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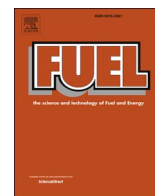
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Corrosion of superheater materials by alkali chloride salt mixtures – The role of the presence of molten phase

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ABSTRACT

In biomass combustion, the presence of alkali chlorides will lower the ash deposit melting temperature. It is also known that aggressive corrosion of superheater materials may occur in the presence of melt in contact with the steel. Therefore, the first melting temperature (T_0) has been used as a guideline for the maximum superheater temperature. However, the impact of the share – or percentage - of molten phase in the salt deposit on corrosion has not been systematically investigated. In this work, the role of the share of molten phase on the corrosion of two stainless steel qualities, AISI 347 and 310, was studied. The salt mixtures used ($\text{NaCl-Na}_2\text{SO}_4$ and $\text{KCl-K}_2\text{CO}_3$) were prepared to produce different amounts of melt at the higher test temperature. The steels were exposed for one week to a salt mixture in a tube furnace, at temperatures both below and above T_0 . After the exposure, the samples were cut to reveal the cross-sections. The cross-sections were analysed by means of SEM-EDX. Remarkable differences in the corrosion tendencies of the materials were observed depending on the percentage of molten phase. The work revealed that for a certain steel quality a given minimum percentage of molten phase was required before observing severe corrosion. For the $\text{NaCl-Na}_2\text{SO}_4$ salt mixtures, around 3 wt% molten phase was sufficient to significantly accelerate the corrosion rate for AISI 347, while the corresponding value was 14 wt% for AISI 310. The criterion of first melting temperature T_0 being the critical limit for severe superheater corrosion requires modification. The amount of liquid phase at T_0 is also essential. The critical amount of liquid phase at T_0 for severe corrosion is steel specific.

1. Introduction

Alkali chlorides are the main cause for superheater corrosion in biomass combustion. Deposits containing chlorides are especially corrosive in the presence of a molten phase [1]. In kraft recovery boilers, i. e., boilers burning pulping industry spent liquor, black liquor, the practice has been to keep the steam temperatures low enough to maintain the superheater tube surface temperatures below the first melting temperature (T_0) of the salt deposits. In recovery boilers, the deposits consist mainly of sodium and potassium sulfates, carbonates, with varying concentrations of chlorides. Thus, the maximum superheater material temperatures in these boilers have been maintained at not higher than around 500 °C, which is just below the first melting temperature of that salt mixture [2].

Superheater corrosion in the presence of alkali chlorides has been studied extensively. There are studies on the role of solid alkali chlorides [3–10] and also the effect of gaseous potassium chlorides [11–14] have been studied to a large extent. In addition, the presence of melt in

corrosive deposits has been discussed [15–19] as well as the role of temperature gradients across the deposit on the deposit chemistry and morphology [20,21]. However, the role of the amount of melt in the corrosive deposit has been in lesser focus.

At T_0 a first molten phase appears in a salt mixture. However, the amount – the percentage - of this first molten phase can be very different at T_0 depending on the composition of the salt mixture. Skrifvars et al. [1] made a study on synthetic alkali salt deposits mimicking those on recovery boiler superheater tubes. The salt mixtures were made of sodium and potassium sulfates and chlorides, and if a melt was formed in a test, the amount of melt was incidental and was not discussed in more detail. One of the key findings was that though, an increased amount of melt in the salt deposit did increase the corrosion, some corrosion took place at temperatures clearly below T_0 , if the salts contained even minor amounts of chlorine [1].

Fig. 1 shows the impact of chlorine on the melt share for a typical kraft recovery boiler deposit with a T_0 of 535 °C. The amount of melt formed just above T_0 increases as the chlorine content is raised in the

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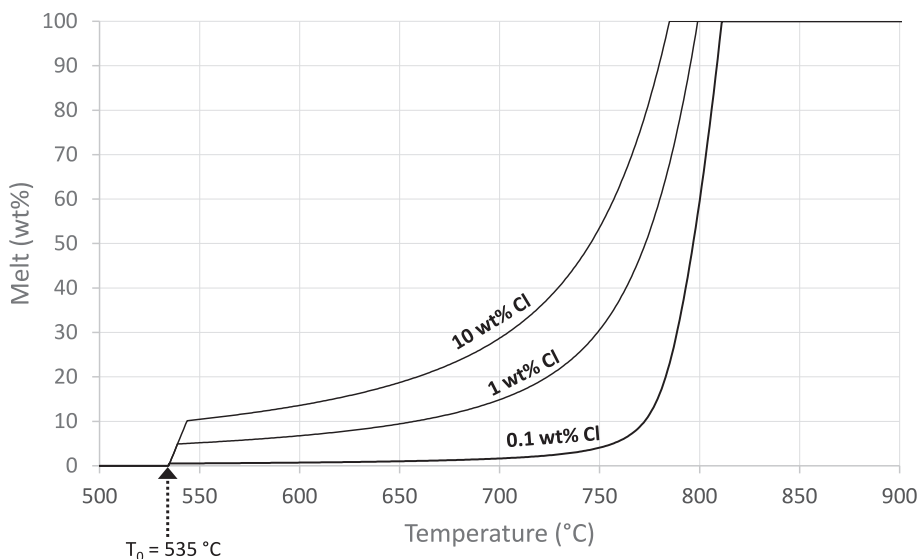


