

# Application of powder injection moulding and extrusion process to manufacturing of Ni-YSZ anodes

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## Manufacturing and processing

### ABSTRACT

**Purpose:** Investigation of the Ni-YSZ cermets for anode supported solid oxide fuel cells (SOFC) prepared by extrusion or powder injection moulding process, sintered and reduced of NiO-YSZ.

**Design/methodology/approach:** Density examination, shrinkage examination, transverse rupture strength tests, microstructure examination.

**Findings:** Results of the rheological and torque investigations have essential importance for further search of the optimum feedstock to injection moulding machines and extruders making forming possible of shapes for fuel cells anodes, which require in addition debinding of the binder, sintering, and reduction.

**Practical implications:** The proposed technological solutions for fabricating anodes as tubes or flat shapes will make connecting the cells into packets possible which will allow increasing the cell power.

**Originality/value:** The presented investigation results confirm purposefulness of employing injection moulding or extrusion for fabrication of fuel cells anodes. These two methods are used for manufacturing elements of devices in a mass scale. Significant interest in fuel cells and rapid development of their production which should take place in the close future may be the reason for searching the inexpensive technological solutions in the manufacturing process of the cells.

**Keywords:** Composites; Powder metallurgy; Sintering

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## 1. Introduction

During the fuel crisis nowadays particular attention is paid to fuel cells which convert the chemical energy of the fuel and

oxidant into the electrical energy. Fuel cells, as the electrochemical devices consist of anode and cathode, separated by the ion conducting material called electrolyte. An interesting concept is the electrolyte in a solid state, i.e., zirconium dioxide

stabilized with yttrium – YSZ. This pertains to the Solid Oxide Fuel Cells type – SOFC [1-3]. However, regardless of the electrolyte type, all fuel cells generate electrical energy without emitting any environment harmful chemical compounds. Moreover, fuel cells are characteristic of a high efficiency, compared to other energy sources, reaching as much as 80%, whereas, e.g., the photovoltaic cells reach the maximum efficiency of about a dozen or so percent only [4, 5]. Another advantage of these cells is their resistance to service conditions. Their main advantage is that they have no moving parts which results in their high reliability, low service costs and long life. They can operate almost intermittently with the continuous supply of fuel and oxidant, and the only noticeable limit is the anode resistance to damages developing during long time service. As an example we may mention the frequent flaw of the cermet anodes in which nickel and zirconium dioxide are used which is coagulation of nickel grains, being the effect of the high cell operating temperature, i.e., of about 1000°C, resulting in deterioration of the cell efficiency.

The disadvantages of the fuel cells are the low voltage obtained from a single cell (below 1V), expensive materials for catalyzers, and obtaining the relatively low power from a module. Therefore, the biggest application potential have the oxide fuel cells because of the possibility of connecting the single cells into stacks and shaping them into various forms (planar, tubular, monolithic), which yields the highest attainable power among all other cells. The main SOFC element is anode, whose function, apart from oxidation the hydrogen, is to carry the mechanical loads which occur in the whole cell. Anode features the cell skeleton supporting electrolyte and cathode.

Due to the rising interest in SOFC a high demand for them in future is expected, therefore, one should use the powder forming method applicable for mass production of such elements. Extrusion or powder injection moulding are the best solutions in this case. Both methods offer the possibility of fabricating tubes or plates which can be assembled into packets making increase of the SOFC power possible. However, the extrusion and powder injection moulding call for using a big amount of binder, especially when forming of the ceramic powder is needed. Wettability of the ceramic powder is usually lower compared to the metallic powder due to its shape. For extrusion or injection moulding metallic powder with the minimum surface area is used, i.e., spherical, atomised with gas [6-14]. The portion of such powder in materials fabricated by injection moulding reaches 70%. In case of the fine grained ceramic powder with the developed surface the portion of the binder is about 50-60%.

The goal of the research carried out was to select the type and portion of the binder making fabrication possible of the Ni-YSZ fuel cells anodes by extrusion and injection moulding of the NiO and YSZ powders, sintering and reduction of the nickelous oxide to the pure nickel form.

