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THE STRUCTURE OF EXTERNAL SURFACES OF SCALE FORMING ON CROFER 22APU STEEL IN ATMOSPHERE CONTAINING H_2/H_2S

BUDOWA ZEWNĘTRZNYCH POWIERZCHNI ZGORZELIN TWORZĄCYCH SIĘ NA STALI CROFER 22APU W ATMOSFERZE H_2/H_2S

The paper presents results of structural tests carried out for scale formed during high-temperature sulphurisation of Crofer 22APU steel within temperature range 600-900°C, in atmosphere containing H_2/H_2S, at partial pressure of sulphur vapours: $p_{S2} 10^{-7}$ up to 10^{-1} Pa. Non-preoxidated and preoxidated (preliminarily oxidated in air atmosphere) samples were put through sulphurisation process. The SEM, EDX and XRD methods were employed to examine scale surface morphology, including its chemical constitution and phase composition. The SEM tests allowed to find that scale structure depends on atmosphere content and temperature. In conditions of high sulphur vapour pressure values (exceeding iron sulphide dissociation pressure), scale has two layers and consists of a mixture of iron sulphides (Fe_nS_m) and chromium sulphides (Cr_xS_y). Outer scale layer is built of large, column-shaped grains with composition corresponding to (Fe_nS_m), whereas its inner layer – fine-grained and porous – is a mixture of chromium sulphides, iron sulphides and sulphospinels. Occurrence of internal oxidation zone has been observed at the temperatures of 800°C and 900°C. Scale has single layer at low sulphur vapour pressure values, that is under FeS dissociation pressure. Preoxidated steel samples undergo sulphurisation process also after incubation period. This period is changeable and depends on sulphur vapour temperature and pressure. The structure and chemical constitution of scale formed on pre-oxidated samples depends on sulphurisation process parameters. Morphology of outer scale surface on preoxidated samples is complicated, because sulphides of all steel constituents are forming on the surface of oxides.

Keywords: Crofer 22APU, preoxidation, sulphurisation, scale, morphology

W pracy przedstawiono wyniki badań strukturalnych zgorzelin otrzymanych w trakcie wysokotemperaturowego siarkowania stali Crofer 22APU w zakresie temperatur 600-900°C w atmosferze H_2/H_2S przy ciśnieniu parcjalnym par siarki $p_{S2} 10^{-7}$ do 10^{-1} Pa. Procesowi siarkowania poddano próbki nie preoksydowane oraz próbki preoksydowane (wstępnie utlenione w atmosferze powietrza). Badania morfologii powierzchni zgorzelin wraz z ich składem chemicznym i fazowym wykonano przy zastosowaniu SEM, EDX i XRD. Na podstawie badań SEM stwierdzono, że budowa zgorzelin zależy od składu atmosfery oraz temperatury. W warunkach wysokich prężności par siarki (powyżej prężności rozkładowej siarczku żelaza) zgorzeliny są dwuwarstwowe i są zbudowane z mieszaniny siarczków żelaza (Fe_nS_m) i siarczków chromu (Cr_xS_y). Zewnętrzna warstw zgorzeliny jest zbudowana z dużych kolumnowych ziaren o składzie odpowiadającej (Fe_nS_m), natomiast wewnętrzna drobno ziarnista, porowata jest mieszaniną siarczków chromu, żelaza oraz sulfospineli. W temperaturze 800°C i 900°C stwierdzono występowanie strefy wewnętrznego utleniania. W niskich ciśnieniach par siarki tzn. poniżej prężności rozkładowej FeS, zgorzeliny są jednowarstwowe. Próbki stali preoksydowane ulegają również procesowi siarkowania po okresie inkubacji. Okres ten jest zmienny i zależy od temperatury i prężności par siarki. Budowa i skład chemiczny zgorzelin otrzymanych na preoksydowanych próbkach zależy od parametrów siarkowania. Morfologia zewnętrznej powierzchni zgorzeliny utworzonej na próbkach preoxydowanych jest skomplikowana, gdyż na powierzchni tlenków tworzą się siarczki składników stali.

1. Introduction

Commercialisation of SOFC (Solid Oxide Fuel Cell) cells is strictly related to the possibility of using in them those fuels, which are available in the market. Usually, these fuels contain sulphur compounds (primarily in form of hydrogen sulphide) at concentrations, which e.g. in case of synthesis gas or carbon, reach even 300 ppm, and in case of methane – up to 1% [1,2]. Sulphur compounds have negative impact on the whole SOFC structure, which reduces its efficiency and degrades it by interconnector corrosion and anode intoxication. Degra-

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dation of interconnector in metallic element of the cell caused by sulphur compounds is a separate issue. In the case of fuels cells working at low temperatures encountered in attempts to use stainless steel for example X20Cr13 on interconnectors [3]. Due to required strength properties and electric conduction at high temperature i.e. SOFC conditions, steel grades from ferritic steel group constitute material that is continuously used to make interconnectors, and Crofer 22APU is one of them.

In conditions of high temperature and atmosphere containing oxidant, this steel forms protective scale layer consisting of chromium oxide. Studies conducted so far in the world focused mainly on the processes involving oxidation of this material and elimination of an adverse effect of volatile CrO_3 formation, whereas available literature contains no information on sulphurisation processes, and in particular on kinetic, morphological and structural studies.