Fig. 1. Melting behaviour of a typical Kraft recovery boiler deposit with three chlorine contents. Calculations were done with FactSage 8.1 using the FTPulp database.

Table 1
Compositions of AISI 347 and AISI 310. The numbers are in wt%.

	Cr	Ni	Fe	C	Si	Mn	P	S
AISI 347	17–19	9–12	69–74	<0.08	<1	<2	<0.045	<0.015
AISI 310	24–26	19–23	51–57	<0.02	<0.7	<2	<0.025	<0.01

deposit. The question is, how does the corrosion behaviour change for alkali salts on stainless steel above T_0 with an increasing amount of molten phase?

The amount of molten phase on corrosion just above T_0 has not previously been studied in a systematic manner. The purpose of this study was to determine the role of the share of molten phase on corrosion of two stainless steel qualities. Two model systems were used: NaCl- Na_2SO_4 and KCl- K_2CO_3 . Experiments were conducted both below and above T_0 with salt mixtures having four gradually increasing percentages of molten phase.

2. Experimental

Corrosion experiments were conducted using two stainless steel qualities: AISI 347 and AISI 310. The main difference between these two qualities is that AISI 310 has higher Cr and Ni contents (Table 1) and is known to withstand corrosion better. The corrosion tests were done according to the Åbo Akademi standard procedure using $2\text{ cm} \times 2\text{ cm} \times 0.5\text{ cm}$ steel coupons [22]. The samples were pre-oxidized at 200 °C for 24 h. A thermally stable paste (Bostik heat seal, heat resistant up to 1200 °C) was applied on the samples to form walls, preventing the salt or melt from running off the sample surface. The salts were pre-melted and crushed to obtain a well-mixed salt mixture. Pre-melting was done the

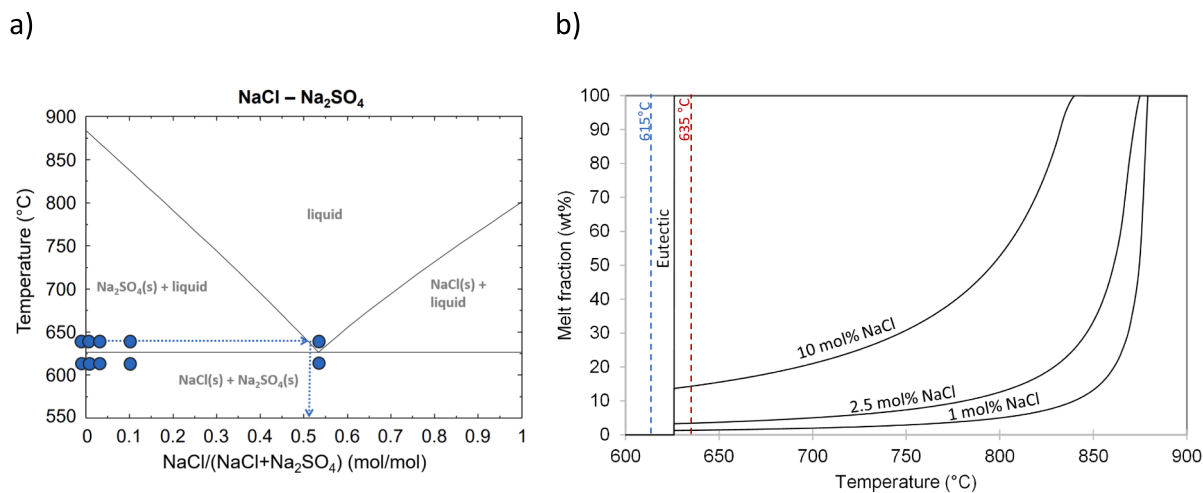


Fig. 2. a) Binary phase diagram for the NaCl- Na_2SO_4 system. Blue dots indicate the experimental salt mixtures and the arrows the melt composition. b) Percentage of melt as function of temperature of the salt mixtures. The experimental temperatures are indicated with the two coloured lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

