 stainless steels

In **Figure 2 (a, b)** the 321 alloy coated with CaCl₂ is shown, the scales formed are rough exhibiting a tendency to deform, wrinkle and microcrack. The formation of metallic chloride may have proceeded through the formation of intermediate volatile species, f.i. CrO₂Cl₂, some of which evaporate and some of decompose and accumulate at the alloy/salt interface in the form of Cr₂O₃.

The SEM micrograph of specimen coated by BaCl₂ exposed at 950 °C for 72 h (**Figure 3 a, b**) showing the presence of internal and pitting corrosion. The specimens exposed at 950 °C were badly deteriorated by layers of oxides and metallic chloride. The deposit film shows the presence of voids and pores especially in the outer layers of the scale.

Energy Dispersive X-Ray Analysis (EDAX)

Figures 4 and 5, the EDAX spectra, elements and compounds had been verified the content of the elements of the specimen coated by calcium chloride and barium chloride exposed at 950 °C for 72 h. The results of spectra and elements showed that the surface was mainly

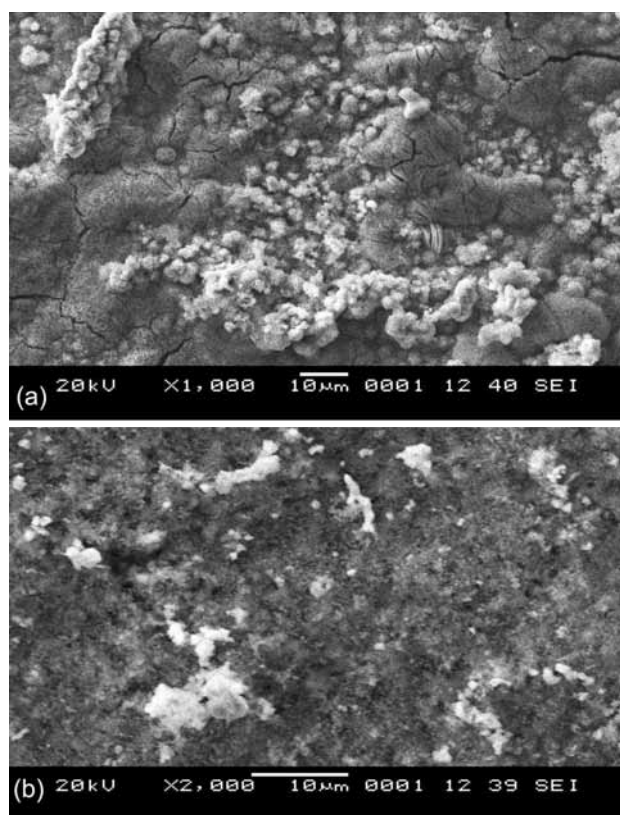


Figure 2: Outer surface of the scale formed on 321 stainless steel coated with CaCl₂, oxidised at 950 °C for 72 h

Slika 2: Zunanja površina škaje, ki je nastala pri 72-urni oksidaciji nerjavnega jekla 321, prekritega s CaCl₂

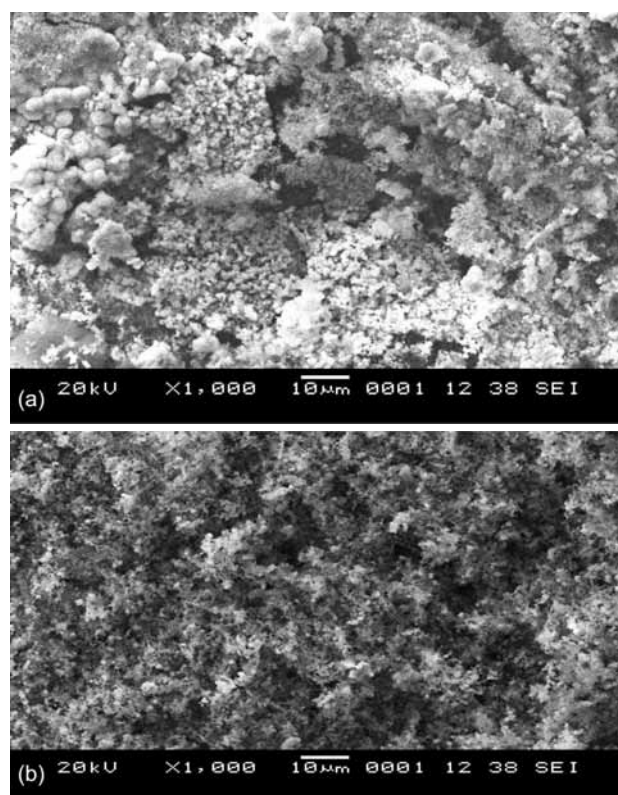


Figure 3: Outer surface of scales formed on 321 stainless steel coated with BaCl₂, oxidised at 950 °C for 72 h

