

Some reasons of the degradation of a fine-grained YSZ–NiO anode material during intense reduction and reoxidation



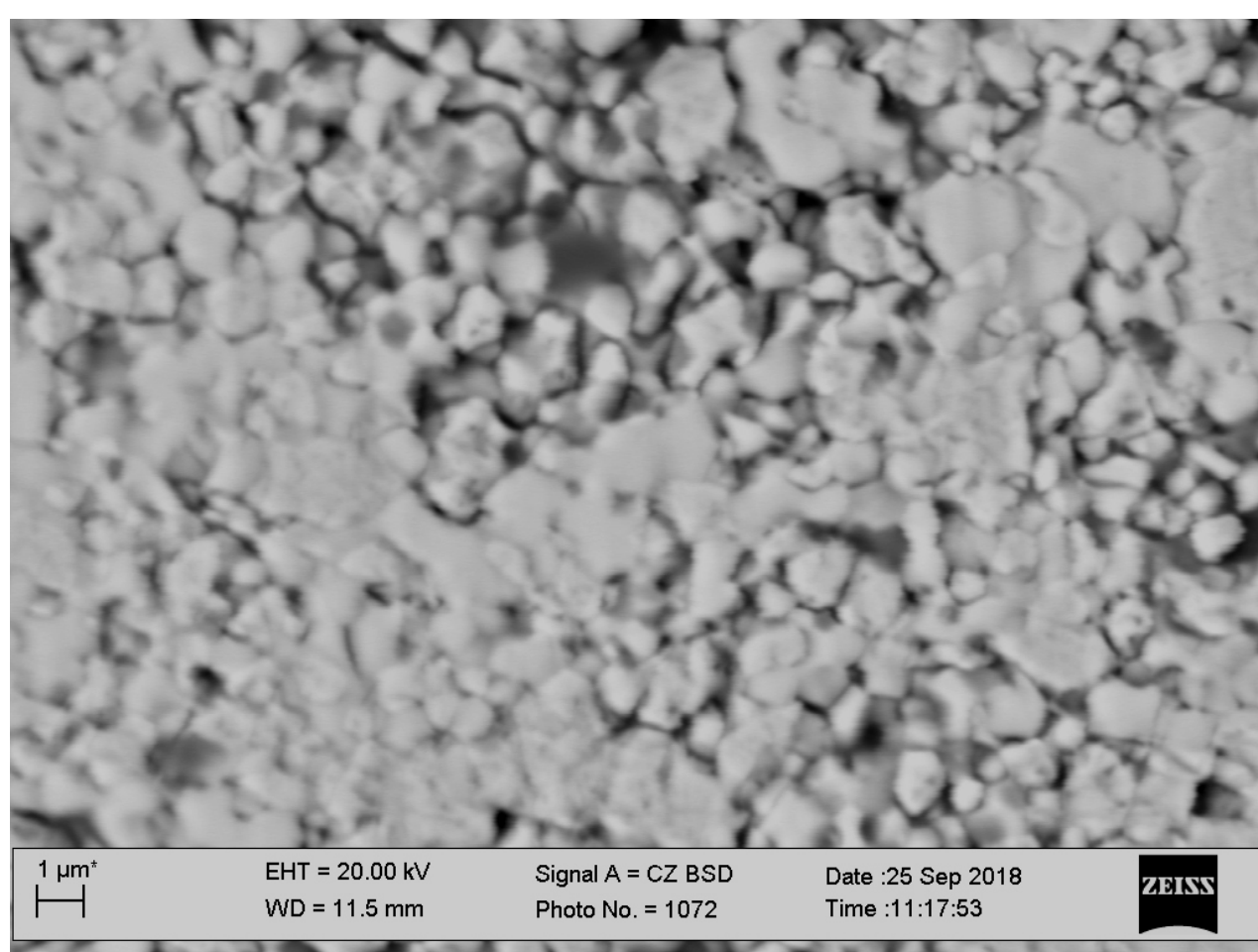
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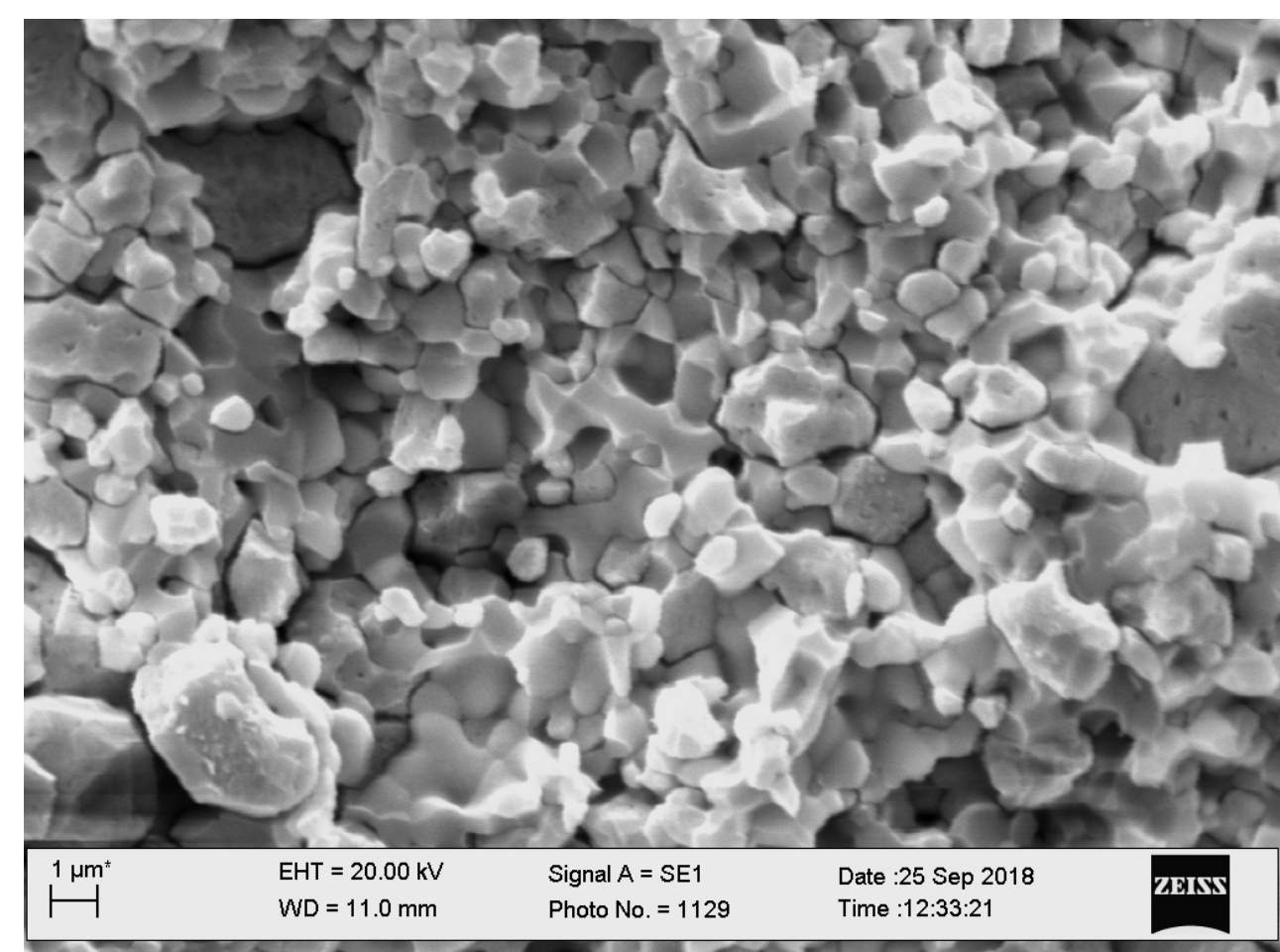
Purpose. This work is aimed at studying the high temperature reduction of nickel oxide and reoxidation of metallic nickel in a fine-grained YSZ–NiO anode material used widely for manufacturing electrodes for solid oxide fuel cells.