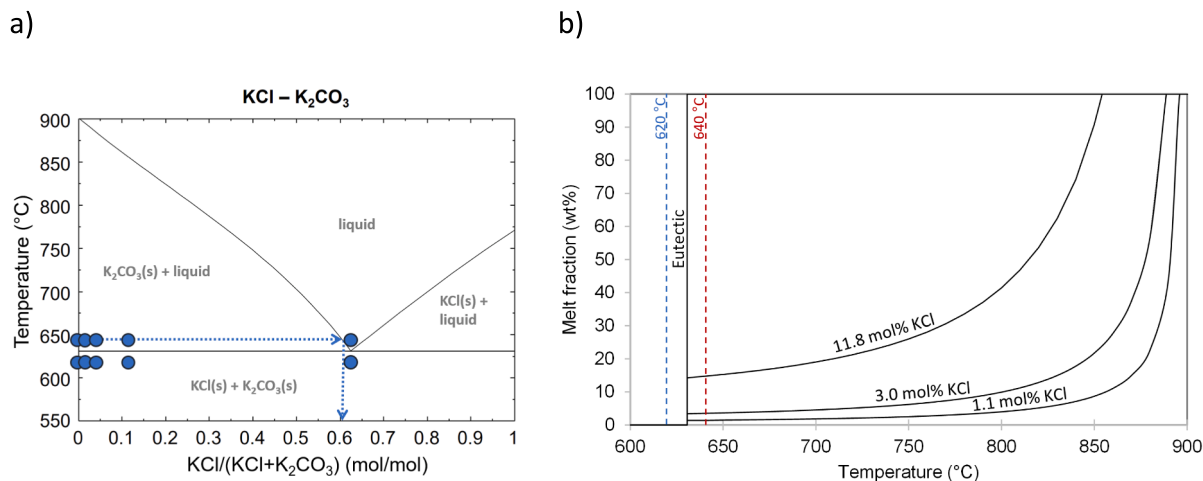


Fig. 3. Binary phase diagram for the KCl-K₂CO₃ system. Blue dots indicate the experimental salt mixtures and the arrows the melt composition. Blue dots indicate experimental points with salt mixtures and grey dots the pure salts. b) Percentage of melt as function of temperature of the salt mixtures. The experimental temperatures are indicated with the two coloured lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