Slika 3: Zunanja površina škaje, ki je nastala pri 72-urni oksidaciji nerjavnega jekla 321, prekritega z BaCl₂

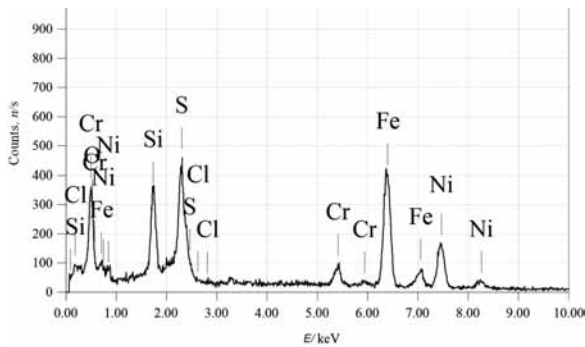
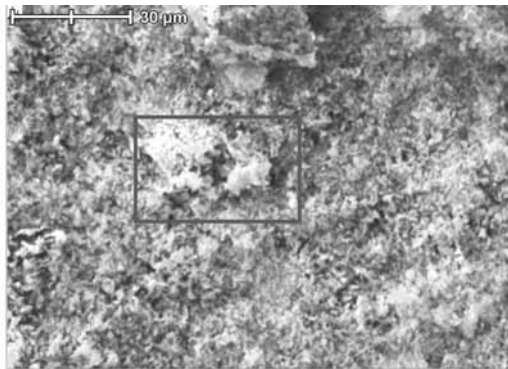


Figure 4: EDAX spectra of the elements on the specimen coated with CaCl₂, oxidized at 950 °C for 72 h in blowing air

Slika 4: Posnetek analizirane površine in EDAX-spekter elementov v vzorcu, prekritem s CaCl₂, ki je bil oksidiran v zračnem toku 72 h pri 950 °C

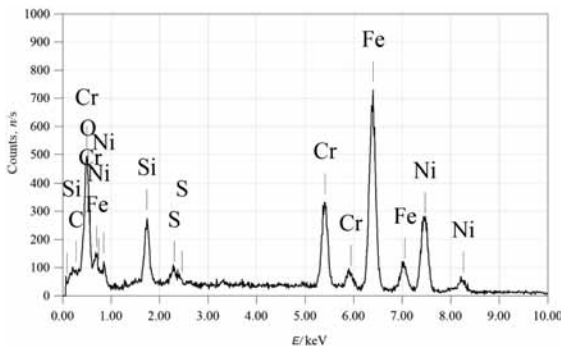
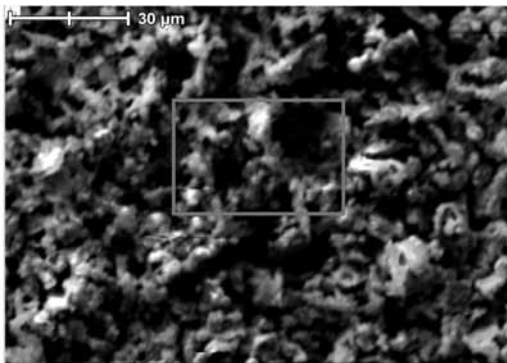
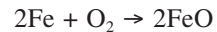


Figure 5: EDAX spectra of the elements and compounds of the specimen coated with BaCl₂, oxidized at 950 °C for 72 h in blowing air

Slika 5: Posnetek analizirane površine in EDAX-spekter elementov v vzorcu, prekritem z BaCl₂, ki je bil oksidiran v zračnem toku 72 h pri 950 °C

composed of nickel (Ni), chromium (Cr), iron (Fe) and oxygen (O). The results were logically acceptable because 321 stainless steel containing 17.5 % of chromium, 10.5 % of nickel and iron as balance.

Tables 1, 2 show the elemental analysis results of specimen coated with calcium- and barium- chloride that exposed at 950 °C for 72 h. According to the results in **Tables 1, 2**, iron oxide, FeO, was the main oxide product, it appearance as the site product while corrosion occur. Iron oxide formed when iron (Fe), reacting with oxygen in air, the equation shown as below:



Besides that, Cr₂O₃ also occur in great quantities as the protective films for the stainless steel. In addition, the surface also accompanied with other oxides such as NiO, Cr₂O₃, SiO₂ and Chloride with small amount.

Table 1: Composition of the scale on the specimen coated with calcium chloride, oxidized at 950 °C for 72 h in blowing air from EDAX. Deduced from the EDAX analysis.