Methods. The YSZ–NiO anode-substrates were manufactured by tape casting. As-sintered material (of mode 1) was undergone to two treatment mode: single reduction in pure hydrogen for 4 h at 600 °C under a pressure 0.15 MPa (mode 2); reduction/oxidation (redox) for five cycles in hydrogen/air atmospheres at 600 °C (mode 3) [1].

Results. As-sintered material (mode 1) showed the strength under three-point bending in a range of 183 to 209 MPa what is high enough for anode materials. However, intense one-time reduction of NiO particles (mode 2) caused a drop of the material strength to a range of 38 to 40 MPa what did not satisfy the requirements to anode materials. In the structure of the specimen reduced in hydrogen, agglomerates of particles (average size about 5 μm) are observed along with small particles (1 μm). The regions with a predominance of small particles contain about 53 wt% Ni and 30 wt% Zr, and agglomerates are characterized by 60 wt% Zr, 30 wt% O, and only about 2 wt% Ni. The low energy-consuming intergranular fracture micromechanism prevails in the specimens tested.

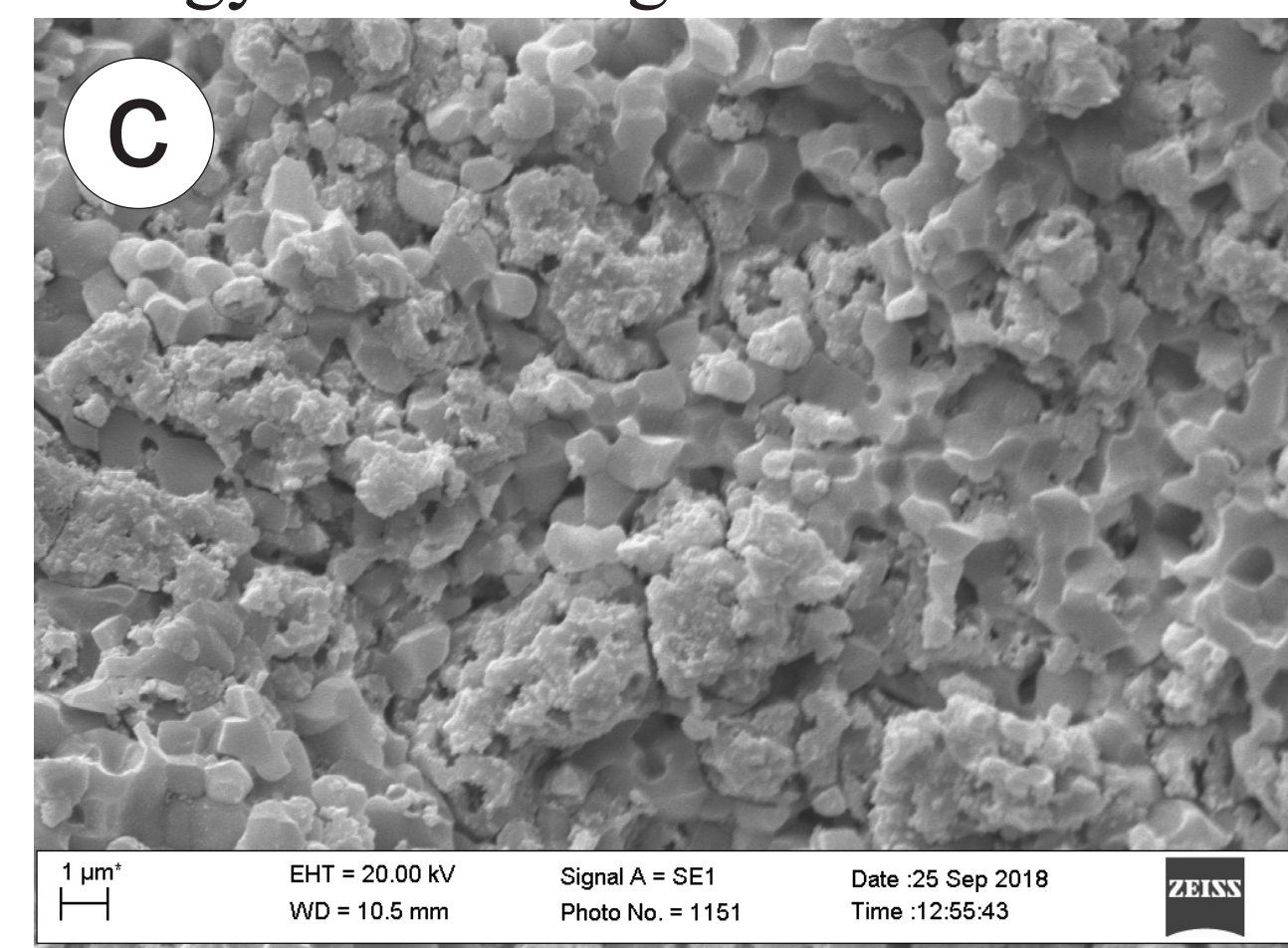
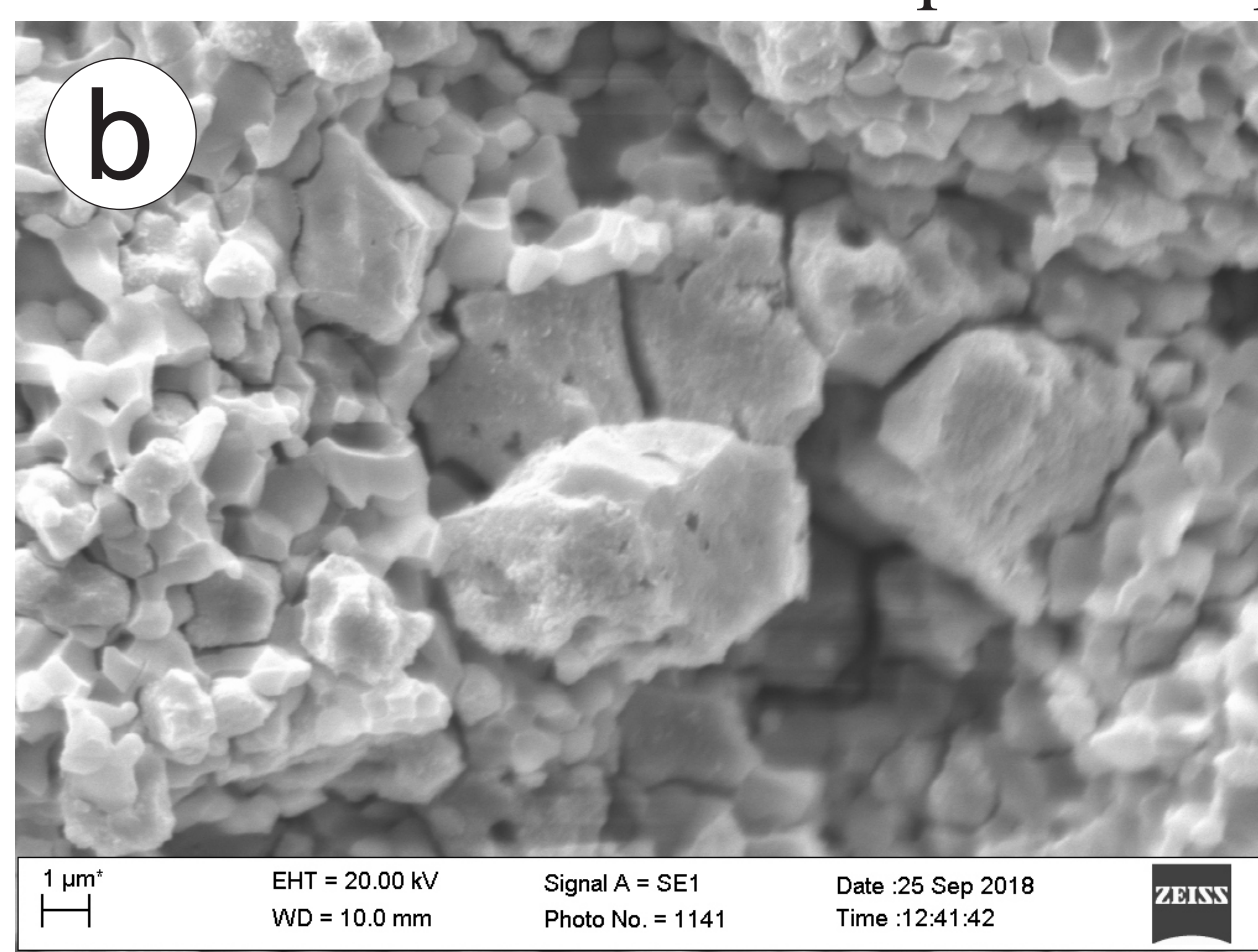
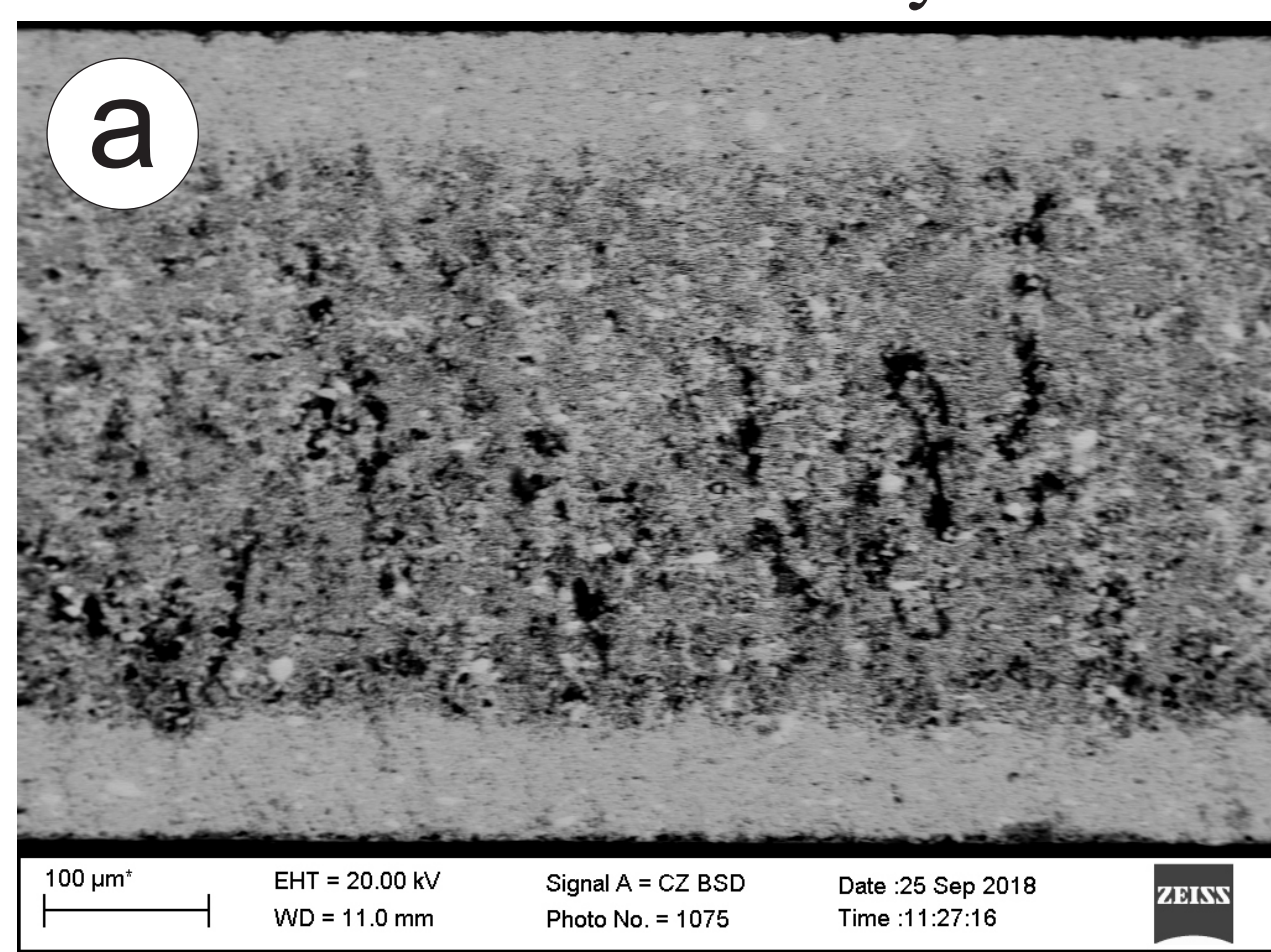


