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MICROSTRUCTURE AND MECHANICAL PROPERTIES OF CROFER 22 APU FERRITIC STAINLESS STEEL

BADANIA MIKROSTRUKTURY I WŁAŚCIWOŚCI MECHANICZNYCH STALI FERRYTYCZNEJ CROFER 22 APU

The objective of this work was to expand the knowledge on mechanical properties of the oxidized Crofer 22 APU Ferritic Stainless Steel. To examine adhesion of oxide scale formed on steel the scratch test was performed. Scratch test as an appropriate method for qualitative evaluation of the film adhesion to substrate has been used in many studies. Scratch properties were investigated before and after oxidation at 800°C for 500 hours in laboratory air.

Keywords: SOFC, Crofer 22 APU, scratch test, high temperature oxidation

Celem niniejszej pracy było poszerzenie wiedzy o mechanicznych właściwościach ferrytycznej stali Crofer 22 APU po procesie wysokotemperaturowego utleniania. Pomiary właściwości mechanicznych utworzonej warstwy tlenkowej wykonano metodą zarysowania – *scratch testu*. Test zarysowania jast najpopularniejszą metodą badania wytrzymałości połączenia powłoki z podłożem. Badania prowadzono na materiale w stanie wyjściowym oraz po utlenianiu przez 500 godzin w temperaturze 800°C – typowych warunkach pracy ogniwa paliwowego typu SOFC.

1. Introduction

The key element responsible for the successful operation of a fuel cell is the interconnect. At present, metallic interconnectors are the most frequently applied type; they not only collect the electrical charge built up in the PEN (Positive – cathode/Electrolyte/Negative – anode) component and transfer it to an external receiver, but they also constitute a key support structure [1].

Metallic interconnect materials, that are usually based on heat-resistant ferritic steels (FSS), need to meet a number of requirements that are either technical or physicochemical in nature, such as: high electrical and negligible ionic conductivity, high thermal conductivity, chemical stability in both oxidizing and reducing environments, a value of thermal expansion coefficient (CTE) that matches to adjacent components, good mechanical properties, low cost and ease of production, resistance to wear and thermal shocks [2-4].

Taking into account the above requirements, ferritic stainless steels (FSS) are intensively studied as potential interconnect materials [4-7]. The ferritic steel with the trade name Crofer 22 APU was specifically designed as an interconnect material for SOFCs operating at temperatures above 800°C[4,5].

In working conditions of SOFC on the surface of interconnect from both cathodic (where air is an operating gas) and anodic (hydrogen/water vapour mixture) side, a scale, which consist of chromia and chromium manganese spinel, is formed. Formation of this passivation layer is extremely important for durability of the interconnect, since its role is to protect material from further corrosion. The knowledge on the adhesive behavior of the scale is of high importance, since it allows to determine the resistivity of the layer for spallation and to select optimal conditions for the SOFC operation.

The main goal of the present study is to evaluate the adherence of the oxide scale formed on the Crofer 22 APU ferritic stainless steel using scratch test technique [8-12].

2. Experimental

Crofer 22 APU ferritic stainless steel (ThyssenKrupp VDM GmBH, Germany) was used as a substrate material. The chemical composition of this steel is presented in Table 1.

TABLE 1

Chemical composition of Crofer 22 APU alloy (wt. %)

Element	Fe	Cr	Mn	Ti	Si	C	P	S	La
from datasheet	bal.	22.0-24.0	0.30-0.80	0.03-0.20	0-0.50	0-0.03	0-0.05	0-0.02	0.04-0.20
as received	76.819	22.0	0.50	0.08	0.50	0.005	0.016	0.02	0.06

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Samples with dimensions of about 20×10×0.9÷1 mm, were ground with 100 to 1200-grid SiC papers, then polished with an alumina slurry and finally ultrasonically cleaned in acetone.

To evaluate the mechanical adherence of the oxide scale formed on the Crofer 22 APU steel, the scratch test was carried out using a commercial CSM Micro Scratch Tester (MST). For the progressive linear type of measurement, the Rockwell diamond indenter with a 50 μm radius hemispherical tip was used. The instrument was equipped with an integrated optical microscope, an acoustic emission monitoring system to detect the crack formation and a device to measure the horizontal Frictional Force in the scratching direction that made it possible to obtain values of the friction coefficient. Figure 1 presents a schematic representation of this instrument and measurement.

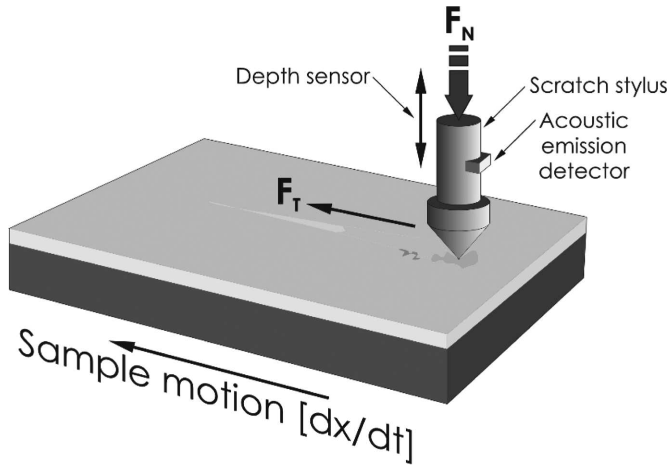

Fig. 1. Schematic of the scratch test method

The values of critical normal load, corresponding frictional force, coefficient of friction, and track width were measured. The tangential force, the penetration depth and the acoustic emission signals were recorded as secondary test data along with the normal force. After completion of the test, the scratch track was microscopically analyzed for specific, well-defined damage such as cracking, deformation, buckling, spallation, or delamination of the coating.

