ORIGINAL PAPER

Oxidation Kinetics of Crofer 22APU Steel in an Atmosphere Containing SO_2

A. Jaroń · Z. Żurek

Abstract The work presents an analysis of the oxidation rate of Crofer 22APU steel intended for the construction of inter-connectors in solid oxide fuel cells. Tests were conducted on two different samples of Crofer 22APU steel: pre-oxidized and unoxidized ones. Kinetic studies were carried out within the temperature range of fuel cells operation (873–1,173 K) in atmospheres with a varying nSO_2 content in the air (where $n = 0.1\%$, 1%, and 10%), as well as in pure air.

Keywords Crofer 22APU · Oxidation · Kinetic parameters

Introduction

A number of ferritic steels are commercially available in a wide range of compositions; however it seems that none of them can fulfil all requirements for SOFC (Solid Oxide Fuel Cell) applications. Crofer 22APU steel has recently been developed for SOFC applications. Studies [1–5] of the behaviour of Crofer 22APU at high temperatures have proved that numerous factors influence the oxidation rate. These include the composition of the atmosphere, temperature, surface treatment, and the thickness of samples. The authors of the present paper report the results concerning the behaviour of Crofer 22APU steel in air atmospheres containing SO_2. The purpose of these investigations was to verify the influence of various concentrations of SO_2 on the oxidation rate of both Crofer 22APU steel and pre-oxidized Crofer 22APU steel. Previous work [6] presented the results of the

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morphology of the scale formed on Crofer 22APU steel oxidized in an atmosphere of air contaminated with SO_2. The results of these studies indicated the presence of a trace amount of sulphur on the scale surface; thus the aim of the present paper is to determine the influence of various amounts of sulphur on the oxidation rate of the steel.

Materials and Methods

Commercial ferritic steel with the Crofer 22APU trade symbol was used for the research. The chemical composition of the steel is presented in Table 1. As follows from Table 1, chromium is the dominant alloy additive. The amounts of minor alloy additives of Al and Si are present because they improved the scale adhesion [5, 7].

Samples of size 15 × 20 × 1.5 mm were cut from sheet metal 1.5 mm thick. A hole of $\varphi = 1$ mm for hanging the sample in the furnace was drilled in the middle, 1 mm from the top edge of the sample, and then the sample surface was ground with 800 grit abrasive paper. The samples were washed in an ultrasonic rinsing device and then degreased with ethanol prior to the experiments.

The samples were exposed in an apparatus for studying the oxidation kinetics of metallic materials at a high temperature [8].

Ground and degreased samples were hung on a quartz hook in the reaction chamber. Then, the reaction zone was flushed with argon and the furnace was heated to the desired temperature. When the appropriate temperature was achieved, the mixture of air + SO_2 was introduced.

The oxidation rate measurements were carried out in the mixture of air + nSO_2 (where n = 0.1%, 1.0%, and 10.0%, without of catalyst) using the periodic method. The rate of gas flow amounted to 10 dm^3/h. The oxidation rate measurements were carried out within the temperature range of 873–1,173 K. After the given exposure time had elapsed, the samples were cooled down in the argon atmosphere. After the furnace temperature reached less than 323 K the sample together with the frame was removed from the furnace and placed for about half an hour in a desiccator until the sample reached room temperature. Then it was weighed with an accuracy of 0.0001 g. This procedure was repeated for each exposed sample for a given period of time.

Table 2 shows the partial pressures of oxygen and sulphur in the examined atmospheres at various temperatures. The values were determined by means of the program FactSage [9].

Table 1 Chemical composition of Crofer 22APU (wt%) [5–7]

Chemical composition (wt%)

Fe	Cr	Mn	Ti	La	Al	Si	Cu	Ce
Bal.	22.3	0.53	0.055	0.10	0.0056	0.10	0.0046	0.0009

**Table 2** Partial pressure of oxygen and sulfur in used atmospheres [6, 9]

Percentage SO$_2$ in air	Temperature							
	873 K		973 K		1,073 K		1,173 K	
	pO$_2$ (Pa)	pS$_2$ (Pa)	pO$_2$ (Pa)	pS$_2$ (Pa)	pO$_2$ (Pa)	pS$_2$ (Pa)	pO$_2$ (Pa)	pS$_2$ (Pa)
0.1	1.9967×10^4	1.8570×10^{-37}	1.9977×10^4	3.4932×10^{-32}	1.9985×10^4	3.5118×10^{-28}	1.9986×10^4	5.0166×10^{-25}
1	1.9672×10^4	1.9508×10^{-35}	1.9787×10^4	3.5956×10^{-30}	1.9890×10^4	3.5588×10^{-26}	1.9941×10^4	5.0464×10^{-23}
10	1.6652×10^4	3.3542×10^{-33}	1.7889×10^4	4.8587×10^{-28}	1.8937×10^4	4.0720×10^{-24}	1.9492×10^4	5.3566×10^{-21}