## 2. Material and research methodology

The YSZ and NiO powders were used for fabrication of the Ni-YSZ cermets being anodes of the fuel cells. The commercial cubic YSZ ceramic powder, containing 8 mol %  $Y_2O_3$  with an average particle size of 0.6 $\mu$ m and reported surface area of 7 m<sup>2</sup>/g, was

produced by Tosoh Corporation. Black NiO grade A, was produced by INCO. Both type of powder were in agglomerate state (Figure 1). Because of the cell efficiency the big surface area between three Ni-YSZ-H<sub>2</sub> phases (TPB -triple phase boundary) is an important factor, therefore, the powders grains should be as small as possible and should not create agglomerates or clusters. In order to break the agglomerate the powders were mixed with a high speed mixer in the liquid medium – methanol. In addition, the surface active agent was added to the bath in the form of the stearic acid (SA) featuring one of the binder constituents. Its goal is coating the ceramic particles with the thin layer of SA which improves wettability during mixing with the other binder elements, i.e., polypropylene and paraffin, and reduces viscosity of the injection moulding machine or extruder feedstock. Taking advantage of the previous investigations of the compacted, sintered, and reduced anodes in which the optimum volume portion of the NiO powder in respect to YSZ was 50%, the same proportions of the mixed powders were used for investigations of the mould injected and extruded materials [15]. The bath mixed for 30 min was put into the drier and soaked at temperature of 60°C to vaporize the methanol. Next the dry mixture of the NiO-YSZ powders coated with the layer of SA with polypropylene (PP) and paraffin (PW) in the form of granulate was poured into the Haake Rheocord Mixer 252p chamber making in addition torque-load measurement depending on feedstock viscosity and mixing time. Mixing of components was done using two blades at the temperature of 170°C at the speed of 40 rpm. Moreover the rheological characterisation of all type of feedstock were performed in a Rheoflizer capillary rheometer (ThermoHaake) at 170, 180 and 190°C over a range of shear rates from 10 to 10000 s<sup>-1</sup>. Portions of the particular components in five selected mixtures of powders with binder are presented in Table 1. Feedstock 1 was injected on the Arburg 220-s injection moulding machine to make the (63 x 12 x 3 mm) test pieces.

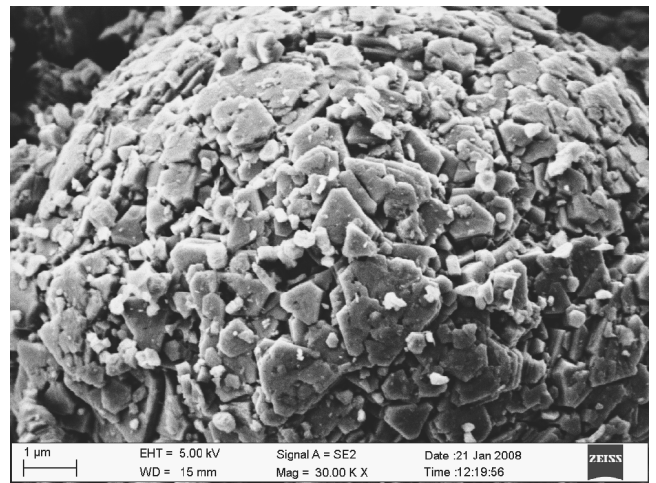


Fig. 1. Powder of NiO in agglomerated state

Test pieces of this shape are used most often for bending strength tests. Feedstock 2 was extruded in the form of tubes on the Haake Rheocord Mixer252p type extruder with a single screw and the die making vertical extrusion of tubes possible. Tubes' length did not exceed 0.5m as it was limited by the vertical extrusion setup, i.e., extruder height. This length was more than

enough for investigations. The injected and extruded test pieces are shown in Figure 2.

The debinding process of green samples was made by two different steps. First the injected and extruded samples were debound in a bath with the heptanol and next by thermal debinding. In order to remove all contents of PW and SA the solvent debinding was investigated at different temperatures and time.

Table 1.  
Proportions of investigated compositions

Designation	Components, % in vol.				
	NiO	YSZ	PP	PW	SA
50NiOYSZ_8SA	25	25	21	21	8
50NiOYSZ_6SA	25	25	22	22	6
50NiOYSZ_4SA	25	25	23	23	4
45NiOYSZ_8SA	22.5	22.5	23.5	23.5	8
55NiOYSZ_8SA	27.5	27.5	18.5	18.5	8