The scratch test was carried out on a sample after isothermal oxidation at 800°C for 500 hours in laboratory air atmosphere.

The phase composition of oxide scale formed on Crofer 22 APU steel after oxidation was analyzed by means of X-ray diffraction (XRD) using the PANalytical X'Pert Pro MPD diffractometer. Morphological observations were carried out via scanning electron microscopy (SEM) using a FEI Nova NanoSEM 200.

3. Results and discussion

3.1. Microstructure and morphology characterization

Observations of the non-etched raw steel revealed the presence of inclusions with a peculiar yellowish-orange or yellowish-gray hue. The size of these inclusions ranged from 12 to 15 μm. The analysis of chemical compositions of inclusions, combined with hardness tests of both inclusions and the matrix conducted during separated studies [13] revealed that the inclusions consisted mainly of titanium nitrades or, in some cases, of titanium carbonitrates.

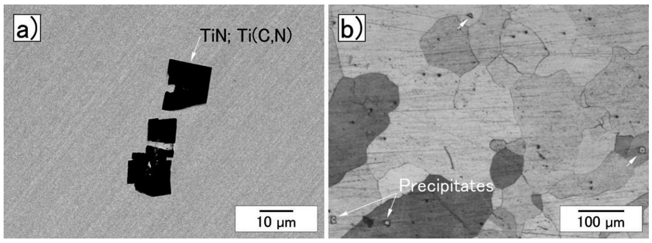

Fig. 2. Microphotographs of the raw Crofer 22 APU steel: a) BSE image, magnified 100×; b) optical microscope image of raw steel etched with Marble's reagent, magnified 20×

Figure 3 shows the X-ray diffraction patterns of the Crofer 22 APU steel oxidized in isothermal conditions in air at 800°C for 500 h. The scale formed on the surface of the Crofer 22 APU steel consisted of Cr_2O_3 and a $MnCr_2O_4$ spinel phase. These results are consistent with those reported in other papers [4,5].

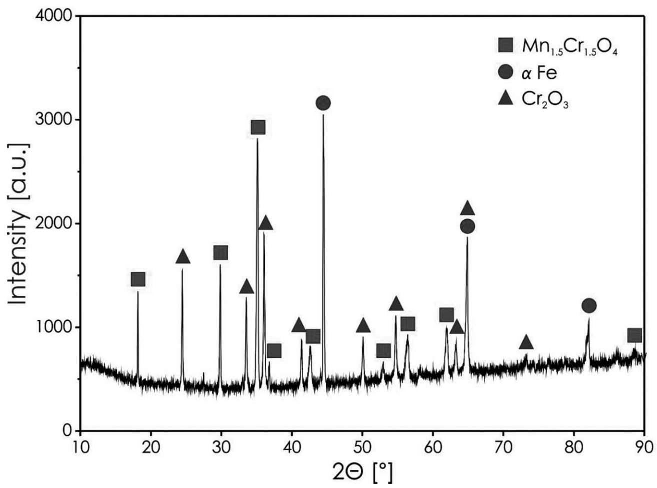

Fig. 3. X-ray diffraction patterns for Crofer 22 APU obtained after 500 h of isothermal oxidation in air at 800°C

3.2. Scratch test

The goal of dimensioning a scratch test is to get as much measurement information from the coating of interest as possible, so that a physical analysis of such tests can explain failure mechanisms of the intended applications – like mode-I fracture or mode-II fracture which are much closer to what happens in a contact situation from practice than a single load component indentation. In order to achieve this, the most relevant degrees of freedom of a scratch test, i.e. the indenter geometry and applied normal force, have to be determined [14].

A scratch tester has to measure a certain information for a physical analysis of a scratch test. Apart from the progressively loaded scratch itself, during which the normal load, the penetration depth under this load, and the lateral force are measured, the profile of the surface prior to the scratch has to be obtained [14]. Difficulties include complicated stress-strain field, different failure modes occurring at the same time, numerous intrinsic and extrinsic parameters. Therefore, the technique is usually regarded as semi quantitative [15].

The first acoustic emission peak observed and the variation of the frictional force provide complementary information for critical load measurements [15]. The multilayered structure of the oxide scale must be accurately known for a correct analysis of scratch-test results. Indeed, the layering of the oxide scale influences the values measured for the critical load [15].

The critical load depends on the combined effect of the oxide scale thickness and the oxide/scale adhesion. The parameters measured during the scratch test for the Crofer 22 APU steel are presented in Table 2.

