

# OXIDATION RESISTANCE AND MICROHARDNESS OF NI-YSZ COMPOSITES, MANUFACTURED BY POWDER METALLURGY TECHNIQUE

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**Abstract.** The paper reports the investigation of corrosion resistance and microhardness of Ni - Y<sub>2</sub>O<sub>3</sub>-92ZrO<sub>2</sub> (YSZ) composites, manufactured by powder metallurgy technique and vacuum annealing at 1250 °C. The structure of the composites was investigated via SEM, XRD, and EDX analysis. Oxidation behavior was studied by thermal treatment in air ambiance. It was shown that the microstructure of nickel based composites predetermines mechanical and oxidation behavior of materials obtained. It was shown that a small YSZ addition of 2-5 wt.% enhances the oxidation resistance of nickel composites in 2-3 times, while the Vickers hardness (HV) remains practically unchanged. The addition of 10 to 20 wt.% of YSZ to nickel matrix leads to almost 8 times increase in the composite hardness.

## 1. INTRODUCTION.

Along with aluminum and copper, nickel is a part of a very important group of light metals widely used for various industrial applications [1-3]. Ni and its alloys possess high ductility, sufficient strength, and thermal stability. However, the significant disadvantage of pure Ni is its low corrosion and oxidation resistance at high temperatures. The fabrication of intermetallic alloys, like, e.g. NiAl or NiCr, is one of the common ways to enhance corrosion resistance and mechanical properties of nickel-based materials [4]. Such alloys possess high strength and viscosity (at least 7 MPa/m) coupled with relatively high oxidation resistance (about  $5 \cdot 10^{-14} \text{ g}^2\text{sm}^{-4}$ ) at 1000-1200 °C. A number of patents [5-7] describe NiAl based material fabrication by powder metal-

lurgy technique; the principal feature of these materials is their elevated mechanical properties at 1100-1200 °C. Nickel aluminide based alloy resistive to oxidation was suggested in [6]. It contains 12 atomic percent of chromium and tantalum in total and at least one element among Fe, Mo, W, Nb, and Hf. The alloy is heat resistant and has strength more than 90 MPa at 1000 °C. However, both the corrosion resistance, and long- and short term strength of the intermetallic alloys decrease considerably at higher working temperatures.

So far it is shown [8-11] that the design of novel nickel based materials with high oxidation resistance and elevated mechanical characteristics is possible via the inclusion of nanosized ceramic particles (oxides, borides, nitrides, carbides, etc.) into Ni matrix. In the recent years, great progress has

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**Table 1.** Physical and chemical characteristics of YSZ precursor.

Phase composition	Mean agglomerate size, nm	Crystallites size, nm	Specific area, $S_{sp}$ , m <sup>2</sup> /g
Zirconia based cubic solid solution	280	7	5

**Table 2.** The composition of Specimens obtained.

Specimen	1	2	3	4	5	6	7
Composition, wt. %	Ni	99Ni+1YSZ	98Ni+2YSZ	97Ni+3YSZ	95Ni+5YSZ	90Ni+10YSZ	80Ni+20YSZ

been achieved in the field of composite nickel-ceramic coatings development. "Ni-SiC" and "Ni-Al<sub>2</sub>O<sub>3</sub>" composite coatings possessing high corrosion resistance, improved mechanical and tribological properties were manufactured via wet chemical techniques in [10,11]. However, few data was reported for bulk nickel-ceramics composites. Papers [12,13] should be mentioned here, they describe the effect of Y<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Si<sub>3</sub>N<sub>4</sub> and SiC ceramic nanoparticles addition on the structural and mechanical properties of 17Cr12Ni2.5Mo2.3Si0.1C and Fe16Cr2Ni0.2C steel alloys. As it is mentioned in [13], a homogeneous dispersion of nanosized oxide particles in the metal matrix resulted in tailored properties in terms of strength.