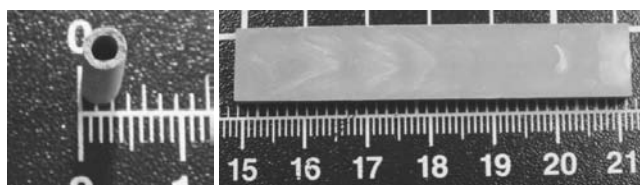


Fig. 2. Extruded and injected samples in green state

Next the thermal debinding in chamber furnace was made at 450°C under flowing air. The sintering process took place immediately after the debinding. Debound bars and tubes were sintered by heating from 1150 to 1450°C, with heating rate not higher than 3°C/min, and by soaking at these temperatures for one hour. The sintered samples were reduced in tubular furnace in a N<sub>2</sub>-10%H<sub>2</sub> atmosphere at 800°C. Structure of the developed materials were examined with SUPRA 25 scanning electron microscope (SEM) equipped with X-ray energy dispersive spectrometer (EDS). Moreover, the X-ray phase analysis of anodes was made in the sintered and reduced states to confirm that the entire NiO contents was reduced to pure nickel. These examinations were made on the PANalytical X'Pert PRO X-ray diffractometer, using the filtered X-ray Co K $\alpha$ , step 0.05, time of counting 10 sec. at the voltage of 40 kV and tube current of 30mA. The flexural strength of sintered and reduced samples was examined by three-point bending test. Density measurements were made using the Archimedes method basing on the product mass and the apparent loss of mass during immersion in water according to standard. Moreover, linear contraction of sintered and reduced samples was measured.

### 3. Results and discussion

Portion of the NiO powder was selected based on previous mechanical - and electrical properties tests of the compacted, sintered,

and reduced anodes at various temperatures in the atmosphere of the flowing N<sub>2</sub>-10%H<sub>2</sub> mixture of gases. The NiO powder portion selected in this way (50%) is connected with the compromise between the relatively high electrical conductivity growing with the NiO portion increase which gets reduced to pure Ni and bending strength growing with the increasing YSZ portion. It was found out based on torque-load characteristic tests and rheological investigations that the portion of the mixture of the NiO-YSZ powders to binder composed of SA, PW, and PP should not exceed 50%. Even coating the powder surface with the surface active agent like the stearic acid, being one of the binder constituents, does not allow to reduce its viscosity to the level making the feedstock injection moulding or extrusion possible. In Fig. 3 the torque-load characteristic is presented versus portion of the ceramic powder in the mixture and mixing time.

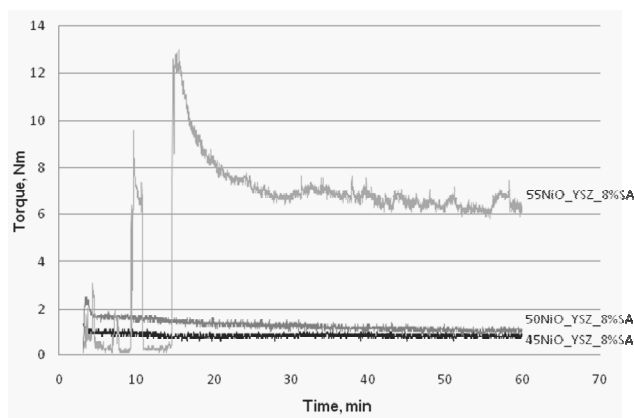


Fig. 3. Torque measurements of feedstock with 8% of SA versus amount of NiO and YSZ powder

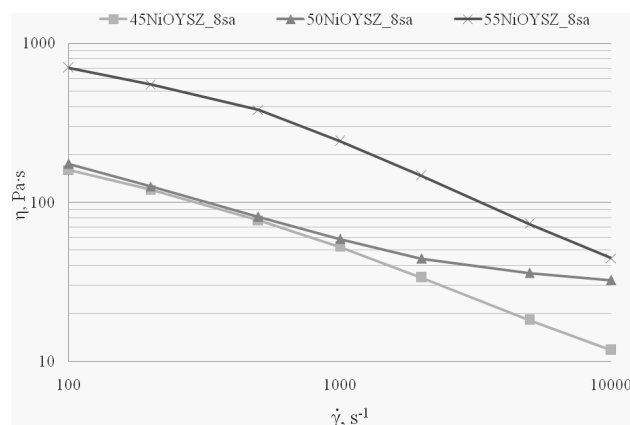


Fig. 4. Rheological behaviour of feedstocks with different amount of NiO and YSZ powder and 8% of SA at 170°C

In each case the ceramic powder was coated initially with the stearic acid amounting to 8% of the total feedstock volume portion. Increase of powder portion from 50% to 55% results in torque growth by 5 Nm. However, the torque-load characteristics for the mixture with the 45% and 50% powder portions are comparable and the curves have a linear character even after a short mixing time. The

mixture viscosity decreases along with the shearing rate increase regardless from the powder portion. Based on the torque-load characteristic and rheological investigations it was assumed that the powder portion towards the binder should be not higher than 50%. Moreover it was found out based on torque-load characteristic tests that application of stearic acid as a coating of ceramic powder powerfully decrease the torque. Torque test results versus SA portion are presented in Fig. 5.

Characteristic curve for the mixture with the 55% powder portion is irregular which attests to the feedstock inhomogeneity in spite of the relatively long mixing time. Long feedstock preparation time at the temperature of 170°C may lead to partial binder degradation, especially of PW and SA. Rheological investigations confirmed high viscosity of the mixture in which 55% of the ceramic powder was used, compared to other mixtures with a lower powder content. Fig. 4 presents viscosity curves depending on shearing rate and ceramic powder portion, while in each case the powder was coated with SA at 8% portion.