Results and Discussion

SO_2 as an impurity may occur in both the anode and the cathode zone of fuel cells, but the amount of SO_2 in the first zone may be infinitely small.
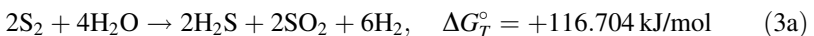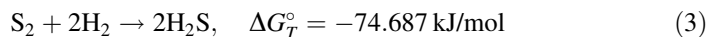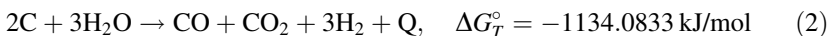
It is assumed that at the inlet of the fuel cell anode zone, the gas (H_2) may be contaminated with H_2S. However, the gas content at the outlet may differ slightly quantitatively and qualitatively owing to the presence of oxygen in the anode zone diffusing through an electrolyte and reacting with hydrogen and contaminants.

The presence of H_2S in the anode zone depends on the hydrogen's source of origin. The reaction (1) of hydrogen obtained through electrolysis or the conversion of hydrocarbons is virtually unable to be contaminated with H_2S due to the substrate's purity (all ΔG_T° for $T = 1,073$ K and $p = 101,325$ Pa values in this paper were calculated using FactSage with thermodynamic databases [9]).
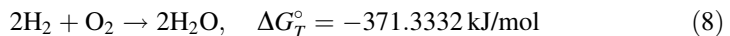
$$CH_4 + H_2O \rightarrow CO + 3H_2, \quad \Delta G_T^\circ = +215.043 \text{ kJ/mol} \tag{1}$$
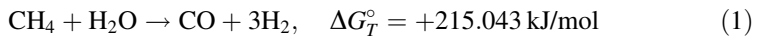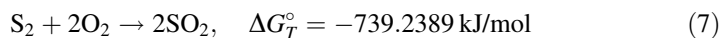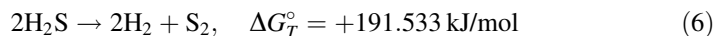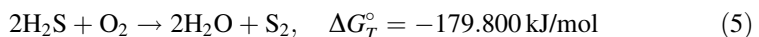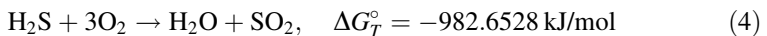
The above reaction takes place in the presence of a nickel catalyst.

However the presence of H_2S is possible if the process of gasification of sulphur-containing carbon is the source of hydrogen. The process of carbon gasification proceeds in accordance with the following reactions:

$$2C + 3H_2O \rightarrow CO + CO_2 + 3H_2 + Q, \quad \Delta G_T^\circ = -1134.0833 \text{ kJ/mol} \tag{2}$$

$$S_2 + 2H_2 \rightarrow 2H_2S, \quad \Delta G_T^\circ = -74.687 \text{ kJ/mol} \tag{3}$$

$$2S_2 + 4H_2O \rightarrow 2H_2S + 2SO_2 + 6H_2, \quad \Delta G_T^\circ = +116.704 \text{ kJ/mol} \tag{3a}$$

Reaction (3a) is not possible $\left(\Delta G_T^\circ > 0\right)$ from the thermodynamics point of view. The presence of H_2S results from the reaction of sulphur, arising from the contamination of carbon with organic and inorganic sulphur-containing compounds, with hydrogen.