Tabela 1: Sestava škake na vzorcu, prekritem s kalcijevom kloridom, ki je bil oksidiran v zračnem toku 72 h pri 950 °C. Preračunano iz EDAX-analize.

Element	E/keV	Mass, w/%	Compound	Mass, w/%
O		30.63		
Si	1.739	5.46	SiO ₂	11.68
S	2.307	4.79	SO ₃	0.96
Cl	2.621	0.36	Cl	0.36
Cr	5.411	3.63	Cr ₂ O ₃	5.31
Fe	6.398	39.03	FeO	50.20
Ni	0.851	16.10	NiO	31.49
Total		100.00		100.00

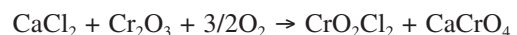
Table 2: Composition of the scale on the specimen coated with barium chloride, oxidized at 950 °C for 72 h in blowing air from EDAX. Deduced from the EDAX analysis.

Tabela 2: Sestava škake na vzorcu, prekritem z barijevom kloridom, ki je bil oksidiran v zračnem toku 72 h pri 950 °C. Preračunano iz EDAX-analize.

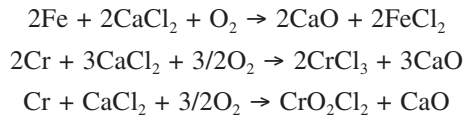
Element	E/keV	Mass, w/%	Compound	Mass, w/%
O		24.78		
Si	1.739	2.24	SiO ₂	4.80
S	2.307	1.20	SO ₃	0.29
Cl	2.621	1.12	Cl	1.29
Cr	5.411	10.18	Cr ₂ O ₃	13.60
Fe	6.398	37.29	FeO	47.98
Ni	7.471	23.19	NiO	32.04
Total		100.00		100.00

4 DISCUSSION

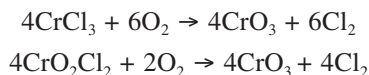
The corrosive environment of calcium chloride and barium chloride effect onto the hot corrosion behavior of 321 stainless steel at 950 °C, exhibiting the breakdown of protection film on stainless steel caused the formation of a volatile, CrO₂Cl₂. The reaction can be described as follows^{12,13}:



The formation of volatile products such as CrO_2Cl_2 and CaCrO_4 , exerts sufficient vapour pressure to break the passivation of oxides on 321 stainless steel. Once the passive film breakdown, the molten CaCl_2 further attacks the stainless steel and lead to corrosion. The equation:



The chlorides formed such as CrO_2Cl_2 and CrCl_3 were released at the salt interface and get oxidized to release chlorine gas:



The chloride might be entrapped between inner oxide layers of the alloy and get condensed on cooling and appear as distinct and discrete phase in the scales¹³. BaCl_2 has undergone the same reaction as CaCl_2 .

Since calcium is more electronegative than barium, the bonding of calcium chloride is weaker than that of the barium chloride. All common metals are very soluble in chloride form and so the reaction rate is increased. The presence of chloride ions in the electrolytic solution affects nearly every aspect of the corrosion behavior. The oxide layer that protects the steel breaks down in the presence of chloride, causing pits to form. This type of corrosion can lead to structural failures³.

Temperature is a factor in activation controlled corrosion. Raising the temperature will also increase the corrosion rate as the activation energy decreases with temperature. Increasing solution temperature increased the susceptibility to both pitting and active dissolution¹.

The corrosion rate of each test decreases with the increasing of exposure times. It is because of the decrease of the concentration of chloride ions with time, most of the chloride ions that leads to corrosion has reacted with the chromium oxide film protecting the surface of the steel and activate the unprotected surface¹². This determined the concentrations of chloride solution will affect the corrosion rate. The chemical reactions of chloride ions are:



At high temperatures in chloride salts increased the susceptibility to both pitting and active dissolution, resulted in increased corrosion current densities and peak current densities⁴.

5 CONCLUSION

The results of the study shown the increased chloride content, the easily the passive region shrinks and simultaneously with the formation of corrosion of

metallic chloride and fluxing products exhibiting the profuse deterioration of the surface of the 321 stainless steel.

The patterns of the graphs follow the kinetic theory of reaction where the reactions rates were directly proportional to the increasing of temperature. It means as the temperature increases in the time for the initiating corrosion attack is decreased. The CaCl_2 coated alloy shown higher weight loss than the coated with BaCl_2 .

Pitting corrosion, internal corrosion and stress corrosion cracking were the commonest corrosion found in 321 stainless steel in presence of chloride.

From the results of EDAX, iron oxide, FeO , Cr_2O_3 and NiO occur in great quantities on the corroded stainless steel surface in addition to other oxides such as SO_3 , SiO_2 and chloride with small composition.

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