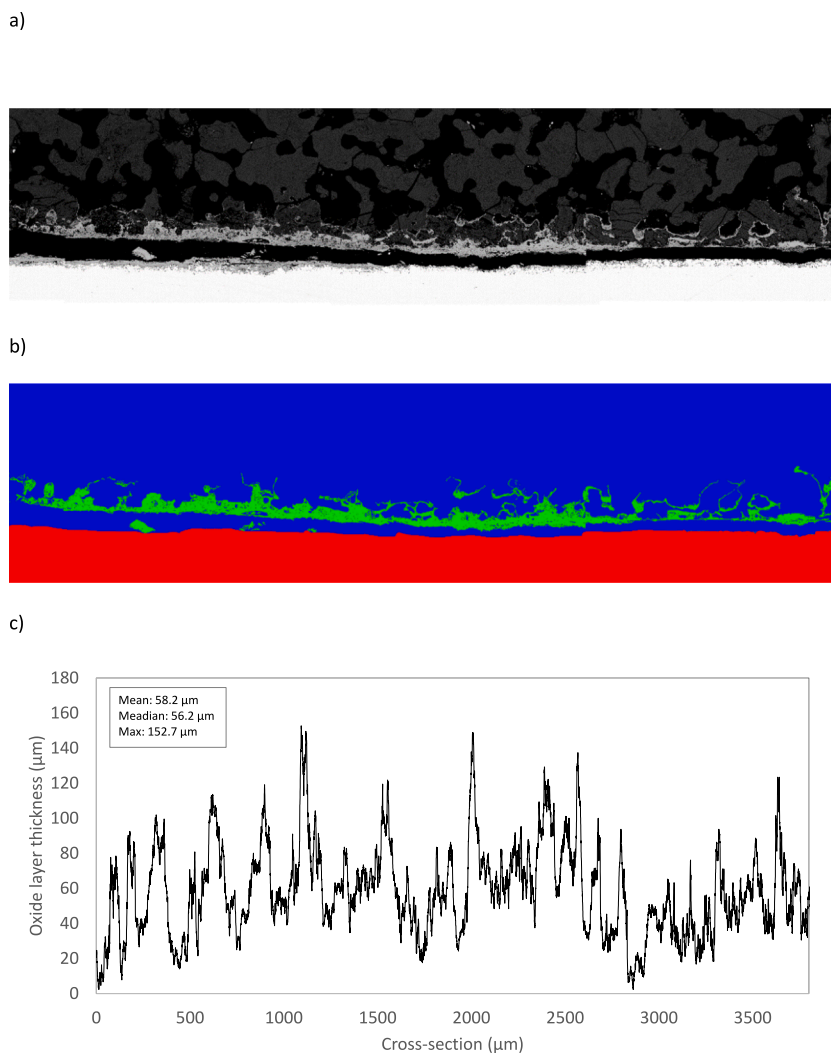


Fig. 4. a) SEM panorama from the middle of AISI 347 exposed to 4.3/95.7 wt% NaCl-Na₂SO₄ mixture at 635 °C, b) oxide layer coloured with green, c) oxide layer thickness along the panorama image. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

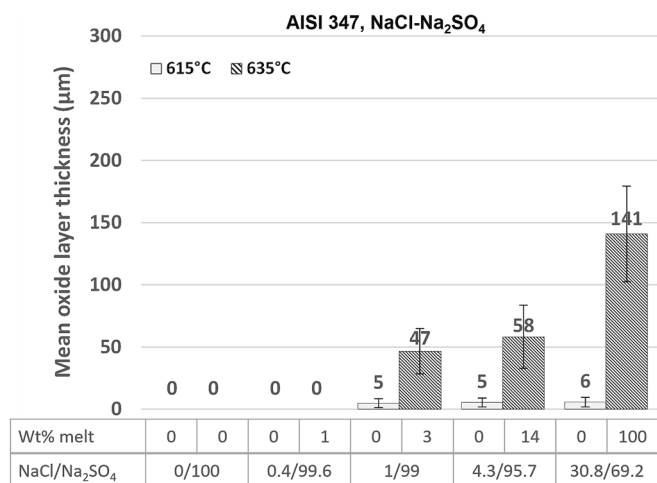


Fig. 5. Mean oxide layer thickness from the experiments with NaCl-Na₂SO₄ salt mixtures on AISI 347 at 615 and 635 °C. Both the salt mixture and wt% melt are given. T₀ for the NaCl-Na₂SO₄ system is 626 °C.

following way. The salt mixtures were placed in a ceramic crucible and inserted in a laboratory furnace at a temperature of 930 °C. Once the temperature reached 930 °C again after the insertion of the crucible, the crucible was kept at 930 °C for 20 min. Then the crucible was removed and the cooled salt mixtures were crushed and sieved to a size between 53 and 250 µm. The compositions of the sieved salt mixtures were controlled with scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), LEO Gemini 1530 with a Thermo Scientific UltraDry Silicon Drift Detector (SDD), and it could be shown that this rapid pre-melting procedure did not cause any significant chlorine vaporization. The samples with the salt on top were placed in a horizontal tube furnace and the exposure time was one week (168 ± 3 h). The gas in the furnace was ambient air. The temperatures were logged at the samples in different locations; all samples had a temperature within ± 2 °C from the set point.

Two model systems were used: NaCl-Na₂SO₄ and KCl-K₂CO₃. The NaCl-Na₂SO₄ and KCl-K₂CO₃ systems have T₀s of 626 and 631 °C, respectively. The temperatures in the corrosion tests were approximately 10 °C below and 10 °C above T₀. Fig. 2a shows the phase diagram for the NaCl-Na₂SO₄ system. The temperatures in the experiments for this system were 615 and 635 °C. Different amounts of NaCl were used so that an increasing share of molten phase and solid Na₂SO₄(s) formed at 635 °C. These are depicted in Fig. 2a as blue dots. The amount of melt formed at 635 °C with the various NaCl amounts were: 0, 1, 3, 14, and 100 wt% (Fig. 2b). In this experimental setup the chemical composition of the molten phase will be the same for the mixtures with 1–14 wt% melt, that is, 52 mol% NaCl – 48 mol% Na₂SO₄ at 635 °C. The eutectic mixture is 53 mol% NaCl – 47 mol% Na₂SO₄.

Similarly, for the KCl-K₂CO₃ system the KCl was increased to form increasing amounts of melt at 640 °C. The salt mixtures used in the experiments with the KCl-K₂CO₃ system are indicated in Fig. 3a with blue dots. The temperatures in the experiments for this system were 620 and 640 °C. The salts were mixed in such way that the same amount of melt was formed at 640 °C for the different cases as for the NaCl-Na₂SO₄ system, that is, 0, 1, 3, 14, and 100 wt% melt (Fig. 3b). The melt composition at 640 °C was 61 mol% KCl – 39 mol% K₂CO₃ for the mixtures with 1–14 wt% melt, while the eutectic mixture is 62 mol% KCl – 38 mol% K₂CO₃.