This work is a continuation of the research on Crofer 22APU steel behaviour in conditions of high-temperature sulphurisation in H_2/H_2S atmosphere presented in studies [4,5]. Authors of this work have focused on comparing and explaining the constitution and structure of sulphide scale forming in hydrogen sulphide atmosphere on non-preoxidated and preoxidated Crofer 22APU steel.

2. Materials and test methods

The material used for test purposes was commercial Crofer 22APU steel characterised by the following chemical composition (wt.-%): Cr-22.3, Mn-0.53, Ti-0.055, La-0.10, Al-0.0056, Si-0.10, Cu-0.0046, Ce-0.0009, Fe-rest.

Sulphurisation process was conducted within temperature range 600-900°C in H_2/H_2S atmosphere, and at varying partial pressure of sulphur (S_2) – from 10^{-7} up to 10^{-1} Pa (Tab. 1). Sulphurisation of preoxidated steel samples (preliminarily oxidated at the temperature of 800°C in air atmosphere, duration 100 h) was carried out in the same conditions as for samples that weren't put through preoxidation process. Test samples sized 10×10 mm were cut out of 0.5 mm-thick sheet. Before the tests sample surface was mechanically polished to bright polish. Using an ultrasonic washer, prepared materials were degreased in bath with a detergent added, and then washed with ethyl alcohol and dried in hot air stream. Sulphurisation tests were carried out using an apparatus, which diagram and principle of operation were described in study [6].

TABLE 1
H_2S concentration in H_2 and sulphur pressure in the mixture

Temperature [°C]	%H_2S w H_2	p_{S2} [Pa]
600	12,00 6,40 0,02	10^{-1} 10^{-3} 10^{-7}
700	11,00 1,82 0,03	10^{-1} 10^{-3} 10^{-6}
800	6,40 0,68 0,07	10^{-1} 10^{-3} 10^{-5}
900	2,8 0,28 0,09	10^{-1} 10^{-3} 10^{-4}

3. Test results and discussion

Phase composition of scale was examined using a Philips X-ray apparatus, PW 1710 type, equipped with $Co_{K\alpha}$ X-Ray filter (Table 2-3).

Identification of phase composition was carried out for surfaces of samples sulphurised at sulphur vapour pressure: p_{S2} =10^{-1} and 10^{-3} Pa, and for low pressure values (p_{S2} =10^{-4}, 10^{-5}, 10^{-6} and 10^{-7} Pa) – for samples from total mass of scale collected in a cuvette (Tables 1-2), because in these conditions scale formed on non-preoxidated samples was coming off metal surface.

TABLE 2
Identification of phase composition for outer surface of scale layer formed on a non-preoxidated Crofer 22APU steel

Temp. [°C]	p_{S2} [Pa]					
	10^{-1}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}
600	Fe_nS_m, Cr_xS_y	Fe_nS_m	–	–	–	Fe_nS_m
700	Fe_nS_m, Cr_xS_y	Fe_nS_m	–	–	$FeCr_2S_4$, Fe_nS_m, Cr_xS_y	–
800	Fe_nS_m, Cr_xS_y	Fe_nS_m	–	Fe_nS_m, Cr_xS_y	–	–
900	Fe_nS_m, Cr_xS_y	Cr_xS_y	Cr_xS_y	–	–	–

TABLE 3

Identification of phase composition for outer surface of scale layer formed on a preoxidated Crofer 22APU steel

Temp. [°C]	**p_{S2} [Pa]**					
	10^{-1}	**10^{-3}**	**10^{-4}**	**10^{-5}**	**10^{-6}**	**10^{-7}**
600	$FeCr_2S_4$, FeS, Cr_xO_y	FeS, Cr_xS_y, TiO_2, Cr_xO_y, Fe_nO_m	–	–	–	Cr_xO_y, Fe_nO_m, $(MnCr)_xO_y$
700	FeS Cr	FeS	–	–	Cr_xO_y, Fe_nO_m, $(MnCr)_xO_y$	–
800	(Mn,Fe)S	(Mn,Fe)S	–	TiS, Fe_nS_m, Cr_xO_y, $(MnCr)_xO_y$, Cr_xO_y	–	–
900	FeS	(Mn,Fe)S	Cr_xS_y	–	–	–

Non-preoxidated samples sulphurised within temperature range 600-900°C and at pressure $p_{S2} = 10^{-1}$ Pa develop on their surfaces scale consisting of iron sulphides, and titanium and aluminium sulphides. In these conditions iron sulphide remains in equilibrium with atmosphere. Alike phase composition is shown by scale formed within temperature range 600-800°C and at the pressure $p_{S2} = 10^{-3}$ Pa. At the temperature of 900°C and partial pressure of sulphur vapours $p_{S2} = 10^{-3}$ Pa chromium sulphide is predominant scale constituent, since iron sulphide formation is impossible. Scale formed during sulphurisation at lowest sulphur vapour pressures within temperature range 700-900°C consists of chromium sulphides and/or iron sulphides, and sulphospinels. Only at the temperature of 600°C and sulphur vapour pressure 10^{-7} Pa it is higher than dissociation pressure of FeS, and thus iron sulphide may form on the surface then.

