316L stainless steel corrosion in molten salts NaNO$_3$ KNO$_3$ NaNO$_2$ simulating storage conditions

A Sandoval-Amador$^1$, A J Santander-Vega$^2$, C C Amaya-Cáceres$^2$, H A Estupiñán-Duran$^1$ and D Y Peña-Ballesteros$^3$

$^1$ DIMAT, Unidades Tecnológicas de Santander, Bucaramanga, Colombia
$^2$ GIC, Universidad Industrial de Santander, Bucaramanga, Colombia
$^3$ Grupo de Tribología y Superficies, Universidad Nacional de Colombia, Medellín, Colombia

E-mail: anderson84f@outlook.com

Abstract. A wide variety of stainless steel is used in concentrated solar plants in different elements as pipelines, pumps, storage tanks, among others, and these are in contact with molten salts, which are used as thermal energy transfer fluids. In this paper, corrosion of stainless steel AISI 316L in molten salt NaNO$_3$ - NaNO$_2$ - KNO$_3$ has been investigated at temperatures of 450, 500 and 550°C, for an exposure period of 150 hours. The salt mixture is sprayed by spray onto the surface of 316L stainless steel, which has been preheated to 170°C. To obtain a thin layer of salt on the samples, these are carried to the furnace in the presence of an oxidizing atmosphere at high temperature for 1, 3, 10, 30, 100 and 150 hours. The results of mass gain and characterization by SEM-EDS and XRD of the surfaces showing the formation of a passive film, composed mainly of hematite Fe$_2$O$_3$. The thickening of the oxide film is according to a parabolic law, whose speed depends on the temperature of the melt.

1. Introduction

In the last years, renewable energies and their application have been widely studied due to the high demand for energy and the need to protect the environment. Solar energy is one of the most evolved types of renewable energy because of the development of energy storage systems that increased plant performance to function under unfavorable weather or night periods [1]. For this have been developed concentrated solar plants (CSP), which operate under a basic principle; solar irradiation is concentrated by means of heliostat mirrors onto the receiver, where the heat is collected by a heat transfer fluid (HTF) [2].

The HTF are used to drive turbines to produce a power or in a heat exchanger to generate steam. Furthermore, these are one of the most important components when it comes to improving the efficiency of CSP [2]. For this reason, the most desired physical and thermodynamic properties of in a HTF are: low melt point, high boiling point and thermal stability, low vapor pressure at high temperature, low viscosity, high thermal conductivity, high heat capacity for energy storage, low corrosion with metal alloys used to contain the HTF and low cost [2-5].

The molten alkali nitrates and nitrites are widely used as heat transfer fluids and storage media in the thermal energy storage system due to its properties [6-8]. Therefore, have been developed multiples studies [9-14] that have analyzed the physicochemical properties of the nitrate salt mixture in order to optimize the efficiency of the thermal energy storage, but have left aside the study of the
effect that have these HTF in degradation of the materials that are usually made the pipelines and storage devices in CSP.

The corrosion is an important problem in CSP systems due to the HTF’s acts as the electrolyte in a corrosive system that attacks the metal containers and pipelines [13]. High operation temperatures are necessary to improve efficiency in the CSP system and molten-salts are the most promising HTF candidates at high temperatures up to 800°C, but the corrosion issues are more significant in CSP plants operated with molten salts compared to other HTF’s, mainly because of the high operating temperatures [2,15].

In this paper, the corrosive effect of 7wt% of NaNO₃ + 53wt% of KNO₃ + 40wt% of NaNO₂ have been tested at 450, 500 and 550°C, in order to simulate the working concentrated solar power CSP plants on stainless steel AISI 316L.

2. Methodology

2.1. Sample preparation
All samples were made with sheets of stainless steel AISI 316L. The composition of the samples was analyzed by optical emission spectroscopy using a Bruker Tasman Q4 spectrometer. The samples were cut with dimensions of 20mm x 15mm x 2mm. Subsequently were roughed mechanically with silicon carbide paper (80, 120, 220, 320, 400 and 600 grit). The samples were subsequently cleaned in ultrasonically bath with ethanol for 10 minutes.

2.2. Preparation and application of ternary salt
A mixture of salt NaNO₃ NaNO₂ and KNO₃ in a weight ratio of 7:53-40% respectively dissolved in deionized water was prepared and applied on the samples following the procedure described by Peña et al in [16].