Among the possible nanosized ceramic additives to Ni, cubic yttria stabilized zirconia powder (YSZ) is regarded as the most promising. Indeed, the elastic modulus of zirconia and nickel are almost the same (200 GPa), while the difference in their thermal expansion coefficients is less than 5% [14]. In the recent works of authors [15-17] the effect of YSZ nanopowder addition and initial nickel powder dispersity (micro- and nanopowder) on the microstructure and mechanical properties of nickel-based composites manufactured by powder metallurgy technique was investigated. It was shown that the use of powder metallurgy technique allows to achieve a homogeneous distribution of the ceramic component in the nickel matrix. It should be noted that the particle size of nickel powder does not change the mechanical properties of Ni-YSZ composites. The typical linear dimensions of YSZ inclusions were estimated as being 70 nm. In case of composites manufactured from microsized nickel, the maximum of compressive strength value was achieved at 3 wt.% of YSZ addition [16], while in case of nanosized Ni powder this amount was 5 wt.% of YSZ [15]. The

present work is the logical extinction of the research initiated in [15-17]. Thus, the goal of the work is the investigation of the microstructure, oxidation resistance and Vickers hardness of (100-x)Ni - xYSZ composites (x = 1, 2, 3, 5, 10, and 20 wt.%), manufactured by powder metallurgy technique.