After the exposure, the samples were cast in epoxy and cut to reveal the cross-section. The cross-sections were analysed by means of SEM-EDX. SEM images of the whole cross-section were taken. These images were stitched together to form a panorama image. A panorama image is presented in Fig. 4a. In this example the corrosion was severe. The oxide layer on top of the steel was coloured green, Fig. 4b. From this, the oxide

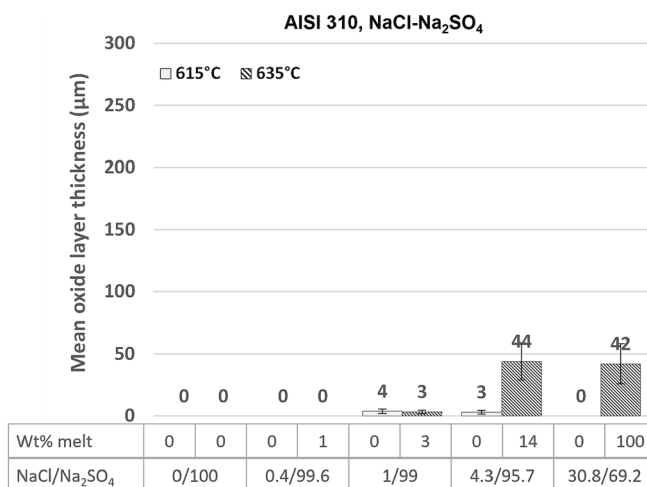


Fig. 6. Mean oxide layer thickness from the experiments with NaCl-Na₂SO₄ salt mixtures on AISI 310 at 615 and 635 °C. Both the salt mixture and wt% melt are given. T₀ for the NaCl-Na₂SO₄ system is 626 °C.

layer thickness along the cross-section can be precisely determined (Fig. 4c), and thus statistics can be obtained. As seen in Fig. 4 the oxide layer in most cases was partly detached from the steel surface during the preparations of the cross sections. The depleted area at the steel surface was not included in the calculations. The corrosion layer thickness after the one-week exposure gives a relative measure of the corrosion rate.

3. Results and discussion

3.1. Tests with NaCl-Na₂SO₄ mixtures

Fig. 5 shows the mean oxide layer thickness from the experiments with NaCl-Na₂SO₄ mixtures below and above T₀. Sodium sulphate was not corrosive under these conditions. This is in line with the finding by Skrifvars et al. [1], who stated that pure Na₂SO₄ is not increasing the corrosion rate at 600 °C. With 1 wt% NaCl and below T₀ at 615 °C, some corrosion (5 µm) was observed. However, above T₀ with 3 wt% melt the corrosion was severe, 47 µm on average. More corrosion was observed with increasing melt amount.

In the experiments with the NaCl-Na₂SO₄ mixtures, the corrosion of AISI 310 was significantly less severe compared to that observed on AISI 347. Only when the melt amount was increased to 14 wt% a clear increase in the corrosion layer thickness was seen (Fig. 6). Interestingly, the amount of corrosion did not increase in the test with the eutectic mixture.

3.2. Tests with KCl-K₂CO₃ mixtures

Pure K₂CO₃ was shown to be corrosive on both stainless steels tested. This is caused by the formation of potassium chromates, leading to a depletion of the protective chromium oxide scale. This has been reported earlier to occur for stainless steel, e.g. Pettersson et al. [23]. Increasing the share of KCl led to an increase in the oxide layer thickness, Fig. 7. Higher corrosion rates for KCl than for K₂CO₃ on ferritic steel and a nickel-based alloy have also been reported by Lehmusto et al. [24]. Above T₀, a significant increase in the corrosion layer thickness was seen with a melt amount of 14 wt%. At eutectic conditions at 640 °C the corrosion was exceptionally severe, with an oxide layer of several hundreds of micrometres. At these conditions, AISI 310 showed better corrosion resistance (Fig. 8) than AISI 347. However, it must be pointed out that at these temperatures the corrosion was significant in all tested conditions. Interestingly though, the amount of melt did affect the corrosion and a threshold melt content was observed when increased