As suggested in the literature [10], H_2S can react with oxygen in the anode zone of SOFC according to the fallowing reactions:

$$H_2S + 3O_2 \rightarrow H_2O + SO_2, \quad \Delta G_T^\circ = -982.6528 \text{ kJ/mol} \tag{4}$$

$$2H_2S + O_2 \rightarrow 2H_2O + S_2, \quad \Delta G_T^\circ = -179.800 \text{ kJ/mol} \tag{5}$$

$$2H_2S \rightarrow 2H_2 + S_2, \quad \Delta G_T^\circ = +191.533 \text{ kJ/mol} \tag{6}$$

$$S_2 + 2O_2 \rightarrow 2SO_2, \quad \Delta G_T^\circ = -739.2389 \text{ kJ/mol} \tag{7}$$

$$2H_2 + O_2 \rightarrow 2H_2O, \quad \Delta G_T^\circ = -371.3332 \text{ kJ/mol} \tag{8}$$

ΔG_T values were determined for the pressure of 101,325 Pa at a temperature of 1,073 K. Reactions (4) and (7) are the source of SO_2, but reaction (5) is the source of sulphur formation which in turn may react (7) with oxygen, yielding SO_2. Reaction (6) cannot proceed towards the dissociation of the H_2S; in the H_2/H_2S mixture the reaction equilibrium is shifted to the left. A slight amount of H_2S will react with oxygen according to reaction (5) with the formation of sulphur, which, reacting with oxygen, yields sulphur dioxide, SO_2. However, sulphur dioxide, SO_2, is more likely to be formed according to reaction (4).

Table 3 The contents of gas mixtures introduced into the inter-connector anode zone and mixture of a different content at the output [9]

	Volume fraction (%)				
	H_2	H_2O	H_2S	O_2	SO_2
Inlet	99.4	0	0,6	0	0
	94.0	0	6	0	0
Outlet	9.4	60.0	0.599	1.26×10^{-15}	7.56×10^{-5}
	4.1	59.98	5.911	6.64×10^{-15}	8.98×10^{-3}

Table 3 illustrates the contents of gas mixtures introduced into the inter-connector anode zone, where, reacting with oxygen diffusing through a stable electrolyte (ZrO_2), they form a mixture of a different content at the outlet. The outlet gas content was calculated assuming that 30% of O_2 diffused into the anode zone through the electrolyte. The calculations were made for a temperature of 1,073 K under pressure of 101,325 Pa and 0.6 and 6.0% H_2S contents in the H_2 atmosphere [9].

As the results of our calculation in Table 3 (very low concentration of SO_2) show, that the amount of resulting SO_2 is negligibly small. Negligible amount of SO_2 form owing to the fact that only a slight amount of H_2S can react with oxygen, which means that H_2S is the prevailing impurity within the anode area.

Thus, sulphur occurs as an impurity in the form of H_2S in the anode zone, but in the form of SO_2 in the cathode area. In the cathode zone the probability of SO_2 presence is significantly higher as its occurrence may result from the contamination of the air with this compound [6].

As can be concluded from the calculations (Table 2), the presence of slight amounts of SO_2 in the air exerts practically no impact on oxygen partial pressure. Oxygen partial pressure changes with temperature only to a small degree. Yet in the case of sulphur, the values of its partial pressure change as a function of the concentration of SO_2 in the gas by approximately three orders of magnitude for each temperature taken into consideration. However, as a function of temperature the values change by as much as ten orders of magnitude [6].

Figures 1, 2, 3, and 4 illustrate the oxidation kinetics of Crofer 22APU in atmospheres of varying SO_2 content. Each oxidation process can be approximately described by a parabolic rate law, which means that in all cases the scale growth diffusion controlled.

The registered differences in samples mass increments, especially at low temperatures, are within experimental errors. At higher temperatures mass increments are so large that the measurement error does not exert such an influence on the observed differences in mass increments for various concentrations of SO_2.

The linear dependence of the parabolic rate constant on temperature indicates that the mechanism of oxidation within the studied range of temperatures is the same for all of the applied SO_2 concentrations (Fig. 5).