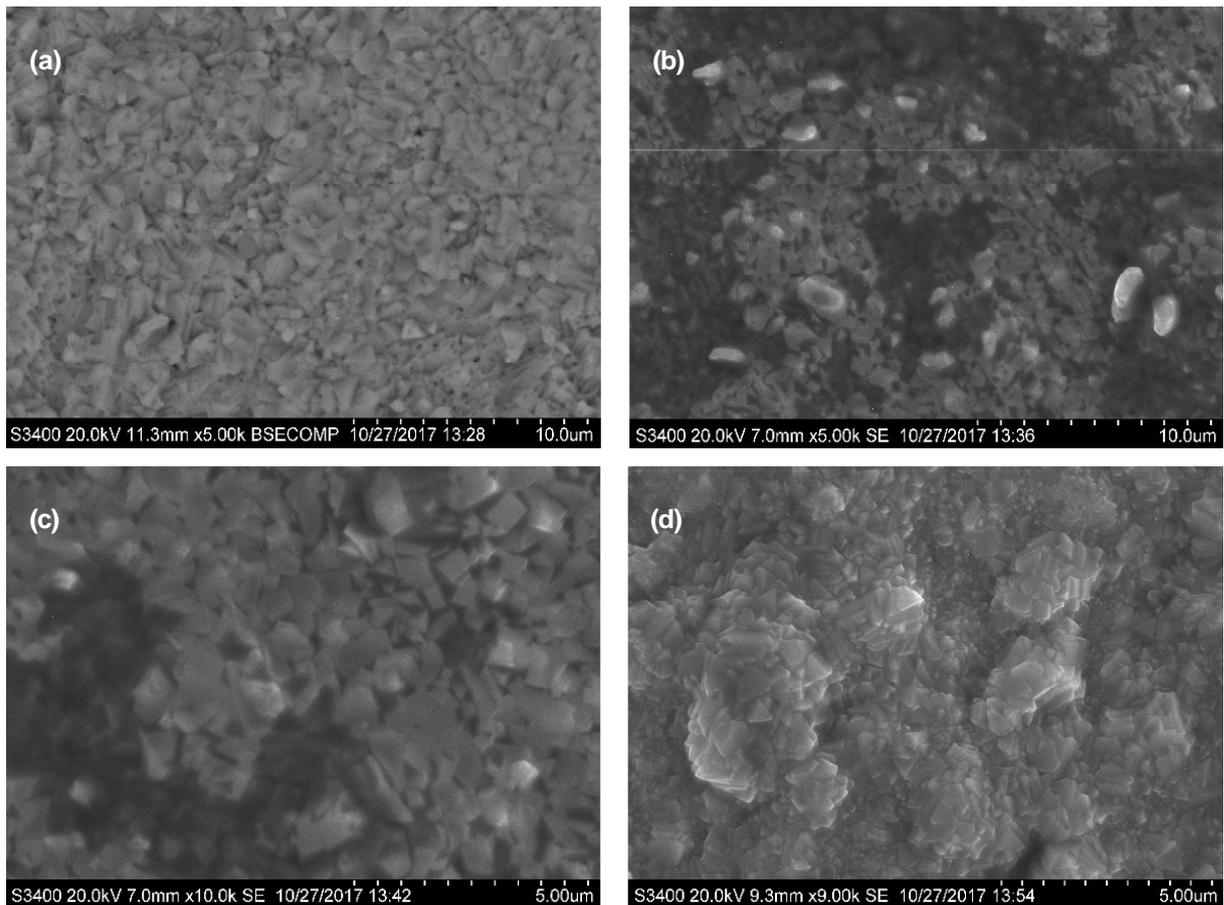
## 2. EXPERIMENTAL

### 2.1. Nanosized precursors synthesis

Nanosized yttria stabilized zirconia powders (8Y<sub>2</sub>O<sub>3</sub>-92ZrO<sub>2</sub>, mol.%, 8YSZ) were obtained by reversed co-precipitation technique, described in details in [18]. In order to prepare 0.1 M aqueous solution, commercially available hydrates ZrO(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Acros organics, Belgium, 99.5%) and Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Vekton ltd, Russia, 99% a.c.s.) were used. 1 M ammonia aqueous solution was taken as a precipitant. Mixed salt solution was added to NH<sub>4</sub>OH by drops with a rate of ~ 2 ml/min. The precipitation has been performed at ~1-2 °C in an ice bath at the constant stirring; pH of the solution was kept at ~9-10 during the synthesis by means of ammonium solution addition. To remove reaction byproducts, the obtained gel was filtered and rinsed until the neutral pH was reached. Then the gel was dehydrated via freeze-drying (Labconco, 1l chamber, 0.018 Torr, 20 °C, 24 hours). Powders were then calcined at 700 °C and mechanically activated in a planetary mill. Physical and chemical characteristics of nanosized YSZ precursor are listed in Table 1.

### 2.2. Composites manufacturing

Commercial fine-grained nickel powder was preliminary sieved, see [16] for details and mixed with YSZ nanopowder in the defined proportions. The mixtures



**Fig. 1.** SEM data of Specimens: (a) - Ni, (b) - 2, 99Ni-1YSZ, (c) - 3, 98Ni-2YSZ, (d) - 6, 90Ni-10YSZ.

were milled in a planetary mill (Pulverisette 6, Fritsch) at 450 rpm for 6 hours. Mechanically activated powders were cold pressed into pellets of 30 mm in the diameter and 15 mm in height under the pressure of 15 tons/cm<sup>2</sup> at room temperature. As a result, tablet-like specimens were fabricated. Specimens were annealed at 1250 °C for 1 hour (heating rate 10 °C/min, cooling with the furnace ~ 6 hours down to 500 °C) in a vacuum furnace with the residual pressure less than 0.003 atm. Table 2 lists the compositions of Specimens obtained.

The obtained Specimens underwent step-by-step oxidation in air atmosphere at 800 °C for 24 hours and then at 900 °C for 24 hours.