One can state based on the torque-load characteristic that about 15 minutes is enough to prepare the homogeneous feedstock regardless of the SA portion.

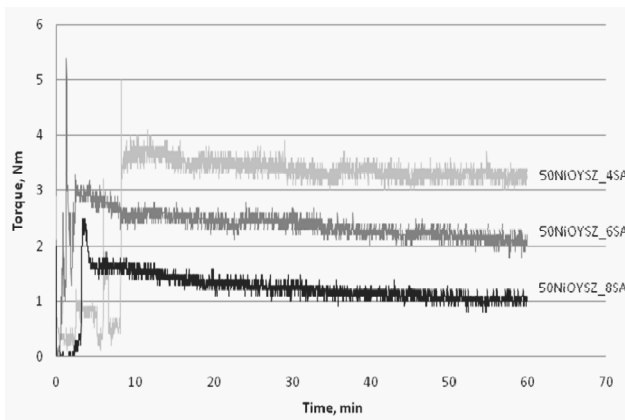


Fig. 5. Torque measurements of feedstock with 50% of NiO and YSZ versus SA amount

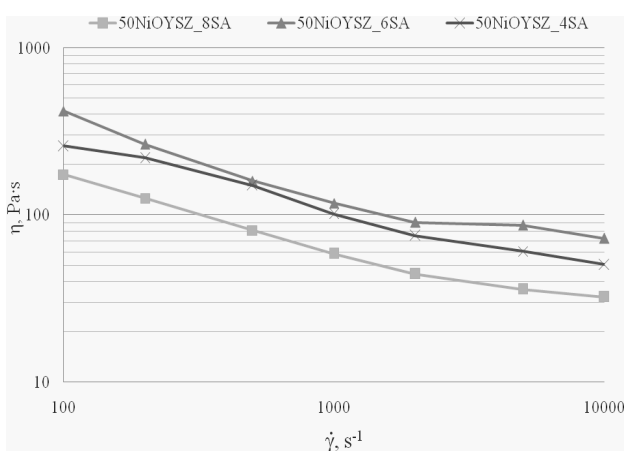


Fig. 6. Rheological behaviour of feedstocks with different amount of SA investigated at 170°C

Extending this time to one hour does not result in a significant reduction of the torque value, as the characteristic curve is close to linear in this range. Moreover, increase of the SA portion from 4% to 8% makes a significant torque value reduction possible from about 3.3 Nm to 1 Nm (Fig. 5). Rheological tests presented in Fig. 6 confirm the effect of SA growth on viscosity decrease. Increase of SA portion decreases the feedstock viscosity regardless of the shear rate. Moreover, regardless of the SA portion increase of the shear rate reduces the feedstock viscosity in each case. Increase of the test temperature affects viscosity reduction in a similar way, which is presented in Figure 7. Further, injection moulding and extrusion were made of the feedstock with the 6% SA portion designated as 50NiOYSZ\_6SA in Table 1. Because of the big difficulties in injection moulding of flat test pieces from this feedstock, the feedstock with a lower viscosity was used, i.e., 50NiOYSZ\_8SA.

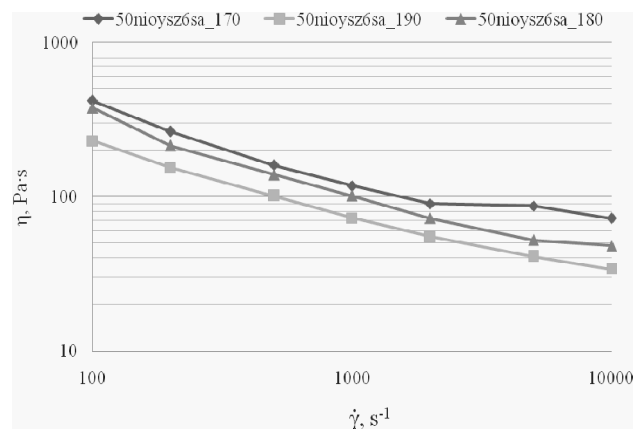


Fig. 7. Rheological behaviour of feedstocks 50NiOYSZ\_6SA investigated at different temperature