Figure 6 illustrates the values of the parabolic rate constant for Crofer 22APU steel as a function of atmospheric content change. The oxidation rate constants at a
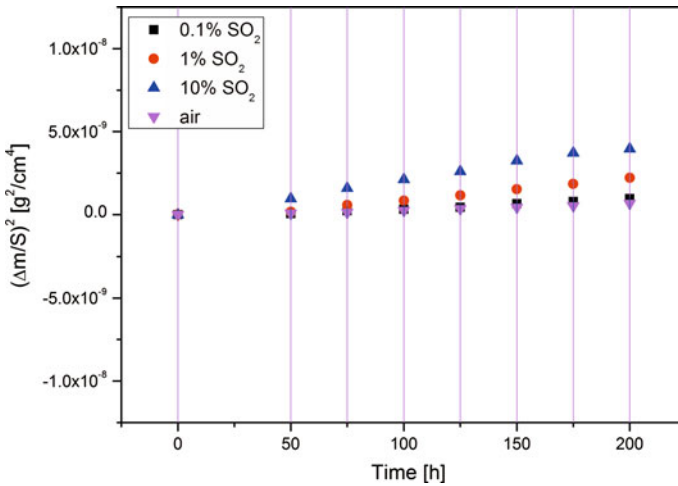
Fig. 1 Kinetic curves of Crofer 22APU oxidized at 873 K in air + nSO$_2$. The total error was around 10^{-7} g^2/cm^4 and the errors bars are outside the scope of scale
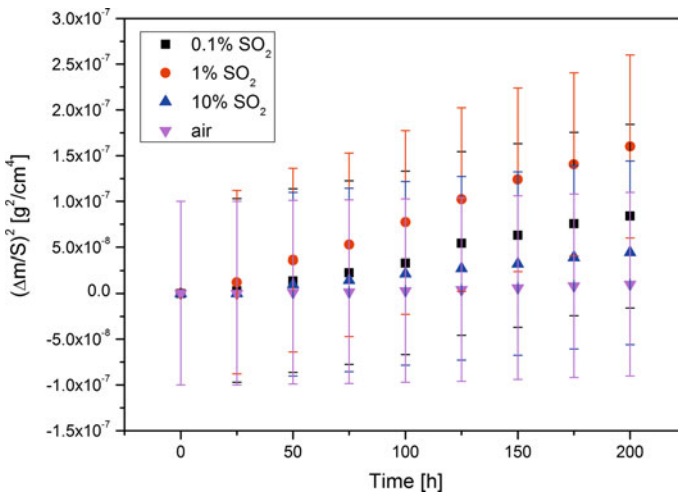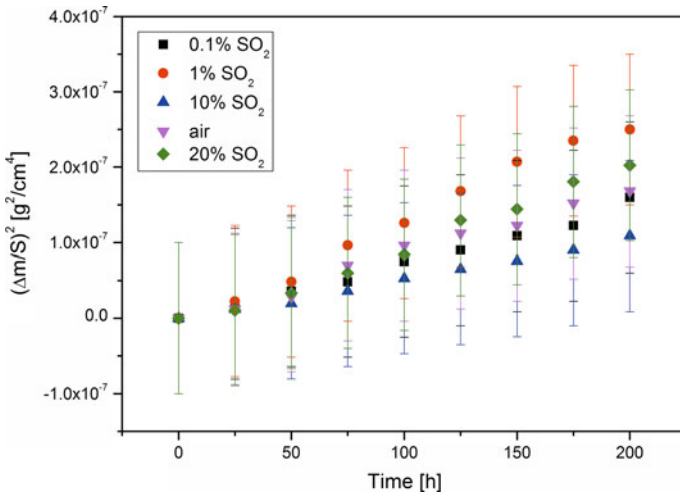

Fig. 2 Kinetic curves of Crofer 22APU oxidized at 973 K in air + nSO$_2$

given temperature do not show distinctive differences, which means that the SO$_2$ content exerts practically small influence on the Crofer 22APU steel oxidation rate within the studied time range. The steel oxidation rate in the air atmosphere is practically comparable with the values obtained in atmospheres containing SO$_2$. Analysing the mass increment of samples oxidized in atmospheres with varying contents of SO$_2$, it may be stated that only at a temperature of 873 K a slight influence of SO$_2$ concentration on the mass increment is observed. At higher temperatures the difference in mass gain was comparable for all of the SO$_2$ concentrations.

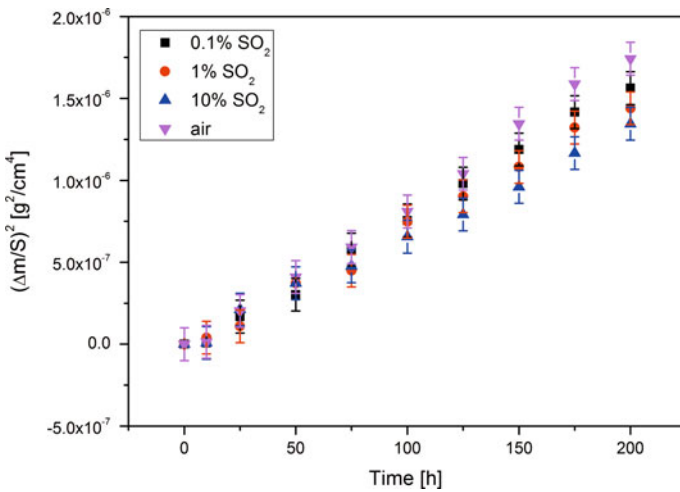**Fig. 3** Kinetic curves of Crofer 22APU oxidized at 1,073 K in air + nSO$_2$