### 2.3. Analysis

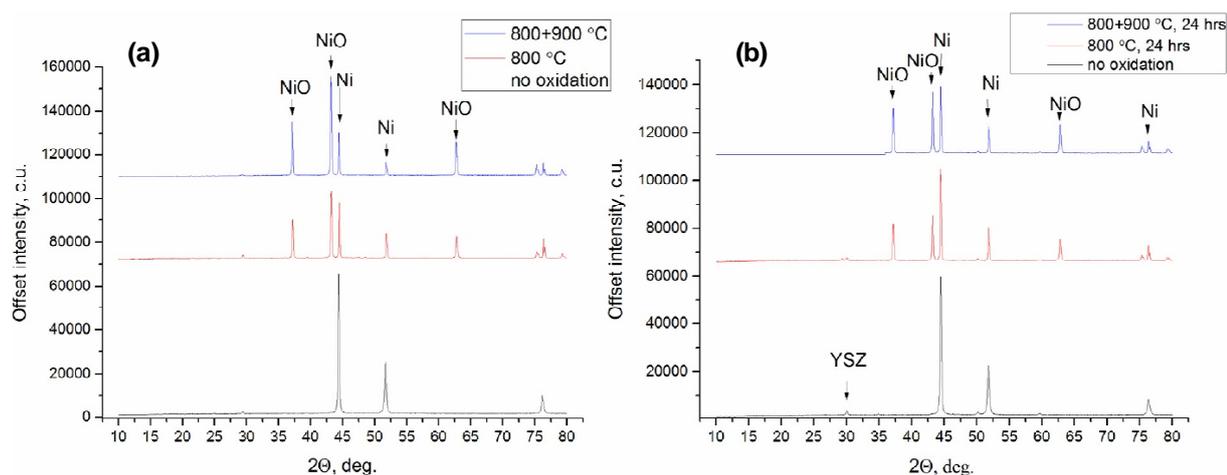
Phase composition of Specimens before and after oxidation was determined via X-Ray diffraction analysis (XRD, Shimadzu XRD-6000). X-ray diffraction experiment for the polycrystalline samples has been performed in air at room temperature using Cu K $\alpha$  radiation,  $\lambda = 1.54 \text{ \AA}$ . Microstructure of samples surface after the synthesis was investigated by scanning electron microscopy (SEM, Hitachi S-3400N

with the equipment for energy dispersive analysis, EDX). Vickers hardness (HV) was determined at the load of 0.5 kg applied for 15 seconds (Shimadzu HMV-G21). The data for each Specimen is averaged over 25 tests.

### 3. RESULTS AND DISCUSSION.

The microstructure of the nickel-YSZ composites was discussed in the recent work of authors [16]. The microstructure of oxidized Specimens 1, 2, and 6 is shown in Fig. 1.

As it is seen from Fig. 1a, homogeneous layer of the trigonal NiO is formed on the surface of pure nickel Specimen after oxidation at 900 °C. Another picture is observed in case of Specimen 2 with 1 wt.% of YSZ addition. Figs. 1b and 1c show the surface of Specimen 2 at the different magnification. Comparing Fig. 1a (pure Ni) with images for YSZ-containing Specimen 2, one can see that ceramics addition even at 1 wt.% level significantly increases oxidation resistivity. Nickel oxide layer formed on the surface of Specimen 2 is discontinuous. The growth of oxide layer is close to epitaxial, which is probably due to higher roughness and re-



**Fig. 2.** XRD patterns of Specimens (a) 2 99Ni-1YSZ and (b) 4, 97Ni-3YSZ before and after oxidation at different temperatures.

duced porosity of composite Specimen 2 comparing to Specimen 1 (nickel with no ceramic inclusions). Similar situation is observed for Specimens 3 and 4 with 2 and 3 wt.% addition of YSZ, respectively. The addition of 5 and more wt.% of YSZ results in highly rough surface of the composite, completely covered by the oxide layer (see Fig. 1d for Specimen 6). Higher surface area of composites is expected to decrease the oxidation resistance of composite Specimens with YSZ content higher than 3 wt.%. The assumption was confirmed by XRD analysis. XRD data for all Specimens before and after step oxidation were obtained. As an example, XRD patterns of Specimens 1 and 4 just after the synthesis and after high-temperature oxidation are shown in Fig. 2.

