



Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

The mechanism of NO_x emissions from binary molten nitrate salts contacting nickel base alloy in thermal energy storage process

Xiaolan Wei^a, Chuntao Yang^a, Jianfeng Lu^b, Weilong Wang^{b,*}, Jing Ding^{b,*}

^a School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China

^b School of Engineering, Sun Yat-sen University, Guangzhou High Education Mega Center, Guangzhou 510006, PR China

HIGHLIGHTS

- The effect of In600, Has X, In625 and HasC 276 on NO_x emissions was studied.
- Chemical thermodynamic of reactions were calculated to study the mechanism of NO_x emission.
- NO_x emission was reduced for treated In625 and HasC 276 due to the oxide film formation.

ARTICLE INFO

Article history:

Received 22 January 2017

Received in revised form 12 June 2017

Accepted 28 June 2017

Available online xxxxx

Keywords:

Binary molten nitrate salts

NO_x emissions

Nickel base alloy

ABSTRACT

This work aimed at investigating the mechanism of NO_x emissions from binary molten nitrate (BMN) salts (an eutectic salt mixture with the component of 60%NaNO₃–40%KNO₃) in its thermal energy storage (TES) process while contacting several kinds of nickel base alloy and determining the optimized temperature range of BMN salts in these metal loops. According to the national environmental protection standard of PR China, HJ479-2009, the concentrations of NO/NO₂ net emissions in tail gases from the heated molten salts while contacting with Inconel 625 (In625), Hastelloy C276 (HasC 276), Hastelloy X (Has X) and Inconel 600 (In600) were measured in TES process, which were deducted the influence of platinum boat while contacting with the molten nitrates. Besides, the In625 and HasC 276 were chosen to test with the same method at 500 °C under the condition that they were corroded at 500 °C after a period of time, SEM/EDS and XRD techniques were utilized to study the surface morphology and corrosion products after a maximum immersion time of 600 h. Furthermore, the chemical thermodynamic calculations of related reactions that between Cr, Ni, Mo, W and nitrate salts were carried out to explain the source of NO/NO₂. The test results show that BMN salts contained in pipes or tanks made of nickel base alloy under air atmosphere in certain conditions can release NO_x in its usage temperature range, and the concentrations of NO_x emissions increase with the rise of the temperature. Below 500 °C, the concentrations of NO_x net emissions that BMN salts contacting with these four kinds of nickel base alloys were under 200 mg/m³, which is in accordance with the emission limit of thermal power plant in China and the emission limit of second directive of EU in coal-fired power plant. Besides, the concentrations of NO_x emissions that BMN salts contacting with corrode materials would decrease to some extent. After a period of corrosion, the formed oxide film on metal surface was very thin but dense. Therefore, the BMN salts were advisable to utilize under 500 °C at the initial stage, and it can be used at higher temperature after the stable oxide film formed in the metal surface.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Solar energy takes a large proportion among various types of renewable energy sources. The concentrating solar power (CSP) with high-temperature thermal energy storage (TES) system becomes

the first choice to provide flexibility for grid electricity supply and service at a large scale (>100 MW) [1–4]. For instance, the Gema solar power plant in Spain which used solar salt in the heat transfer (HT) and TES system, which can offer an annual capacity factor of 55% with the decreased levelized cost of energy (LCOE) [5–8]. Heat transfer fluids (HTFs) in commercial CSP plants include air, water/steam, mineral/synthetic oils, and inorganic molten salts. To date, synthetic oils and molten salts are the most widely used sensible

* Corresponding authors.

E-mail addresses: wwlong@mail.sysu.edu.cn (W. Wang), dingjing@mail.sysu.edu.cn (J. Ding).

<http://dx.doi.org/10.1016/j.apenergy.2017.06.109>

0306-2619/© 2017 Elsevier Ltd. All rights reserved.

heat storage and transfer materials in commercialized CSP systems. By comparison, heat transfer oil will take a risk of being degraded when temperature is higher than 393 °C, which restrains the maximum temperature of the superheated steam and decreases the turbine efficiency [9–11]. The molten salt prepared from KNO₃ (40 wt%)-NaNO₃ (60 wt%) is a desired candidate for heat transfer due to its high specific heat, high thermal conductivity, low melting point, low vapor pressure, and wide operating temperature range [9,12–14]. However, the thermodynamic efficiency of the solar thermal power station mainly depends on the operating temperature range of HTF and TES medium, and the maximum operation temperature are limited by the chemical stability of the salt and the compatibility between salts with containers or capsule shells.