Constitution of scale formed on preoxidated samples depends on sulphurisation conditions (Tab. 2) as well. Continuous layer of iron sulphides is formed on the surface of oxide scale within the entire temperature range and at the pressure of $p_{S2} = 10^{-1}$ Pa. At lower temperature values (600, 700°C) under pressure $p_{S2} = 10^{-3}$ Pa, oxide scale surface gets covered with "blooms" consisting of a mixture of iron sulphides (Fe_nS_m) and chromium sulphides (Cr_xS_y), manganese (MnS) and sulphospinel ($FeCr_2S_4$ and/or $MnFe_2S_4$). At higher temperatures original oxide scale is covered with a layer of iron sulphides (Fe_nS_m) or a mixture consisting of iron sulphides and chromium sulphides (Cr_xS_y). Whereas, at the temperature of 900°C and sulphur vapour pressure $p_{S2} = 10^{-3}$ Pa, the surface is covered mainly with (Cr_xS_y) and a mixture of iron and chromium sulphides $(Fe,Cr)_nS_m$. Chromium sulphide grains were only sporadically identified on scale surface during sulphurisation of pre-oxidated samples under sulphur vapour pressure $p_{s2} = 10^{-7}$ and temperature of 600°C. With increasing temperature and pressure of sulphur vapours the scale gets covered with chromium sulphide blooms. At the temperature of 900°C the entire surfaces were covered with compact chromium sulphide layer.

The mechanism involving formation of sulphides of steel ingredients on oxide layer surface is connected with their core diffusion through oxide layer. Whereas, sulphides formation depends only on whether thermodynamic conditions for their formation are met or not. Oxide layer does not decompose, only its compactness is deteriorated by growing sulphide grains.

Surface morphology and lateral microsection were examined using a scanning electron microscope, STEREOSCAN 420 type, equipped with X-ray microanalyser - EDS LINK ISIS 300 and FEI Nora 200 Nano SEM. Examination results for non-preoxidated samples are shown in Figures 1-2.

In the atmosphere under sulphur vapour pressure $p_{S2} = 10^{-1}$ Pa, formed scale consists of regular grains. Their dimensions change with temperature. At the temperature of 600°C grains are not larger than 20 μm (Fig. 1a), while within temperature range 700 to 800°C grain size reaches tens of μm (Fig. 1b-1c).

The structure of regular grains decays at the temperature of 900°C (Fig. 1d). The layer of reaction products shows cracks along grain boundaries.

The SEM observations of scale formed at the atmosphere under pressure of $p_{S2} = 10^{-3}$ Pa have proven that morphology of outer scale layer depends on temperature and pressure of sulphur vapours (Fig. 2a-2d). At the temperature of 600°C grains are not larger than few μm (Fig. 2a), while within temperature range 700 to 800°C grain size reaches tens of μm (Fig. 2b-2c). At the temperature of 900°C, morphology of scale differs from morphology of scale formed at lower temperatures and the same sulphur vapour pressure. The scale is fine-grained and porous, with strongly developed "spongy" surface (Fig. 2d).

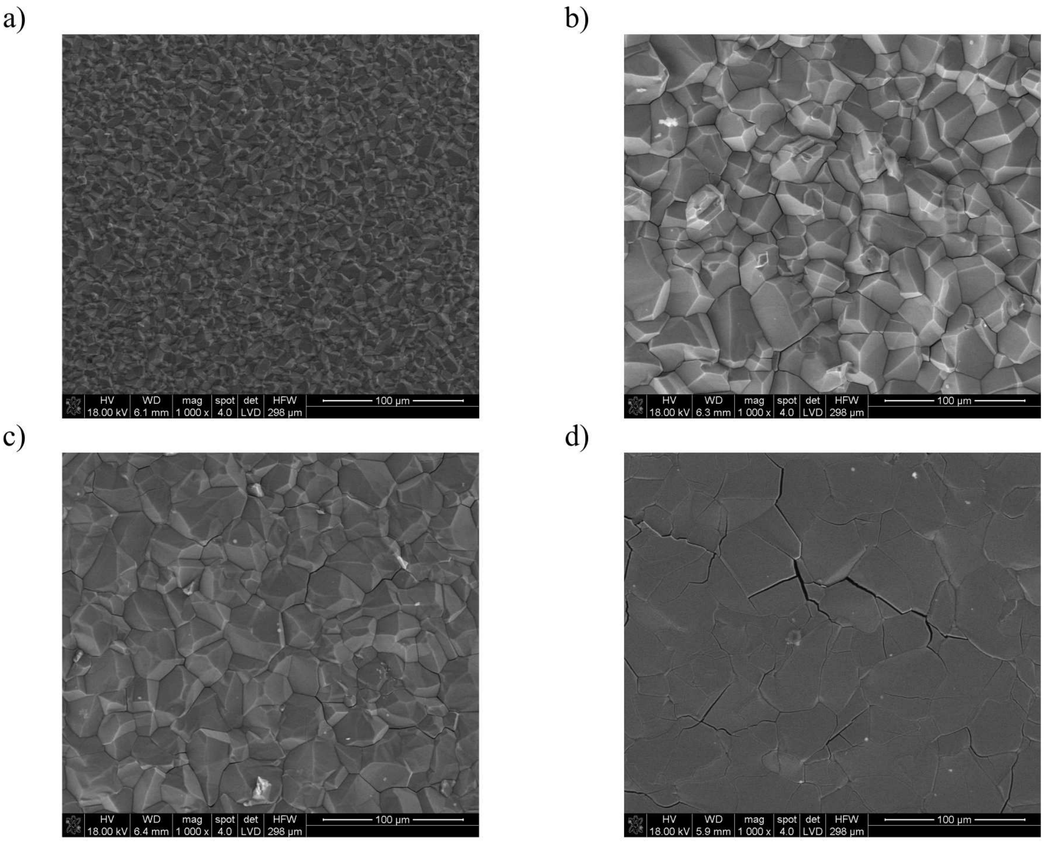

Fig. 1. Surface morphology in scale formed on non-preoxidated Crofer 22APU steel sulphurised in H_2/H_2S atmosphere at partial pressure of sulphur vapours 10^{-1} Pa and temperature: a) 600°C, b) 700°C, c) 800°C, d) 900oC