As it is seen from Fig. 2a, Specimen 1 after synthesis corresponds to single phase nickel. Thermal treatment at 800 °C in air for 24 hours results in fast nickel oxidation to nickel oxide. Indeed, much lower intensity of peaks, corresponding to nickel phase i.e.  $2\theta = 44, 52, 76^\circ$ , is observed in XRD pattern after oxidation. The peaks at  $2\theta = 37, 43, 63^\circ$  correspond to NiO phase. The estimated Ni to NiO ratio

is 35:65 (see Table 3). Additional annealing at 900 °C leads to the increase in peaks intensity of nickel oxide phase, the estimated amount of NiO in Specimen 1 is 81 wt.%. In contrast to pure nickel, Ni-YSZ composites show significantly higher oxidation resistance. The identification of 1 and 2 wt.% of YSZ is beyond of XRD identification limit. The peak corresponding to the second phase of cubic zirconia solid solution ( $2\theta = 29.5^\circ$ ) is observed for the first time in the XRD pattern of Specimen 4 (see Fig. 2b and Table 3). The addition of YSZ phase significantly enhances the oxidation resistance of the Ni-based material both at 800 and 900 °C. As one can see from Fig. 2b, the intensity of Ni peaks after oxidation in case composite with 3 wt.% YSZ addition is about 2 times higher than that detected for Specimen 1 (pure nickel). The amounts of nickel, YSZ, and nickel oxide after Specimens oxidation at different temperatures estimated from XRD analysis are presented in Tables 3 and 4.

As it is seen from Table 3, the lowest NiO amount after the oxidation at 800 °C is observed in case of Specimens 2, 3, and 6. In case of these Specimens the amount of nickel oxidized to NiO is ap-

**Table 3.** The amount of nickel, YSZ, and nickel oxide after Specimens oxidation at 800 °C for 24 hours.

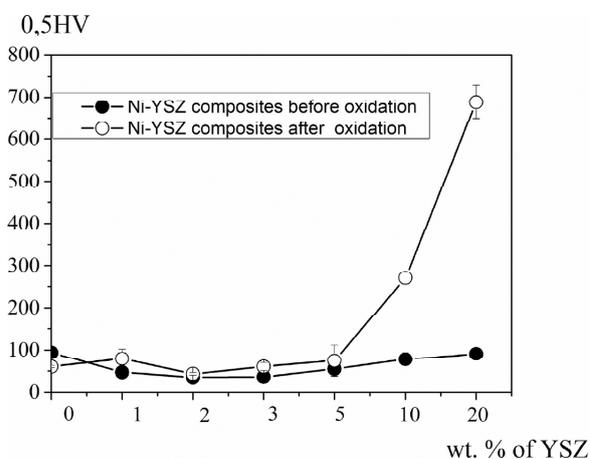
Specimen number	Composition, wt.%	Ni, wt.%	NiO, wt.%	YSZ, wt.%
1	Ni	35	65	-
2	99Ni+1YSZ	67	33	-
3	98Ni+2YSZ	67	33	-
4	97Ni+3YSZ	56	43	1
5	95Ni+5YSZ	61	36	3
6	90Ni+10YSZ	67	28	5
7	80Ni+20YSZ	36	52	12

**Table 4.** The amount of nickel, YSZ, and nickel oxide after Specimens oxidation at 800 and 900 °C for 24 hours.

Specimen number	Composition, wt. %	Ni, wt%	NiO, wt. %	YSZ, wt. %
1	Ni	19	81	-
2	99Ni+1YSZ	43	57	-
3	98Ni+2YSZ	51	48	1
4	97Ni+3YSZ	40	59	2
5	95Ni+5YSZ	40	57	3
6	90Ni+10YSZ	23	72	5
7	80Ni+20YSZ	-	87	13