Some work has been conducted regarding the decomposition of single NaNO₃ or KNO₃ [15–20]. Freeman [21,22] studied the thermal decomposition of sodium nitrate in oxygen and argon atmosphere, explored the thermal decomposition of potassium nitrate in the oxygen atmosphere, and the reactions between NaNO₂ and O₂ at 600 °C ~ 780 °C; Hoshino and Bond [23,24] also studied the thermal decomposition of NaNO₃ in argon atmosphere; Bartholomew [25] did a research about the thermal decomposition reaction of KNO₃ under the condition of 550 °C ~ 750 °C, the results show that, when the nitrate salt is heated in stainless steel or silver container, due to some side reactions, the thermal decomposition products has some nitrogen oxides except for O₂; Stern [18] studied the thermal decomposition of K/NaNO₃ and the K/NaNO₂, the N₂, O₂, NO, NO₂, N₂O₃, N₂O₄, N₂O₅ are all likely to come from the decomposition of molten nitrate and nitrite salt, The reason for the decomposition of nitrate and nitrite salts depends on the salt itself, the temperature, and the experimental conditions. Wei et al. [14] studied the NO_x emissions and the effect of 45# carbon steel (1045, ASTM) on it in thermal energy storage (TES) process of binary BMN salts and found the total concentrations of NO_x emissions and nitrite ion in molten salts increased, in addition to monitoring gas products, the ion changes after thermal decomposition of nitric acid molten salts were tested, the mass fractions of NO₂⁻ increase rapidly with the increase of temperature, and the mass fractions of NO₂⁻ in the samples increase with the temperature compared with that without contacting with carbon steel. Peng et al. [26] studied the nitrogen oxides from molten nitrates contacting with SS316, SS304 and SS201 in nitrogen and air atmosphere, the formation rate of NO in nitrogen is higher than the rate in air, and the SS316 has the most significant effect on decomposition of solar salt in nitrogen. Nissen and Meeker [17] monitored the concentration of nitrite ion (NO₂⁻) in solar salt at 550 °C and 600 °C at different oxygen partial pressures (21–100 vol%). The percentage of NO₂⁻ was found to increase with the increase of temperature and the decrease of oxygen partial pressure. Consequently, corrosion behavior of nickel base alloy in molten salts was also widely studied [27–32]. Vignarooban et al. [31] studied the Hastelloys C-276 and C-22 and stainless steel 304 in a eutectic molten salt consisting of 13.4 mol% NaCl, 33.7 mol% KCl and 52.9 mol% ZnCl₂, results show that Hastelloy C-276 has the best corrosion resistance. Dorcheh et al. [28] have studied the corrosion behavior of BMN salts on two ferritic steels P91 and X20CrMoV11-1, two austenitic steels SS316 and SS347H and a Ni-alloy IN625 at 600 °C and found the

IN625 showed the best protective behavior among alloys. Lu et al. [32] have studied the corrosion behavior of Fe, Cr, Ni-base alloys in 850 °C molten NaCl. The corrosion rate ranked from the maximum is: Cr base, Ni base and Fe base alloys. According to the above literatures, most works has been done experimentally on the decomposition of molten nitrate salts or the corrosion behavior of metal materials in molten salts. However, quite few work has been done to make a comprehensive understanding on the mechanism of NO_x emission from the viewpoint of thermodynamics, and the effect of various component and metal substrate on NO_x emission has no adequate discussion, which play a key role for operating safety of practical concentrating solar power.

In this paper, NO_x emission of BMN salt while contacting several kinds of nickel base alloy materials in the operation temperature range has been investigated, and the appropriate usage temperature range was also determined. Besides, the NO_x emissions of BMN salt contacting nickel base alloy after a certain corrosion treatment were investigated at 500 °C. Meanwhile, the content of nitrite ion, corrosion products and surface morphology of metal samples were also investigated to explore the mechanism of NO_x emissions.

2. Experiment

2.1. Materials

The binary eutectic salt mixture (60% NaNO₃-40% KNO₃) was prepared by fully mixing the two salt components according to the mass fraction ratio above. The purity of reagents obtained from Guangzhou Chemical Regent Factory is more than 99%. Amounts of salts were held in two separate glass pans and placed in a drying oven for at least 48 h at 120 °C before cooling in desiccator for being weighed. Four kinds of nickel base alloys including IN625, HasC 276, Has X and IN600 were studied as candidate materials for solar salt applications. The compositions of the alloys are listed in Table 1. The alloys were cut into 40 mm × 1.0 mm × 15 mm by cutting machine. The samples were ground successively with a series of 320 grit, 600 grit, 800 grit and 1000 grit silicon carbide papers, then, they were cleaned in ethanol, then in distilled water, and dried eventually. Finally, each sample was measured with micrometer to calculate its surface area and weight their mass.

2.2. Apparatus and procedure

The standard working curve of absorbance and the concentration of NO₂⁻ obtained as follows: $A = 0.00997 + 0.92221 \cdot C$ (μg/ml), the linear correlation coefficient R² was 0.9998. The research method of NO/NO₂ in tail gases from BMN salts during thermal storage process accorded to the national standard (HJ479-2009) of PR China [33], in which the accumulated concentration of NO/NO₂ may be measured for 1 h or 24 h average, and the 1 h average was selected in this paper. The method for determination of nitrite ion and the apparatus were designed according to the standard HJ479-2009 as described in Wei's article [14], the schematic diagram of the experimental device is shown in Fig. 1, and the experimental flow chart is shown in Fig. 2.

Table 1
Chemical composition of the studied alloys.

Alloy	Cr	Fe	Si	Ni	Mo	W	Mn	Other
Has X	22	18	–	49.5	9	0.5	–	Co 1
IN600	15.5	8	0.005	<75.5	–	–	<1	Co
IN625	21.5	<5	<0.005	60.8	9	–	–	Nb + Ta 3.65
Has C276	13–17.5	4.5–7	–	52.2–62.8	16–18	3.7–5.3	–	

Download English Version:

<https://daneshyari.com/en/article/6681889>

Download Persian Version:

<https://daneshyari.com/article/6681889>

[Daneshyari.com](https://daneshyari.com)