Fig. 4 Kinetic curves of Crofer 22APU oxidized at 1,173 K in air + nSO$_2$

Mass gain connected with the formation of MnS is greater than in the case of MnO but in the presence of SO$_2$ taking part in the oxidation of steel it is very small and therefore practically unmeasurable. The reaction processes on the surface of the scale can be written as [11]:

$$Mn + SO_2 \rightarrow MnS + 2MnO \tag{9}$$

$$MnO + Cr_2O_3 \rightarrow MnCr_2O_4 \tag{10}$$
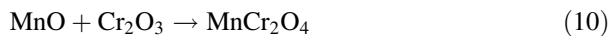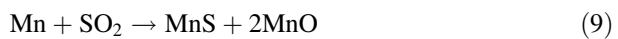
The scale formed on Crofer has a good adherence to the metallic core (Fig. 7).
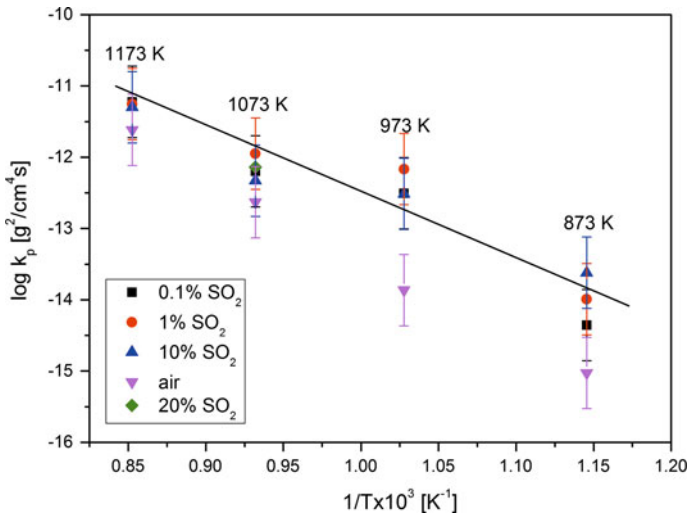
Fig. 5 Parabolic oxidation rate constant for Crofer 22APU steel as a function of temperature in nSO_2 + air atmospheres (oxidation time: 100 h)

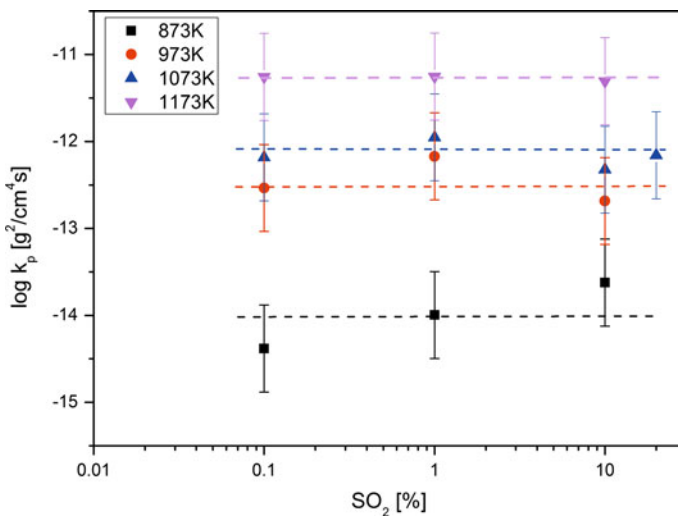

Fig. 6 Parabolic oxidation rate constant for Crofer 22APU steel as a function of atmospheric content of nSO_2 + air