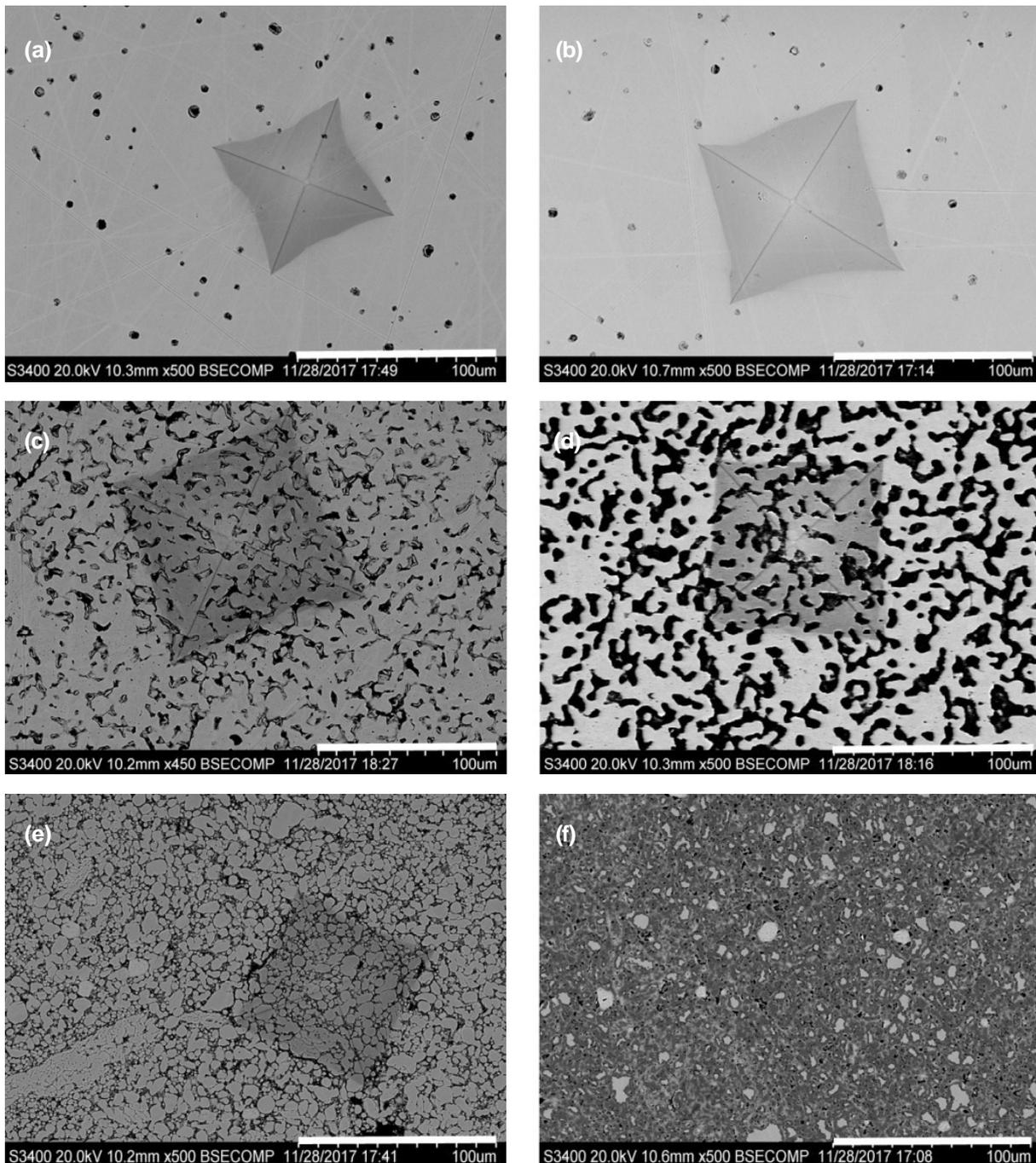
proximately two times less than comparing to pure nickel (Specimen 1). Additional treatment at 900 °C leads to the increase of NiO in all the Specimens. It should be noted that Specimen 7 with 20 wt.% of YSZ is fully oxidized. As it is seen from Table 4, only nickel oxide and yttria stabilized zirconia are present in that Specimen. Oxidation resistance of Specimen 6 with 10 wt.% of YSZ addition is close to Specimen 1 manufactured from pure nickel. The best results are obtained in case of nickel based composite with 2 wt.% of YSZ (Specimen 3), where oxidation resistance is almost 3 times higher than that of pure nickel. The observed difference in Specimens oxidation is most probably due to their microstructure features. The dependence of Specimens microhardness (HV) on the amount of YSZ addition before and after step-by-step oxidation is shown in Fig. 3.