2.3. Corrosion and gravimetric test
The corrosion tests were performed in Carbolyte CWF 1200 furnace at 450, 500 and 550°C for 150 hours; three specimens were removed from the furnace at 1, 3, 10, 30, 100 and 150 hours for the examination and analysis. After the samples were removed from the furnace, they were slowly cooled and weighed on an analytical balance with 0.00001g responsiveness; the average weight was obtained from 5 weight values. Equation 1 was used to calculate the mass gain:

\[ \frac{m_f}{s_0} = \frac{m_i - m_f}{s_0} \]  

3. Results
The stainless steel under analysis at temperatures of 450, 500 and 550°C is an AISI 316L (see the chemical composition in Table 1) which was exposed to the ternary salt for 150h. The results of the gravimetric test in the presence of the ternary salt 7%wt of NaNO₃ + 53%wt of NaNO₂ + 40%wt of KNO₃ are compared in Figure 1.

| Table 1. Nominal composition of stainless steel AISI 316L |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| AISI 316L   | %C          | %Si         | %Mn         | %P          | %S          | %Ni         | %Cr         | %Mo         | %N          |
|             | 0.020       | 0.506       | 0.852       | <0.150      | 0.003       | 10.11       | 16.43       | 1.896       | 0.221       |

As shown in Figure 1, the mass gain of the steel is adjusted to a parabolic behavior, also can be clearly seen that the increase in temperature leads to greater mass gain obtained to 0.6mg/cm² at 550°C.
Figure 1. The gravimetric behavior of stainless steel AISI 316L in 7%wt of NaNO₃ + 53%wt of NaNO₂ + 40%wt of KNO₃.

The steel surface is covered by a poor adhesive film having flaking possibly due to handling. The most external film (Figure 2(a)) is mainly composed of iron and oxygen as shown in EDS (Figure 3(a)). In the inner part of the film (Figure 2(b) and 3(b)) shows the presence of elements such as nickel and chrome, these elements are characteristic of steel alloy. The oxide film thickness is approximately 800µm as seen in cross-section in Figure 4.

Figure 2. Surface view of stainless steel AISI 316L after 150 h test at 550 ºC

Figure 3. Elemental composition of the film formed on the stainless steel AISI 316L after 150 h test at 550ºC. (a) external film (b) Inner part of the film.
The corrosion products detected by DRX on the surface of stainless steel AISI 316L after 150h test at 450, 500 and 550°C are showed in Table 2. Accordingly, there is variation in the composition of the oxide layer due to the temperature. Appearing mainly hematite Fe₂O₃, and the transition to mixed oxides of iron, chromium and nickel.

### Table 2. Corrosion products obtained at different temperatures after 150h of exposure.

| Compound at 450°C | Compound at 500°C | Compound at 550°C |
|-------------------|-------------------|-------------------|
| Fe₀.₆₄Ni₀.₃₆      | Fe₀.₆₄Ni₀.₃₆      | Fe₀.₆₄Ni₀.₃₆      |
| Fe₁₀.₈Ni          | Na₁₄.₀₃Ni₀.₉₅O₂   | Fe₂.₉₄₂O₃         |
| FeO(OH)           | FeOCr₂O₃          | Fe₂O₃             |
| NiCr₂O₄           | Fe₃O₄             | NaO               |
| Fe(OH)₃(H₂O)₀·₂₅  | Na(NO₂)           | (CrNi₃)           |
| Fe₂O₃             | Fe₂O₃             | -                 |

### 4. Discussion

According to the results recorded, it may indicate that the corrosion presents a direct increase with temperature. Besides the formation of a protective film, which in most external part is mainly composed of hematite and also in the inner of the film the hematite and mixed oxides of iron, nickel and chromium were found. These results are consistent with those reported by Tz. Tzvetkoff and J. Kolchakov in [17].

In addition, when comparing the results with those reported by Bradshaw and Goods in [18] can infer than steel AISI 316L has a good resistance to corrosion when in contact with the mixture of salt ternary study. Similarly, these authors reported that 316L has greater corrosion resistance than steel AISI 316 and 304 in the presence of molten salts [15].