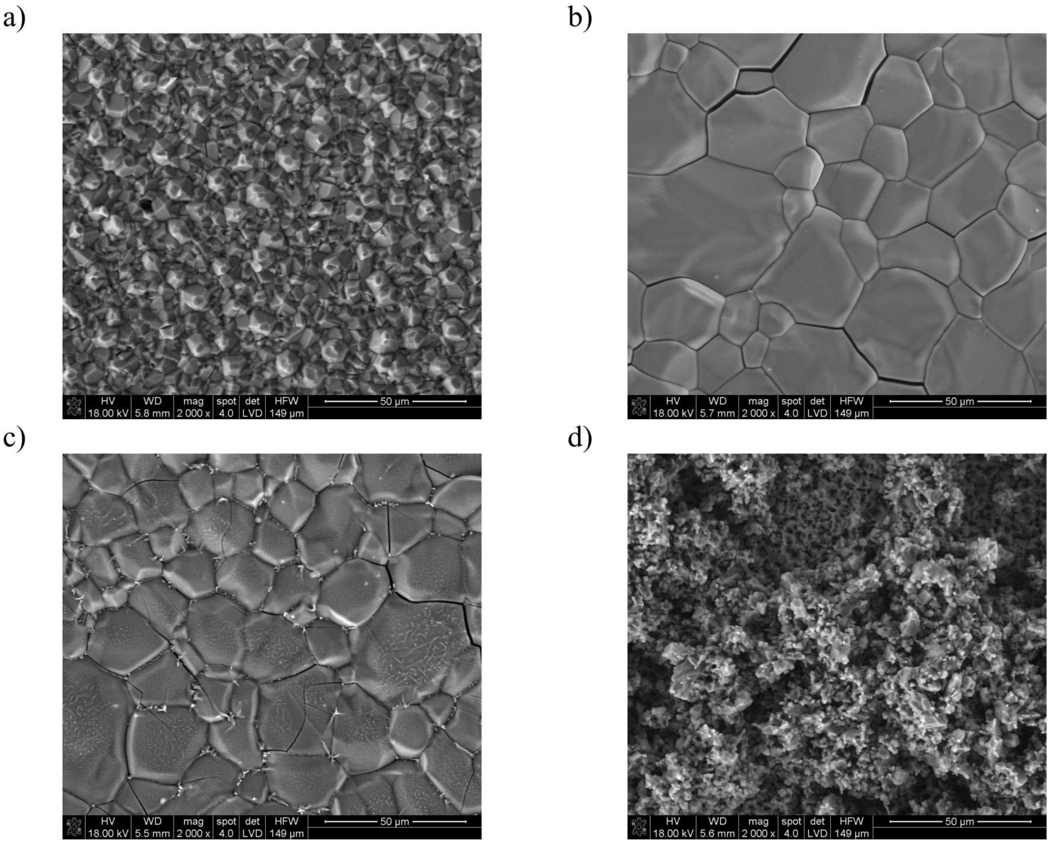

Fig. 2. Surface morphology in scale formed on non-preoxidated Crofer 22APU steel sulphurised in H_2/H_2S atmosphere at partial pressure of sulphur vapours 10^{-3} Pa and temperature: a) 600°C, b) 700°C, c) 800°C, d) 900°C

Sulphurisation at low sulphur vapour pressures within temperature range 600-900°C allowed to observe that surface appearance of scale formed on non-preoxidated samples depends on process conditions (temperature, pressure) (Fig. 3a-3d). At partial pressure of sulphur vapours 10^{-7} Pa and the temperature of 600°C, formed scale consists of regular Fe_nS_m grains. Their dimensions reach a dozen or so μm (Fig. 3a). At the temperature of 700°C and $p_{S2} = 10^{-6}$ Pa, the surface consists of fine-grained Cr_xS_y and grain size does not exceed 1-2 μm. Grains sized 5-6 μm occur sporadically (Fig. 3b). With increasing temperature and partial pressure of sulphur vapours, the surface of samples becomes covered with more and more compact Cr_xS_y layer showing the structure of large crystallites (Fig. 3c, 3d).

In case of preoxidated samples sulphurised in atmosphere under sulphur vapour pressure $p_{S2} = 10^{-1}$ Pa, the researchers were sporadically observing manganese enriched chromium sulphide grains after the examined time only at the temperature of 600°C (Fig. 4a). With increasing temperature the surface of samples gets covered with compact sulphide layer and/or manganic-ferric sulphospinel (Fig. 4b-c).