As it is seen from Fig. 3, microhardness of pure nickel is rather low and is about 75 HV. Overall, microhardness value of specimens slightly changes upon YSZ addition. The minimum is observed for Specimen 3 with 2 wt.% YSZ content, being ~50 HV. The microhardness values of oxidized samples

**Fig. 3.** Microhardness of specimens before and after oxidation.

with low YSZ content (up to 5 wt.%) are rather similar to those for Specimens before oxidation. However, it significantly increases in case of oxidized composite with higher YSZ content. Microhardness value measured for Specimen 7 (20 wt.% YSZ) becomes ~700 HV. Note that the hardness of cubic stabilized zirconia is 1100-1400 HV [19]. In order to reveal the nature of the observed mechanical and oxidation behavior of nickel based composites, SEM and EDX data were obtained for all Specimens after indentation. Fig. 4 shows the surface of non-oxidized and oxidized Specimens 1, 4, and 6 after indentation.

Comparing Figs. 4a and 4b, one can see that polished surface of pure nickel before and after oxidation is characterized by slight open porosity. Oxidation takes place on all the surface of Specimen, including open pores. As a result, some pores in Specimen 1 are getting filled by NiO after oxidation. According to EDX data (see Table 5), indenter penetrates Ni phase in Specimen 1 before oxidation and mostly NiO phase after oxidation. The addition of 3 wt.% of YSZ (Specimen 4) leads to porosity increase and to the formation of the surface consisted of coarse grains divided by pores (see Fig. 4c and data of previous work [16] for details). Step-by-step thermal treatment results in microstructure rearrangement. Grain coarsening and pore size increase takes place along with Ni oxidation to NiO. This process, likely, prevents nickel based composite from fast oxidation. As it was observed via EDX analysis, the indenter penetrates Ni phase for Specimen 1 before oxidation and mostly NiO phase after its oxidation. In spite of some grains coarsening, the mechanism of indenter penetration in case of Specimens 2-5 with small YSZ content is considered being similar to the above discussed case of pure Ni sample. Upon the addition of 10 wt.% YSZ nanopowder, the microstructure of composite corresponds to rather small grains divided



**Fig. 4.** Left row: the surface of non-oxidized Specimens (a) – 1, Ni, (c) – 3, 98Ni-2YSZ, (e) – 6 90Ni-10YSZ; right row: the surface of oxidized Specimens (a) - 1, (c) - 4, (e) - 6. Scale bar corresponds to 100 μm.

by interconnected porous network. It should be noted that thermal treatment induces significant structural rearrangement and porosity reduction (see Fig. 4f). Magnified indentation zone of Specimen 6 is shown in Fig. 5.

As it is seen from Fig. 5, bright non-porous allocated zones appear in the composite structure. According to EDX data, presented in Table 5, they correspond to pure nickel phase. Bright porous and

light grey zones are YSZ with small admixture of non-oxidized nickel, whereas dark grey zones are mostly NiO with YSZ admixture. The indenter penetrates to the mix of YSZ and nickel. It is worth to note that a number of cracks are seen around the indentation zone in case of composite Specimen 6, indicating some increase of the brittleness of the material.