Extrusion of tubes based on the 50NiOYSZ\_6SA feedstock was not problematic. The extruded and injection moulded test pieces were presented above in Fig.2. Next, solvent debinding in heptanol at different temperatures was carried out. Figs. 8a and 8b show the paraffin dissolving rate depending on the test piece shape and solvent temperature. Because of the considerable surface of the thin-walled extruded tubes the nearly complete dissolution of paraffin in heptanol heated to the temperature of 60°C takes place already after about 15 minutes. Fig. 8b present the effect of temperature on binder removal rate one can notice that after about 3h of dissolving the volume portion of the dissolved binder is above 5% and is comparable. Basing on the fact that one may infer that the solvent debinding may be done without the need to heat the solvent up, especially when the solvent used often is flammable. Therefore, thermal debinding carried out at the ambient temperature rules using the drier out, makes electrical energy cost saving possible, and reduces the solvent ignition risk. Next, the test pieces were thermally debound, sintered, and NiO was reduced to pure Ni form. Test pieces after thermal debinding did not reveal cracks or gas cavities on surface, which attests to the correctly selected debinding parameters. Excessively fast thermal debinding process leads often to development of cavities and cracks on the test piece surface.

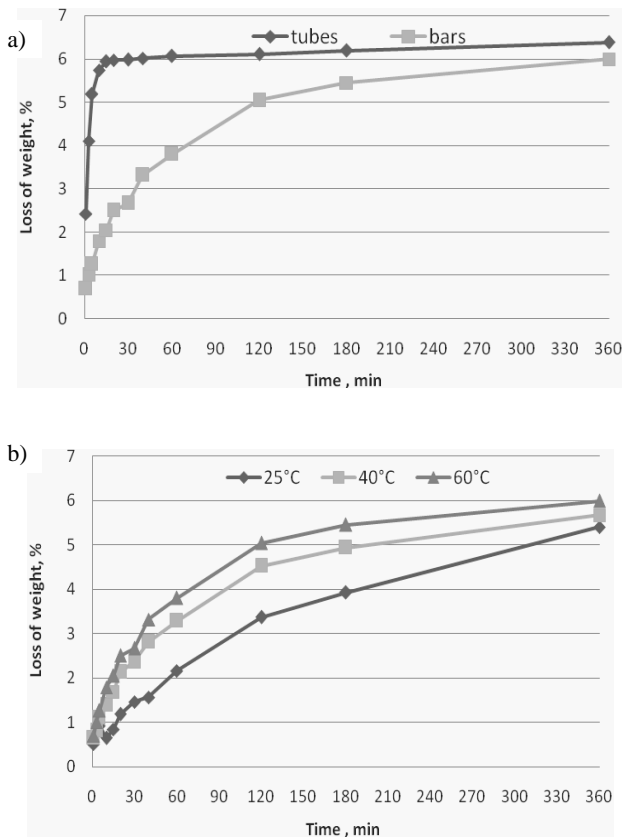


Fig. 8. a) Influence of solvent debinding time on loss weight of tubes and bars, b) influence of solvent debinding temperature and time on loss weight of bars

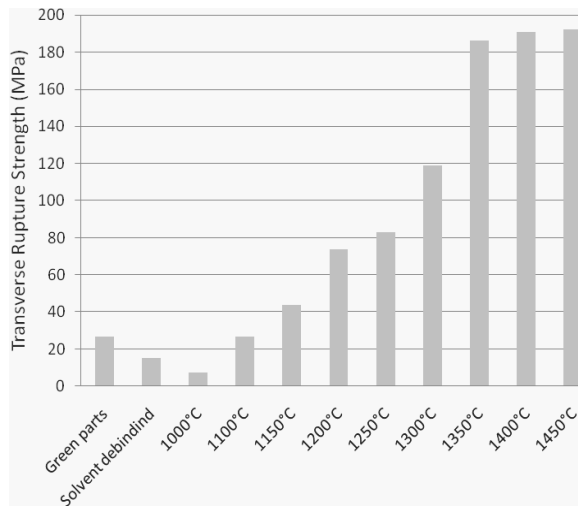


Fig. 9. Influence of sintering temperature of injected anodes on Transverse Rupture Strength

Testing results of the mechanical properties based on three-point bending in the sintered state and reduced state are presented in Figure 9. Based on the test results one can state that the NiO reduction process does not result in deterioration of the anodes mechanical properties. However, bending strength grows with the sintering temperature increase. Bending strength at the maximum temperature, i.e., of 1450°C, is about 100MPa and is double the strength of a test piece sintered at the temperature of 1150°C. To retain the relatively high mechanical properties the sintering temperature of anodes should not be lower than 1250°C.

Because of retaining of about 40% porosity of anodes indispensable for the fuel gas transport the sintering temperature cannot be too high. The effect of the sintering temperature on density and contraction is presented in Figure 10.