Same as in case of samples preoxidated and sulphurised at $p_{s2} = 10^{-1}$, the researchers have observed for $p_{s2} = 10^{-3}$ Pa original oxide layer occurring at lower temperatures (Fig. 5a, 5b). With increasing temperature this layer gets covered with sulphurisation products (iron-manganese sulphides). Within temperature range 800-900°C the scale consists of regular grains exceeding 100 μm in size. Deep cracks and gaps are visible in reaction products layer.

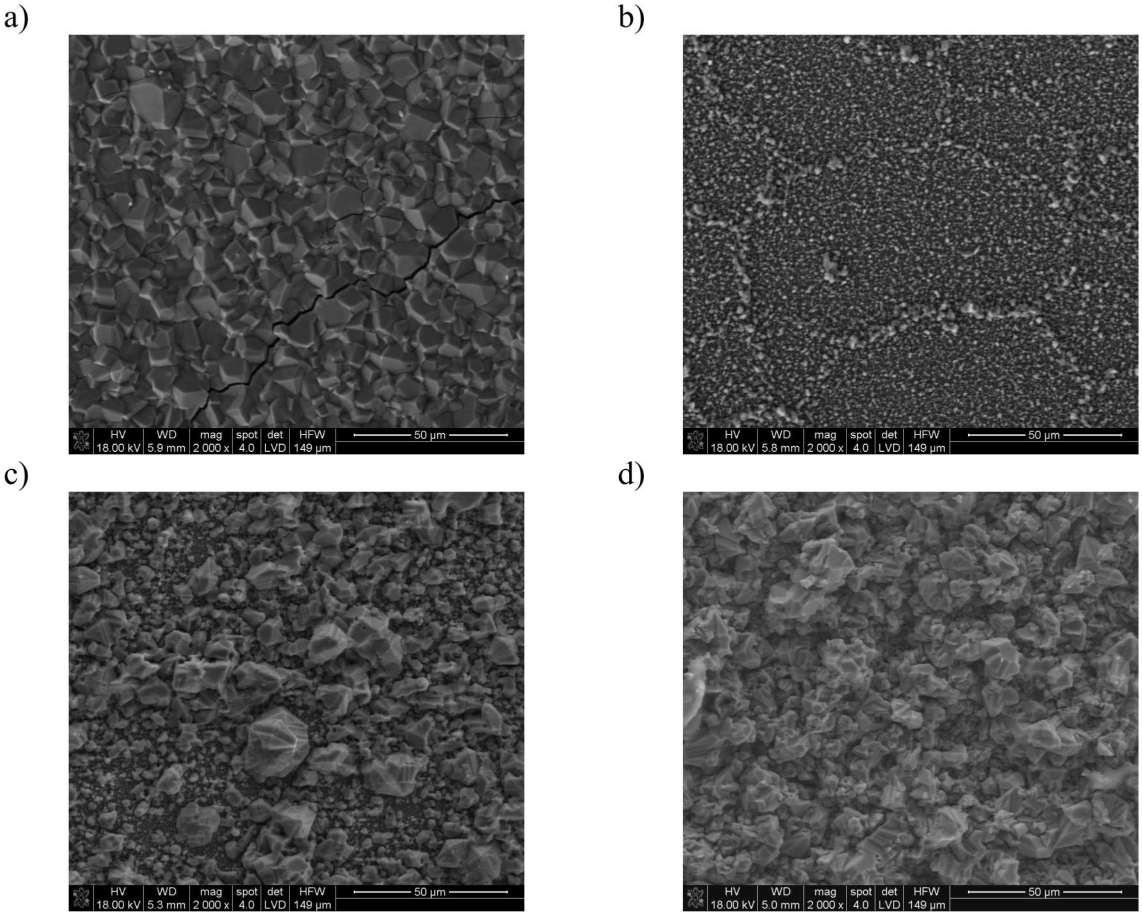

Fig. 3. Surface morphology in scale formed on non-preoxidated Crofer 22APU steel sulphurised in H_2/H_2S atmosphere: a) 600°C and $p_{S2}=10^{-7}$ Pa, b) 700°C and $p_{S2}=10^{-6}$ Pa, c) 800°C and $p_{S2}=10^{-5}$ Pa, d) 900°C and $p_{S2}=10^{-4}$ Pa