**Table 5.** EDX data on the element composition (wt.%) of Specimen 6 after oxidation.

Spectrum	Ni	O	Zr	Y	Hf
814	100	-	-	-	-
815	53.9	23.7	19.1	2.8	0.5
816	79.9	19.3	0.7	-	-
817	24.9	22.1	44.5	7.4	1.1
818	3.5	22.6	62.4	10	1.6

Summarizing the data obtained, one can see that powder metallurgy technique allows to produce composites with homogeneous distribution of ceramic phase, i.e. YSZ powder. Indeed, the peaks corresponding to YSZ phase appear in the XRD pattern of Specimen 4 with 3 wt.% YSZ content (see Table 3 and the data of [16]). Microstructure of the composites significantly varies with YSZ content and predetermines mechanical and oxidation behavior of materials obtained. Namely, the addition of 1-2 wt.% of YSZ reduces porosity and slightly enhances the roughness of composite comparing to pure nickel Specimen. Oxidation takes place simultaneously with grain coarsening and pore size redistribution. That, likely, results in discontinuous NiO layer on the surface of composite, i.e. reduced oxidation of Ni. Weight percentage of Ni, NiO and YSZ phases, evaluated from XRD patterns for all Specimens after step-by-step oxidation allows to conclude that oxidation resistance increased by 3 times in case of composite with 2 wt.% YSZ content comparing to pure nickel Specimen (see Table 4). As it is seen from Table 4, for nickel based composites containing 1, 3, and 5 wt.% of YSZ, that value increases in about 2 times. Oxidation of Ni-based composites with 10 wt.% YSZ content is comparable to the case of pure nickel Specimen; this is probably due to

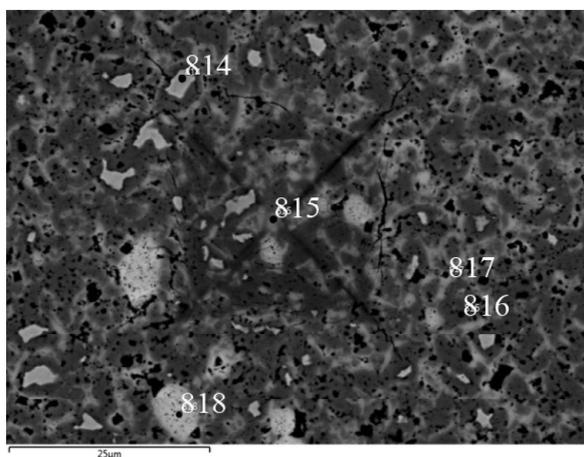
high surface area of the material. At the same time, oxidation induces significant structural rearrangement and porosity reduction of composites containing 10 and 20 wt.% of YSZ. According to SEM photos (see Figs. 1, 4, and 5), it is most likely nickel oxide that grows in the pores of the composite filling them up. Oxidation is followed by the allocation of zones consisting of pure nickel and mix of Ni and YSZ phases for Specimen 6 and NiO with YSZ for Specimen 7. Allocation of YSZ and Ni phases, most probably, results in increased hardness of the composite 6 up to ~700 HV. So, in case of Specimen 6 (90Ni-10YSZ, wt.%) the required combination of high plasticity and sufficient hardness is observed, which could open the new bright prospective in materials science.

#### 4. CONCLUSIONS

Via XRD, SEM, and EDX analysis, it was shown that the oxidation resistance of "98Ni-2 wt.% YSZ" composite is 3 times higher than that of the bulk material produced from pure nickel due to grain coarsening and pore size redistribution taking place during oxidation. For nickel based composites containing 1, 3, and 5 wt.% of YSZ, that value increases in about 2 times with almost no change in Vickers hardness (HV). Vickers hardness testing of nickel based composites containing 10 and 20 wt.% showed the hardness increase up to ~700 HV coupled with high plasticity. SEM and EDX data revealed that for "90Ni-10 wt.% YSZ" composite, oxidation is followed by the allocation of zones consisting of nickel and mix of Ni and YSZ phases, nickel oxide grows in the pores of the composite filling them up.

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**Fig. 5.** Magnified SEM data taken in the indentation zone of Specimen 6, 90Ni-10YSZ.

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