### 5. Conclusions

In this study, the corrosive effect on Stainless steel AISI 316L of the ternary salt 7% wt of NaNO₃ + 53% wt of NaNO₂ + 40% wt of KNO₃ at 450, 500 and 550°C during 150h was evaluated. The results of the gravimetric tests were supplemented using SEM-EDS and XRD, this allowed determining that the stainless steel AISI 316L shows an excellent corrosion resistance due the formation of an inner protective film composed of hematite and mixed oxides of iron, nickel and chromium. Additionally, on this film a second layer is formed, which is mainly composed of hematite. Therefore, stainless steel AISI 316L presented a mass gain of mg/cm² and a thickness of oxide film of about 800μm to 550°C. This validated the use this steel to build pipelines or storage tank using in CSP.
References

[1] Fernandez A G, Galleguillos H, Fuentealba E and Pérez F J. 2015 Corrosion of stainless steels and low Cr in molten Ca(NO3)2-NaNO3-KNO3 eutectic slat for direct energy storage in CSP plants Sol. Energy Mater. Sol. Cells 141 7-13

[2] Vignaroonban K, Xinhai Xu, Arvay A, Hsu K and Kannan A M 2015 Heat transfer fluids for concentrating solar power systems - A Review Appl. Energy 146 383-396

[3] Ren N, Wu Y T, Ma C F and Sang L X 2015 Preparation and thermal properties of quaternary mixed nitrate with low melting point Sol. Energy Mater. Sol. Cells. 127 6-13

[4] Oliwares R J 2012 The thermal stability of molten nitrite/nitrates salt for thermal energy storage in different atmospheres Sol. Energy 86 2576-2583

[5] Fernandez A G, Cortes M, Fuentealba E and Pérez F J 2015 Corrosion properties of a ternary nitrate/nitrite molten salt in concentrated solar technology Renewable Energy 80 177-183

[6] Singh B, Venkatachari G and Balakrishhana K 1994 Electrochemical studies on the oxidation behaviour of iron in NANO3-NaNO2 melt Corros. Sci. 36 1787-1794

[7] Shingh B and Sen U 1993 The effect of NaCl addition on the corrosion of mild steel in NaNO3 melt Corros. Sci. 34 1773-1742

[8] Calvet N, Gomez J C, Faik A, Roddatis V V, Meffre A, Glautzmaier G C, Doppiu S and Py X 2013 Compatibility of a post-industrial ceramic with nitrate molten salts for use as filler material in a thermoclave storage system Appl. Energy 109 387-393

[9] Peng Q, Ding J, Wei X, Yang J and Yang X 2010 The preparation and properties of multi-component molten salts Appl. Energy 87 2812-2817

[10] Bradshaw R W and Meeker D E 1990 High-temperature stability of ternary nitrate molten salts for solar thermal energy systems Sol. Energy Mater. 21 51-60

[11] S. Ushak, A. G. Fernandez, M. Grageda 2015 Using molten salts and others liquid sensible storage media on thermal energy storage (TES) systems Advances in Thermal Energy Storage Systems ed Cabeza L F (Sawston: Woodhead Publishing) chapter 3 pp 49-63

[12] Gaggioli W, Fabrizzi F, Fontana F, Rinaldi L and Tarquini L 2014 An innovative concept of a thermal energy storage system based on single tank configuration using stratifying molten salts as both heat storage media and heat transfer fluid, and with an integrated steam generator Energy Procedia 49 780-789

[13] Gimenez P, Fereres S 2015 Effect of heating rates and composition on the thermal decomposition of nitrate-based molten salts Energy 69 654-662

[14] Mohd Faizal T, Wan Nur Azrina W M, Md Nor Annuar M and Farazila Y 2017 Characterization and thermal properties of Nitrate based molten salts for heat recovery system J. Phys.: Conf. Ser. 914 012016

[15] Goods S H and Bradshaw R W 2004 Corrosion of stainless steels and carbon steel by molten mixtures of commercial nitrate salts J. Muter. Eng. Perform. 13 78-87

[16] Peña Ballesteros D Y, Estupiñan Duran H A, Caceres A and Camargo N 2013 Corrosion a alta temperatura de un acero 2.25Cr-1Mo en contacto con una mezcla de sal K2SO4 - NaCl Informador Técnico 77 147-156

[17] Tzvetkoff TZ and Kolchakov J 2004 Mechanism of growth, composition and structure of oxide films formed on ferrous alloys in molten salt electrolytes - a review Mater. Chem. Phys. 87 201-211

[18] Bradshaw R W and Goods S H 2001 Corrosion resistance of stainless steels during thermal cycling in alkali nitrate molten salts Sand2001-8518 consulted on: https://prod.sandia.gov/techlib-noauth/access-control.cgi/2001/018518.pdf