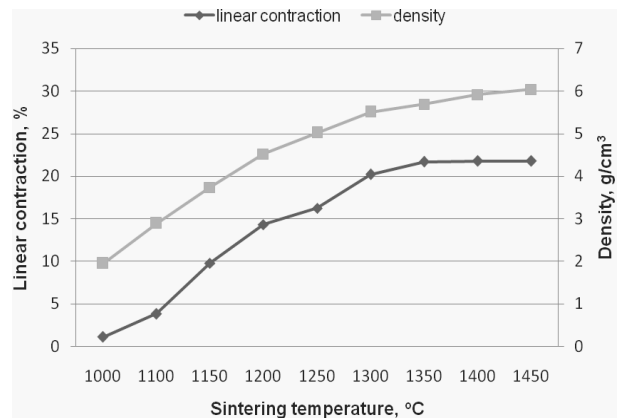


Fig. 10. The effect of the sintering temperature on density and contraction

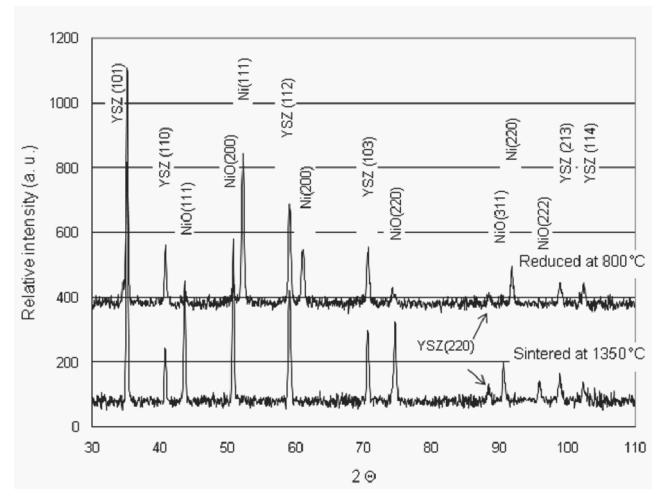


Fig. 11. XRD patterns of injected samples sintered at 1350°C and reduced at 800 °C

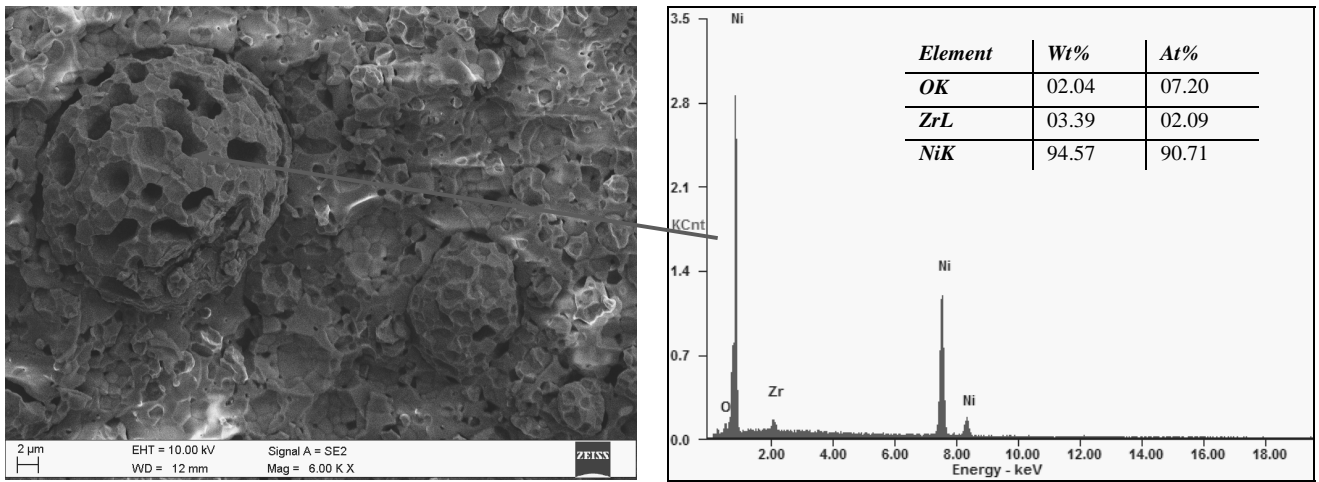


Fig. 12. The structure and EDS analysis of extruded tube sintered at 1350°C and reduced at 800°C