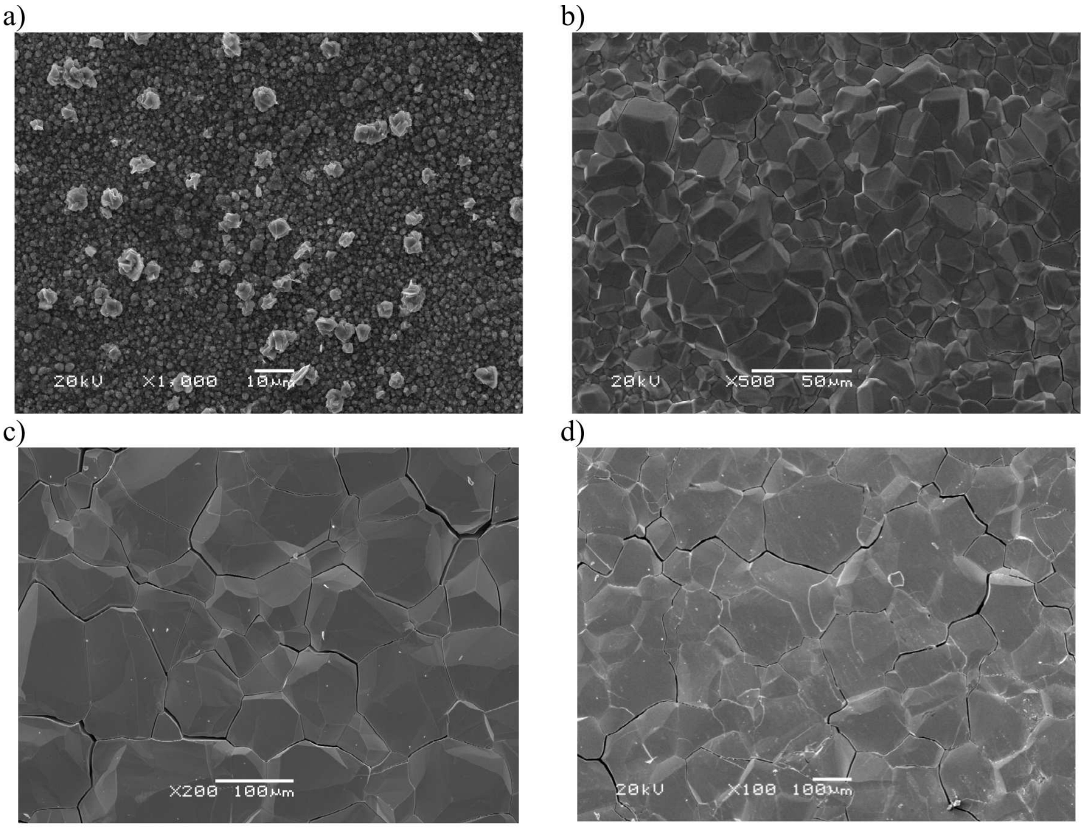

Fig. 4. Surface morphology in scale formed on preoxidated Crofer 22APU steel sulphurised in H_2/H_2S atmosphere at partial pressure of sulphur vapours 10^{-1} Pa and temperature: a) 600°C, b) 700°C, c) 800°C, d) 900°C

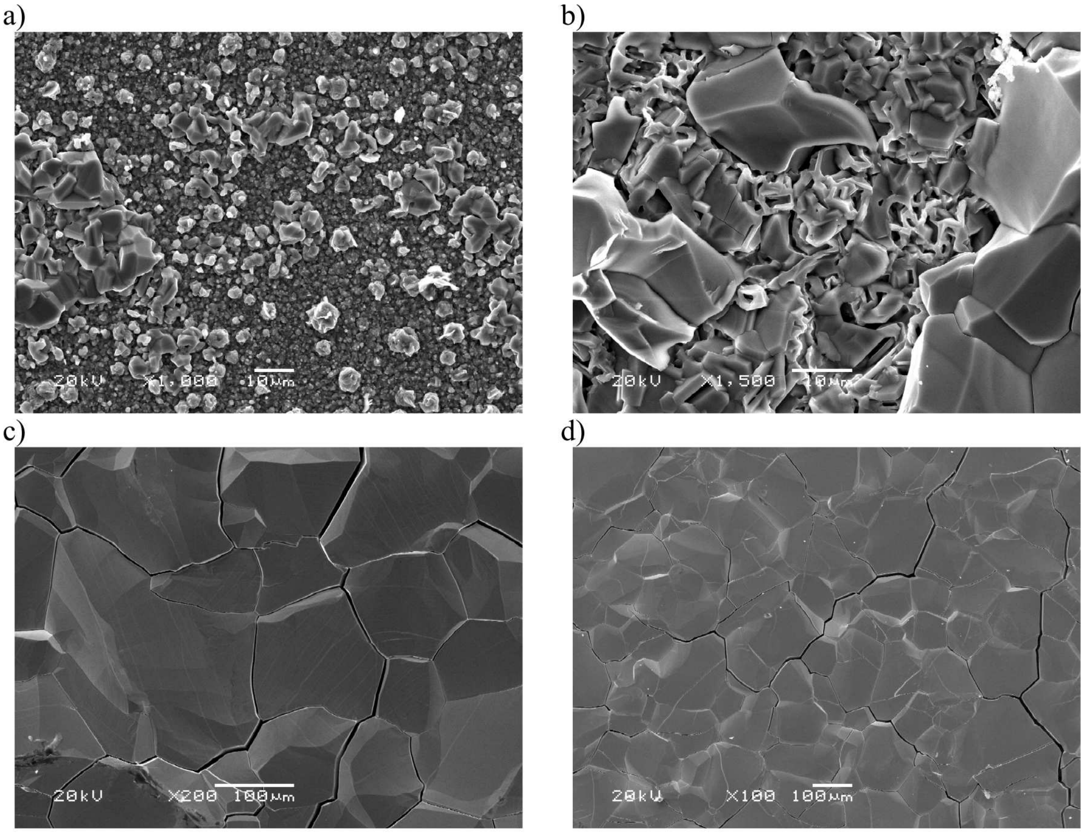

Fig. 5. Surface morphology in scale formed on preoxidated Crofer 22APU steel sulphurised in H_2/H_2S atmosphere at partial pressure of sulphur vapours 10^{-3} Pa and temperature: a) 600°C, b) 700°C, c) 800°C, d) 900°C