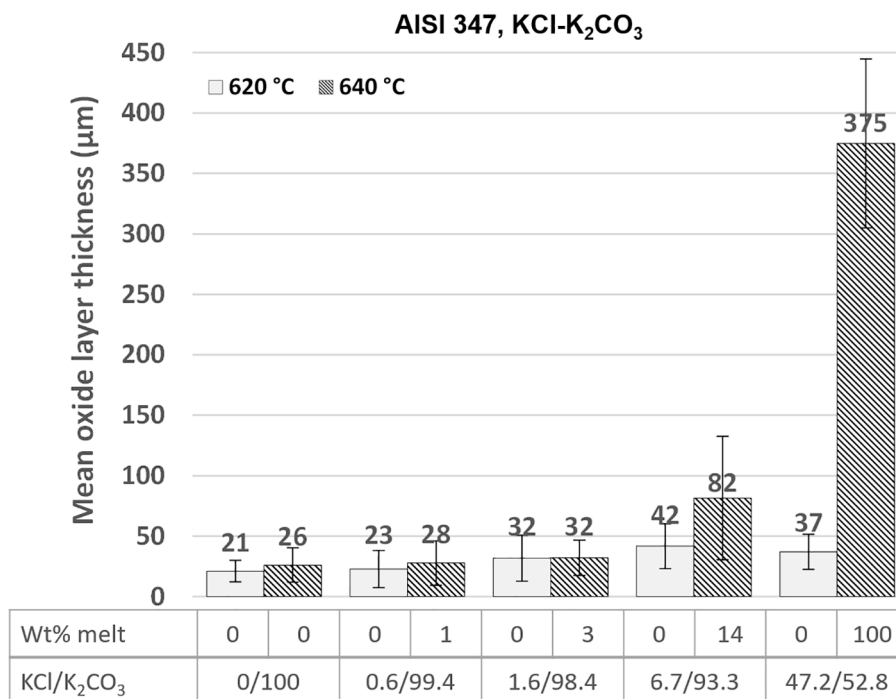


Fig. 7. Mean oxide layer thickness from the experiments with KCl-K₂CO₃ salt mixtures on AISI 347 at 620 and 640 °C. Both the salt mixture and wt% melt are given. T₀ for the KCl-K₂CO₃ system is 631 °C.

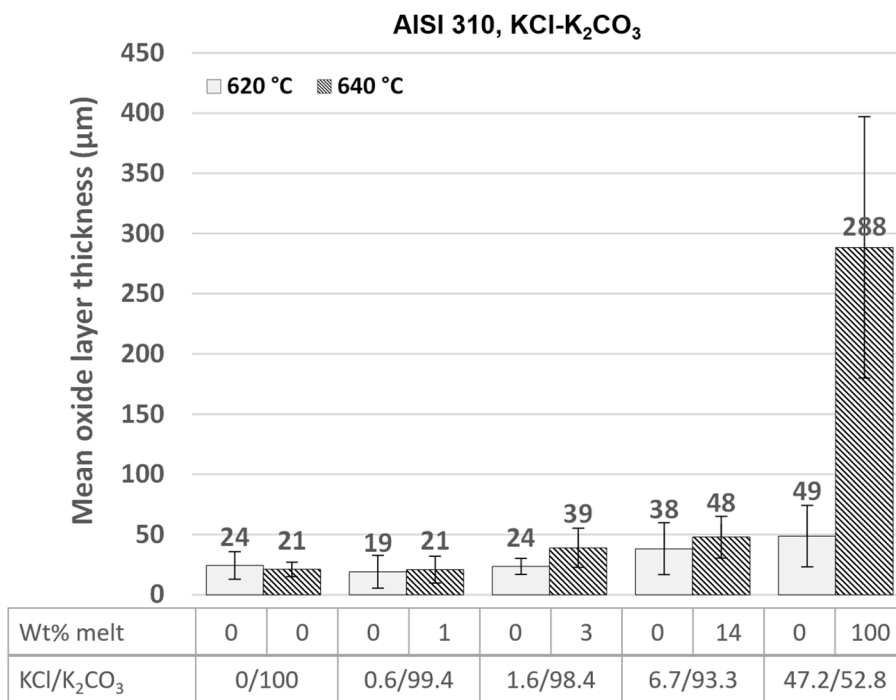


Fig. 8. Mean oxide layer thickness from the experiments with KCl-K₂CO₃ salt mixtures on AISI 310 at 620 and 640 °C. Both the salt mixture and wt% melt are given. T₀ for the KCl-K₂CO₃ system is 631 °C.

corrosion was observed compared to the sub-T₀ experiments.