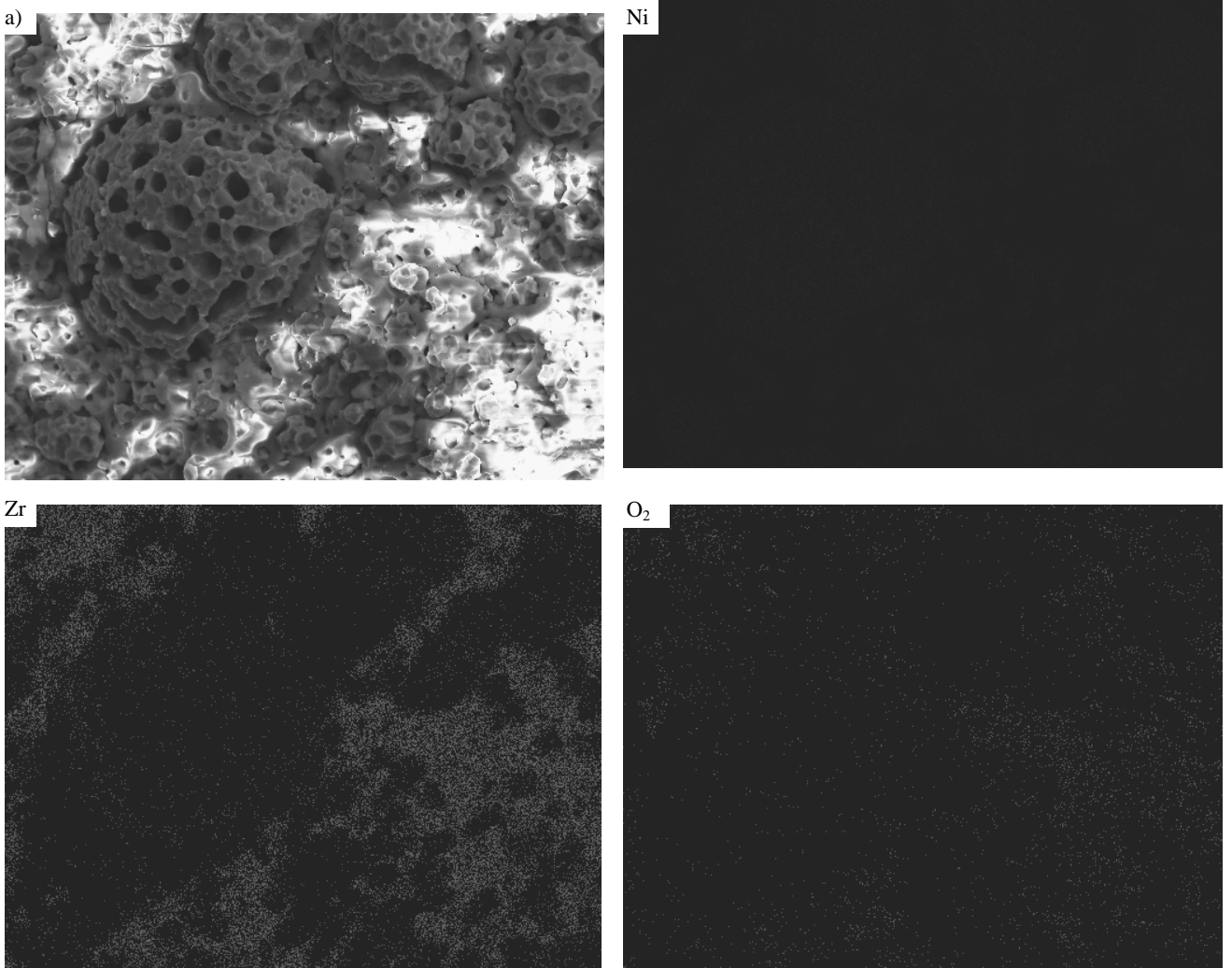


Fig. 13. The structure and distribution of Ni, Zr and O<sub>2</sub> in injected bars sintered at 1350°C and reduced at 800°C