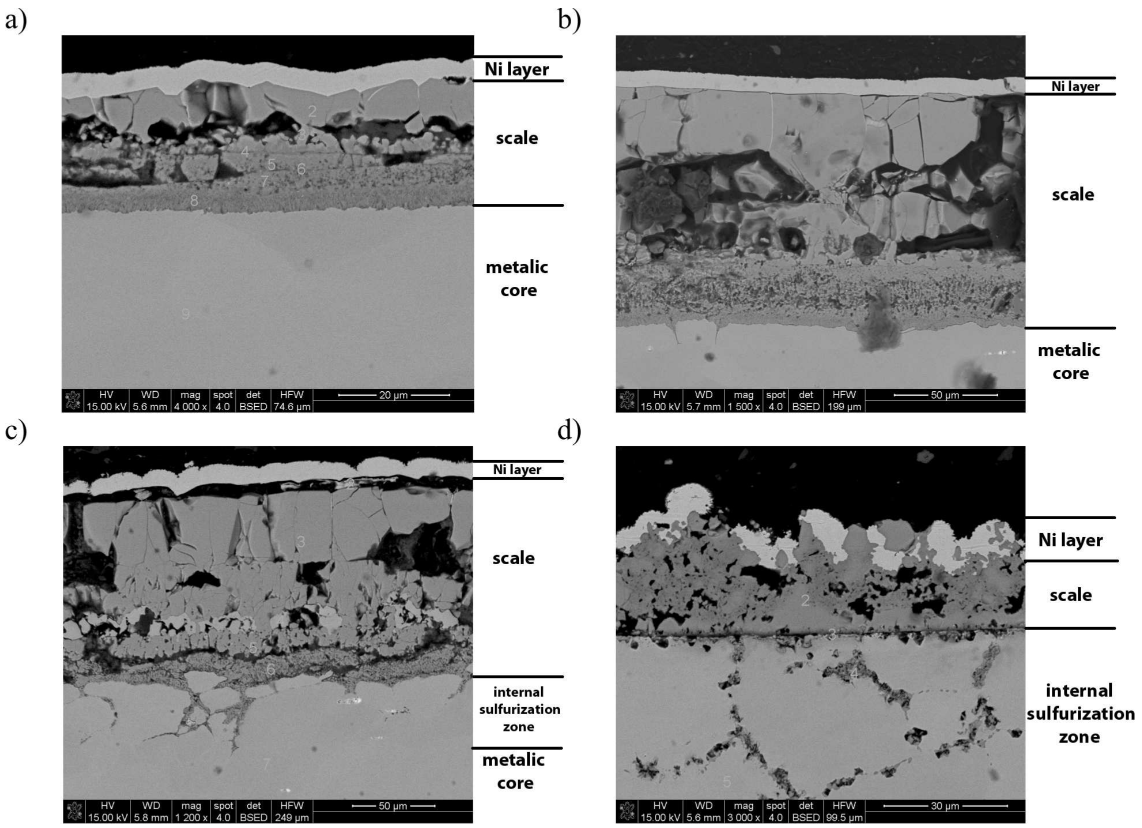

Fig. 6. SEM image showing fracture of Crofer 22APU steel sample sulphurised in H_2/H_2S atmosphere at partial pressure of sulphur vapours 10^{-3} Pa and temperature: a) 600°C, b) 700°C, c) 800°C, d) 900°C