3.3. Role of melt amount on corrosion and salt/steel contact

The amount of molten phase had a clear effect on the thickness of the

formed oxide layer. Fig. 9 summarizes the effect of the presence of a molten phase on corrosion for the two steel qualities. Low percentages (≤ 1 wt%) of melt did not yet show an increase in corrosion layer thickness. The chloride content also increases with the melt amount, and both factors impact the corrosion, hence the results should for each salt

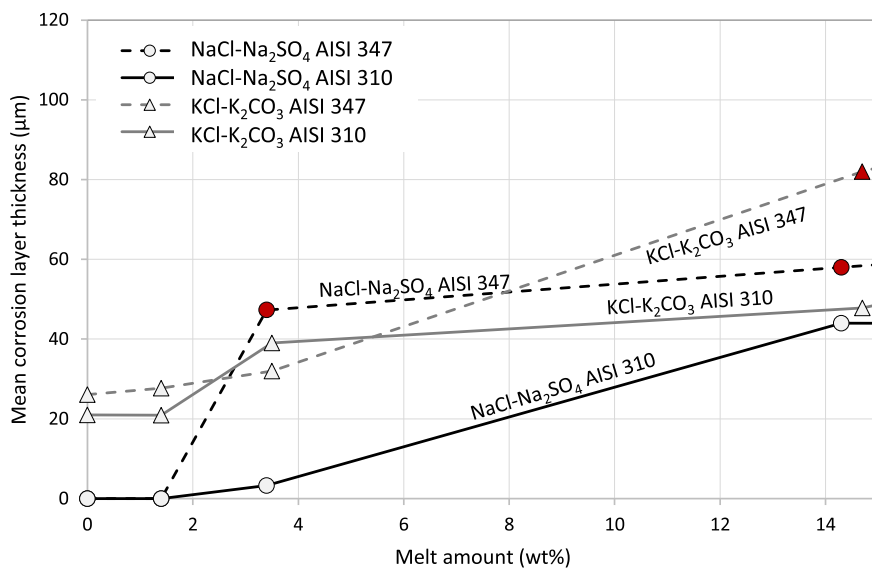


Fig. 9. Effect of melt amount on corrosion layer thickness for the various cases. Markers with red showed increased corrosion layer thickness compared with the reference (experiments below T_0). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