SEM microstructure of a singly-reduced specimen



Fracture surface of a singly-reduced specimen

On the fracture surface of the redox treated specimen, dense external (top and bottom) layers and a porous core of the specimen have been revealed. The increased concentration of nickel in the surface layer (64.74 wt.%) as compared to the singly reduced material (43.67 wt.%), is probably a consequence of diffusion of nickel from the subsurface region toward the surface, and the intensity of this process decreases significantly when approaching the middle of the specimen. The distinct intergranular fracture mechanism in the specimen core was noted. Thus, the redox treatment led to the degradation of the core of the specimen by forming large pores, their coalescence into cracks, and loss of material integrity. Coagulated spongy particles with an average size of 5–7 μm are occasionally detected in the structure of the surface layer, in contrast to the uniform distribution of the small nickel particles (0.5–3 μm). The mixed (trans- and partly intergranular) fracture mechanism in the surface layer of the specimen was noted that corresponds to quite energy-consuming fracture conditions.



Fracture surface of a redox-treated specimen: (a) general view; (b) core; (c) surface layer.

Conclusions. Despite too “rigid” mode of redox cycling in pure hydrogen and air at 600 °C, according to the level of strength (85 MPa) the cermet is not inferior to those obtained using other techniques. The obtained close values of electrical conductivity (of about $7.4 \cdot 10^5$ S/m), in addition to some positive tendency in strength, indicate the potential of the tape casted material in the case of the optimization of its treatment mode, in particular, reduction in Ar–H₂ gas mixture instead of pure hydrogen.

References.

[1] Vasyliv B.D. et al. A method of treatment of NiO-containing anodes for a solid oxide fuel cell. UA Patent 78992, April 10, 2013. [in Ukrainian].

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