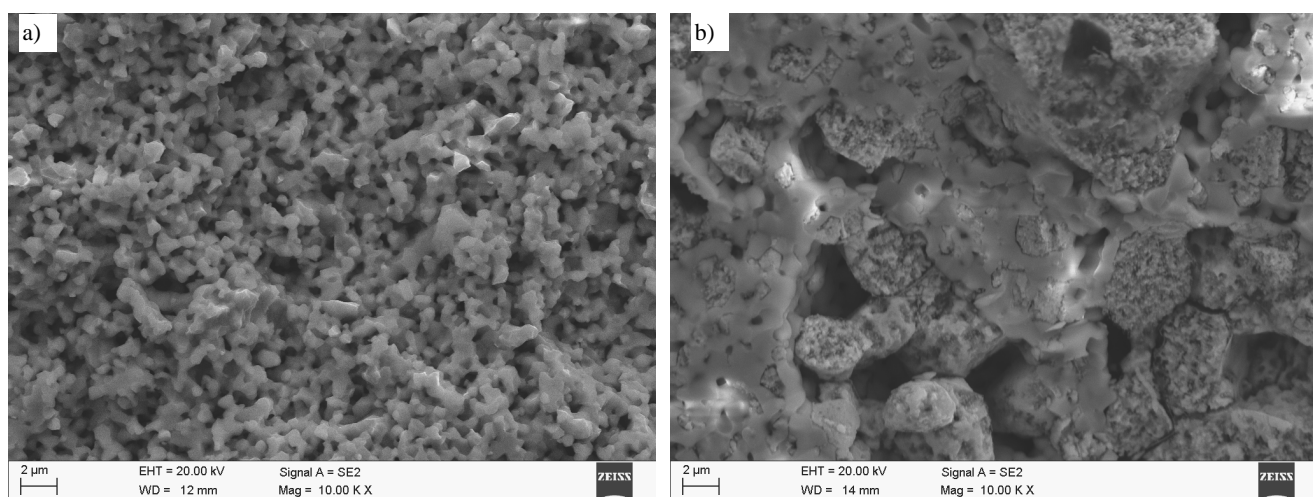


Fig. 14. The structure of anodes sintered at 1300°C and reduced at 800°C; a) NiO and YSZ powders were grinded b) NiO and YSZ powders were mixed

Basing on the fracture structure examinations of the sintered and reduced test pieces it was found out, that the essential factor is their reduction time. Lasting two hours process does not allow for the complete NiO reduction to Ni form in the entire volume of anodes. Extending the reduction time to 10 hours allowed NiO reduction in the entire volume of the injection moulded and extruded test pieces. The EDS analysis on the scanning microscope and the X-ray phase analysis did not reveal occurrences of NiO in the test pieces sintered and reduced for 10 hours (Figs.11-13). Moreover, the quantitative analysis of oxygen on the scanning microscope revealed that the volume portions of this element in the surface layer and inside of the test piece are comparable and are 12.8 and 12.6 respectively, which corresponds to oxygen content in the YSZ phase.

## 4. Conclusions

The presented investigation results confirm purposefulness of employing injection moulding or extrusion for fabrication of fuel cells anodes. These two methods are used for manufacturing elements of devices in a mass scale. Significant interest in fuel cells and rapid development of their production which should take place in the close future may be the reason for searching the inexpensive technological solutions in the manufacturing process of the cells. The consumer market will certainly be interested in cutting manufacturing costs of fuel cells, which instead of the classic heat and power plants will choose fuel cells - economically comparable yet more ecological. It seems that the proposed technological solutions for fabricating anodes as tubes or flat shapes will make connecting the cells into packets possible which will allow increasing the cell power.

Results of the rheological and torque investigations have essential importance for further search of the optimum feedstock to injection moulding machines and extruders making forming possible of shapes for fuel cells anodes, which require in addition debinding of the binder, sintering, and reduction. High viscosity

of the feedstock in which there are hard ceramic particles causes fast wear of screws, dies, heads, and cylinders of injection moulding machines and extruders, therefore binder portion increase is required. Moreover, a big amount of pores will develop due to binder degradation, needed for the fuel gas transport. On the other hand, due to the technologically difficult binder degradation process and big contraction after sintering the injection moulded or extruded elements one strives to minimise the binder portion retaining the relatively low feedstock viscosity. The extruded mixture viscosity may be higher compared to the injection moulded one; therefore, the feedstock was prepared separately for extruder and injection moulding machine, striving to reduce the binder portion to a maximum.

One may state based on bending strength tests and density examinations of the sintered and reduced anodes that the sintering temperature should not be lower than 1250°C. Lower sintering temperature deteriorates significantly mechanical properties of anodes which perform also the mechanical load carrying function for the whole fuel cell. Growth of the sintering temperature to about 1350 °C or 1450 °C increases the bending strength to value of about 5MPa; whereas, it significantly lowers the sinter porosity which may reduce flow of the fuel gas. Grinding of the NiO-YSZ powders mixture is planned in the forthcoming investigations because of the unpowdered NiO conglomerates which can be observed in the sintered and reduced test pieces. The inhomogeneous structure in the form of local clusters of Ni grains may reduce the anode's electrical conductivity.

The quantitative analysis of oxygen in various areas on fracture of the test pieces sintered and reduced for 10 hours revealed that portions of O<sub>2</sub> are the same, which attests to the correctly conducted reduction of NiO in the entire volume of anodes.

Grinding if the NiO and YSZ powders is planned in the next investigations to break up completely agglomerates and testing of the electrical properties of the fabricated anodes. The first results and difference between grinding and mixing of powder mixture is presented in Figure 14. The samples are in sintering and reducing state.

## Acknowledgements

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