TABLE 2

Parameters investigated during scratch measurements and results

Measurement parameters		
Scratch parameters	**Value**	
Begin load/Scanning load [mN]	500	
End load [mN]	15000	
Loading rate [mN/min]	14500	
Speed [mm/min]	5	
Results		
Parameter	**Critical Load [mN]**	**Distance [mm]**
L_{c1} (First critical load - it corresponds to the point at which first damage is observed)	2151.36	0.58
L_{c2} (Second critical load - the point at which the damage becomes continuous and complete delamination of the coating starts)	3672.05	1.10

The first critical load L_{c1} (referred also as crack initiation resistance) shown at Fig. 4a appear almost at the beginning of the scratch test. Shortly afterwards the second critical load L_{c2} (point at which the damage becomes continuous and complete delamination of the coating starts) has been sighted – Fig. 4b.

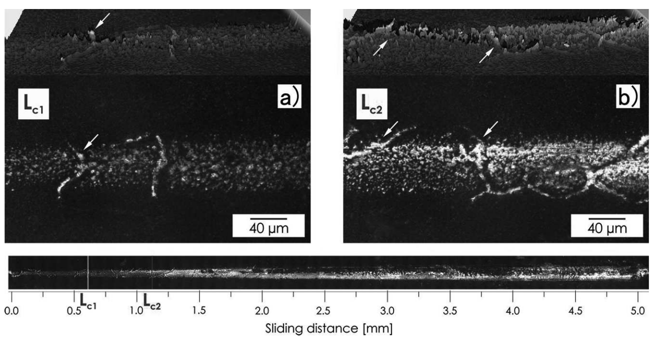

Fig. 4. Microphotographs of scratching track on Crofer 22 APU steel after isothermal oxidation: a) the first critical load L_{c1}; b) the second critical load L_{c2}

In this study, the values of L_{c1} and L_{c2} are relatively low indicating that the oxide scale formed on the Crofer 22 APU steel has a low adhesion and high fragility. This results show that the oxide scale is susceptible to spallation under mechanical stress.

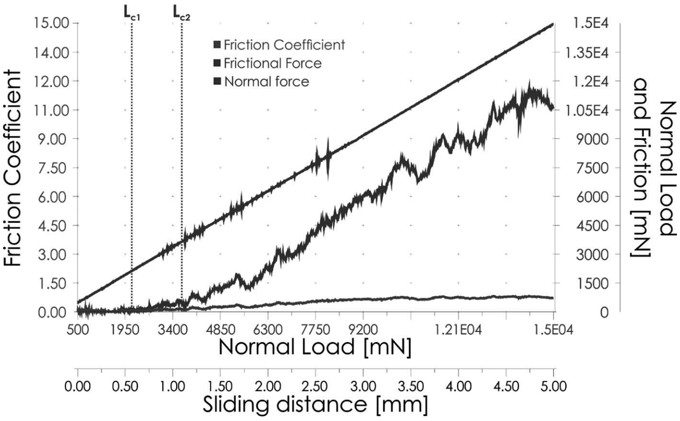

Fig. 5. Friction behaviour during scratch test against Crofer 22 APU stainless steel

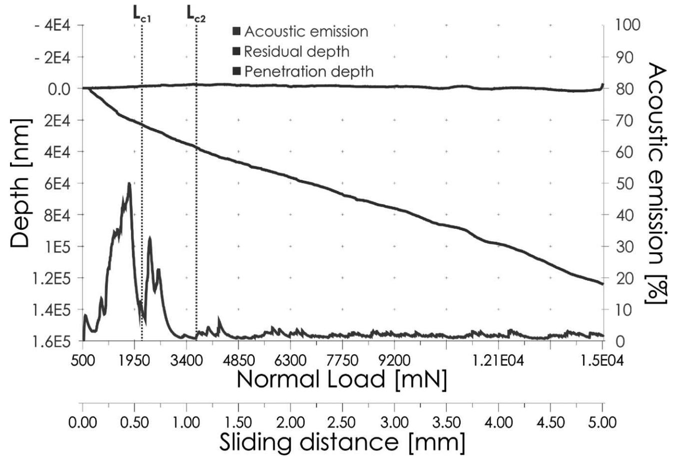

Fig. 6. Profiles of measured information along the scratch track together with an acoustic emission events with increasing load

It is important to point out that the studied case of the oxide scale adherence on a steel is more complex than that of a film deposited on a substrate. For a thermally grown oxide, it may be necessary to distinguish the effect of oxide scale thickness and the effect of oxidation duration on the adhesion behavior [15].

4. Summary

The scales formed on the Crofer 22 APU steel after isothermal oxidation consisted mainly of a Cr_2O_3 layer and a $MnCr_2O_4$ spinel in the form of a thin external layer.

Scratch measurement used as efficient technique to the evaluate adhesion of coatings to, revealed some very interesting data. In this study, values of first (L_{c1}) and second critical load (L_{c2}) were relatively low which indicate that oxide scale formed on Crofer 22 APU steel has a low adhesion and high fragility. This results show that the oxide scale is susceptible to spallation under mechanical stress. It is also worth to note that the received results are unique and would serve as benchmark data for further research.

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