The results of the oxidation rate of the pre-oxidized sample are presented below (Fig. 8). A Crofer 22APU steel sample was pre-oxidized in an air atmosphere at a temperature of 1,073 K for 100 h. A 1.5–2.5 μm thick scale formed on the sample surface [5, 6]. The pre-oxidized sample was placed in a furnace and a mixture of gases, air + SO_2, was introduced. Oxidation of preoxidized samples was carried out in air + SO_2 gas mixture only at 1,073 K. These results have demonstrated that the
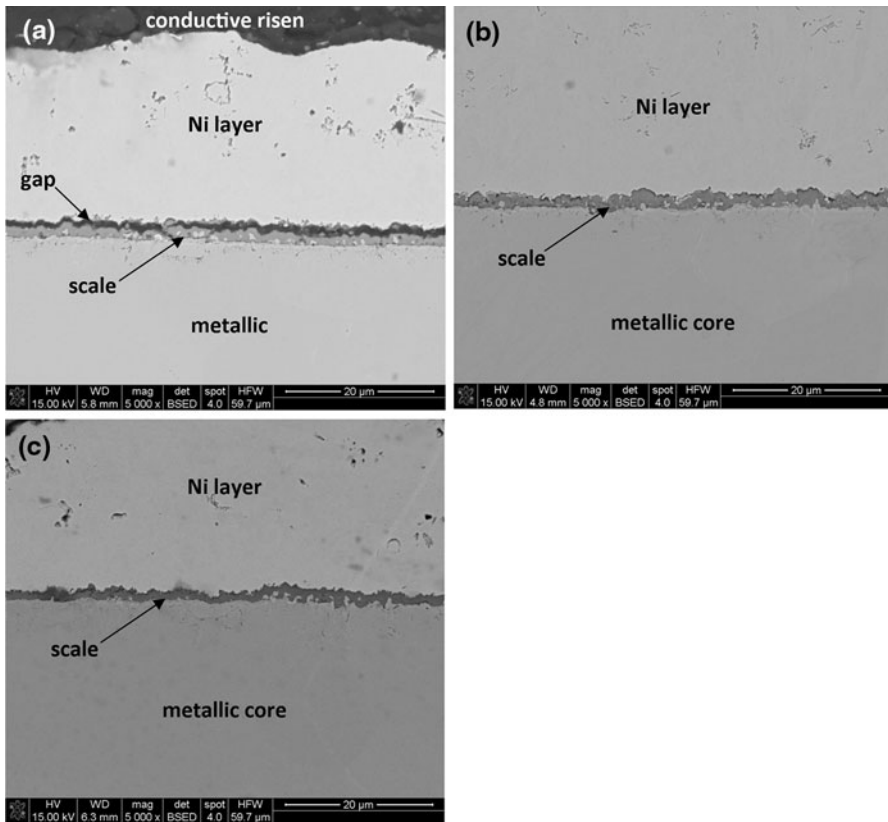
Fig. 7 SEM cross section image of Crofer 22APU oxidized at 1173 K in **a** air + 0.1% SO$_2$, **b** air + 1% SO$_2$, and **c** air + 10% SO$_2$
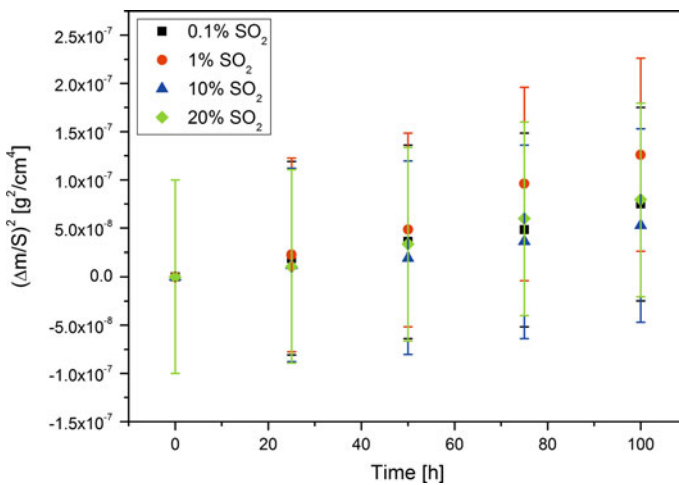

Fig. 8 Kinetic curves of pre-oxidized Crofer 22APU steel oxidized at 1,073 K in air + nSO$_2$

preformed scale layer hindered the rate of further sample oxidation only to a slight degree (Fig. 8). Moreover, these results confirmed that the small amount of SO_2 present in the atmosphere practically did not influence the oxidation rate.

Conclusions

On the basis of the conducted studies it may be established that:

(1) The Crofer 22APU steel oxidation rate is practically independent of the oxidizing atmosphere content (nSO_2 + air).
(2) An influence of SO_2 concentration on the oxidation rate practically was not observed.
(3) The scale formed demonstrates good adherence to the steel.
(4) Pre-oxidization of the samples lowers the rate of steel oxidation in atmospheres containing SO_2 to a slight degree.

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