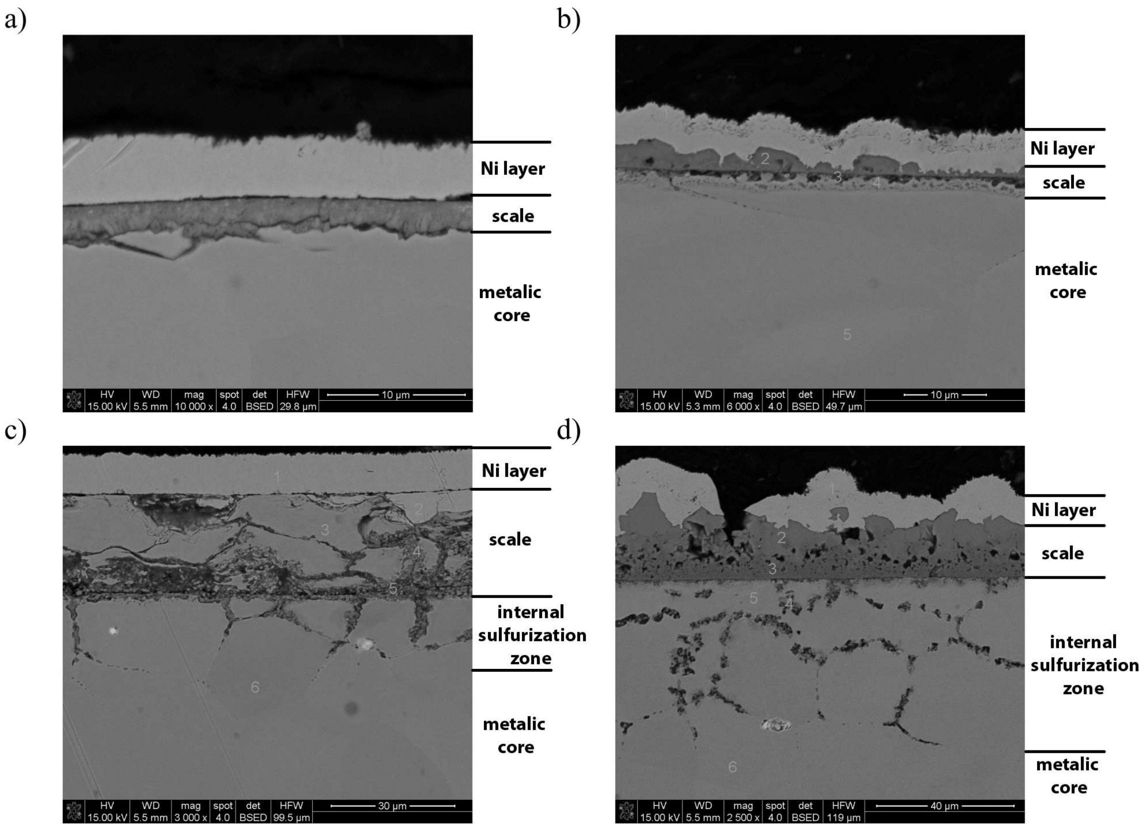

Fig. 7. SEM image showing fracture of Crofer22APU steel sample sulphurised in H_2/H_2S atmosphere: a) 600°C and $p_{S2} = 10^{-7}$ Pa, b) 700°C and $p_{S2} = 10^{-6}$ Pa, c) 800°C and $p_{S2} = 10^{-5}$ Pa, d) 900°C and $p_{S2} = 10^{-4}$ Pa

Figures 6-7 show microsections of non-preoxidated samples sulphurised within temperature range 600°C to 900°C in H_2/H_2S atmosphere at partial pressure of sulphur vapours 10^{-3}Pa (the samples with scale was covered by nickel layer). Two-layer scale forms on non-preoxidated samples in the examined atmosphere at the temperatures of 600, 700 and 800°C (Fig. 6a-6c). Outer layer consists of large column-shaped crystals, and inner layer constitutes a mixture of fine-grained sulphides. Constitution analysis has proven that the external, compact layer consists primarily of iron sulphide, and the internal layer – of a mixture containing chromium sulphides (Cr_6S_7), iron sulphides (FeS) and probably sulphospinels ($MnFe_2S$, $FeCr_2S_4$) or mixed sulphides (Fe,Cr)S (Table 1). At the temperature of 600 and 700°C the researchers did not observe any zone of internal sulphuring in metallic core subsurface layer, which was found at 800°C. Visible voids (holes) in scale are the result of microsection preparation, because scale is fragile. One-layer porous scale consisting primarily of chromium sulphide (Cr_6S_7) forms at the temperature of 900°C (Fig. 6d). Internal oxidation zone running along grain boundaries is visible in metallic core subsurface layer. Internal sulfurization zone occurs only at 800 and 900°C and reaches up to ca. 45 μm deep into the metal.

Analysis of microsections for non-preoxidated samples sulphurised in atmosphere under low partial pressures of sulphur vapours (10^{-7} - 10^{-4} Pa) within temperature range 600-900°C has proven that scale has laminar structure (Fig. 7a-7d). Scale formed at the temperature of 600°C and partial pressure 10^{-7} Pa is approximately 5 μm thick. External layer consists primarily of iron sulphide, and very thin internal layer is built of chromium sulphide (Fig. 7a).

At the temperature of 700°C, 800°C and 900°C and sulphur vapour pressure 10^{-6} Pa, 10^{-5} Pa and 10^{-4} Pa, respectively, the scale has single layer and its constitution corresponds mainly to chromium sulphides and/or chromium sulphides enriched with iron and manganese $(Fe,Cr)_nS_m$, $(Mn,Cr)_nS_m$. In all cases the researchers observed internal oxidation zone running along grain boundaries. With increasing temperature the depth of this zone grows from 3 μm at the temperature of 700°C to 50 μm at 900°C (Fig. 7b and 7d).

4. Conclusions

Completed research allows to draw the following conclusions:

1. In case of non-preoxidated and preoxidated Crofer 22APU steel samples put through sulphurisation in H_2/H_2S atmosphere, formed scale structure and its chemical constitution depends on process conditions (temperature and pressure).
2. Scale formed on non-preoxidated samples at the temperatures of 600°C-900°C in atmosphere under partial pressure of sulphur vapours $p_{S2} = 10^{-1}$ Pa has two layers. External layer consists of large column-shaped grains of iron sulphides (Fe_nS_m), while internal, fine-grained layer is a mixture of chromium and iron sulphides, sulphospinels (Cr_xS_y) and sulphospinel ($FeCr_2S_4$).
3. At temperatures of 600°C-800°C in atmosphere under partial pressure of sulphur vapours $p_{S2} = 10^{-3}$ Pa, scale structure is practically the same as in case of sulphurisation under sulphur vapour pressure $p_{S2} = 10^{-1}$ Pa.
4. In case of sample sulphurisation in atmospheres under lowest sulphur vapour pressures, within temperature range 700-900°C, the surface is covered with scale consisting of chromium sulphides. At 600°C and partial pressure 10^{-7} Pa, scale has two layers and its external layer is built of iron sulphides.
5. Oxide layer formed during preoxidation process does not make protective barrier for Crofer 22APU steel to safeguard it against sulphurisation process. Iron, chromium and manganese sulphides form on the surface of oxide scale as a result of core diffusion of iron, chromium and manganese ions. Formation of these sulphides depends on process parameters (temperature and pressure of sulphur vapours).
6. Formation of internal sulphurisation zone was observed at higher temperature values. Chromium sulphide is the product of internal oxidation.

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