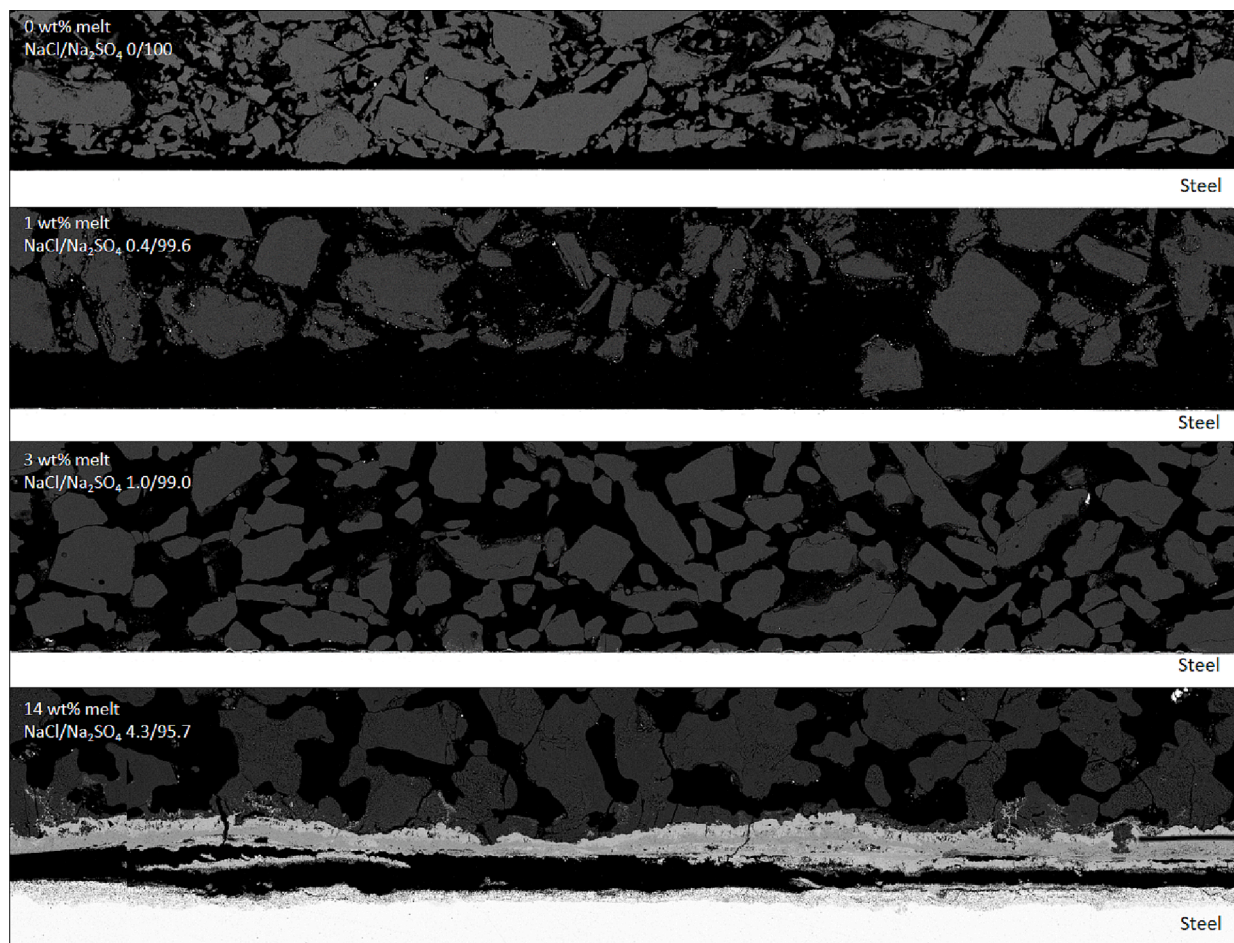


Fig. 10. SEM panorama images of cross-sections of AISI 310 exposed to four different mixtures of NaCl-Na₂SO₄ at 635 °C and increasing melt amount. The amount of melt for the different salt mixture is 0, 1, 3, and 14 wt-%.

be compared to the corresponding experiment performed below T_0 . The effect of the molten phase on corrosion was significant when the melt amount was above 3 wt% for AISI 347 and 14 wt-% for AISI 310.

The increase in the corrosion layer thickness with the share of the molten phase could relate to the contact with the steel and the corrosive melt. Fig. 10 shows panorama SEM images from experiments with NaCl-

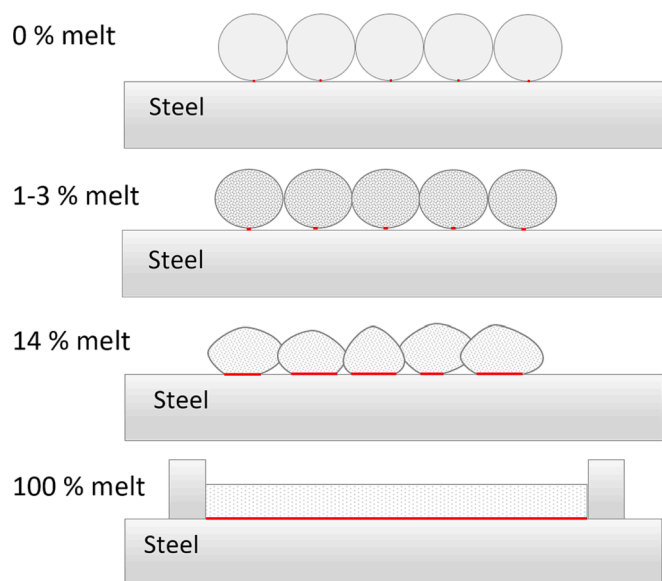


Fig. 11. Illustration of the increase of salt contact to the steel with an increasing amount of molten phase. Salt/deposit contact to steel indicated with red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Na_2SO_4 on AISI 310 at 635 °C. The salt particles become rounder, and agglomerates are formed, as the melt amount increase with the increased share of NaCl. The contact of the salt and melt to the steel is improved and this is thought to be the cause for the increased corrosion. The effect of increasing melt fraction and the subsequent increase in melt is schematically illustrated in Fig. 11.

4. Conclusions

The role of the presence of a molten phase on superheater corrosion was studied in the laboratory using two model salt systems: NaCl- Na_2SO_4 and KCl- K_2CO_3 . Experiments with an increasing amount of molten phase for the two systems were done. Additionally, tests just below the first melting temperature were conducted. Two stainless steel qualities were studied: AISI 310 and AISI 347, with AISI 310 having higher chromium and nickel contents.

The work showed that there appears to be a threshold content of melt above which the corrosion rate increases. This is believed to be caused by the increased steel/salt-melt contact. For the NaCl- Na_2SO_4 salt mixtures, already 3 wt% molten phase was sufficient to significantly accelerate the corrosion rate for AISI 347, while the corresponding value was as high as 14 wt% for AISI 310. Pure solid Na_2SO_4 did not show any corrosion while solid K_2CO_3 showed significant corrosion. The criterion of first melting temperature T_0 being the critical limit for severe superheater corrosion requires modification, as the amount of liquid phase at T_0 is also essential. The critical amount of liquid phase at T_0 for severe corrosion is steel specific.

CRediT authorship contribution statement

Elisa Hupa: Investigation, Writing – original draft, Visualization, Funding acquisition. **Emil Vainio:** Supervision, Conceptualization, Visualization, Writing – original draft, Funding acquisition. **Patrik Yrjas:** Writing – review & editing, Funding acquisition. **Markus Engblom:** Writing – review & editing. **Mikko Hupa:** Conceptualization, Visualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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