

## Material Science and Engineering with Advanced Research

# Surface Degradation of Composites Prepared by Al<sub>2</sub>O<sub>3</sub> and Ni Nanopowders

AG Lekatou\*, I Kenanoglou, K Kalantzis, AE Karantzalis, D Sioulas, KLentzaris and AK Sfikas

Laboratory of Applied Metallurgy, Department of Materials Science & Engineering, University of Ioannina, 45110 Ioannina, Hellas

\*Corresponding author: AG Lekatou, Laboratory of Applied Metallurgy, Department of Materials Science & Engineering, University of Ioannina, 45110 Ioannina, Hellas, Greece; Tel: (+30) 2651007309; Fax: (+30) 2651007309; E mail: alekatou@cc.uoi.gr

Article Type: Research, Submission Date: 06 February 2017, Accepted Date: 17 February 2017, Published Date: 16 May 2017.

**Citation:** AG Lekatou, I Kenanoglou, K Kalantzis, AE Karantzalis, D Sioulas, et al. (2017) Surface Degradation of Composites Prepared by Al<sub>2</sub>O<sub>2</sub> and Ni Nanopowders. Mater. Sci. Eng. Adv. Res Special Issue: 7-18. doi: https://doi.org/10.24218/msear.2017.2S.

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#### Abstract

Nowadays, in most engineering fields, there is a high need for the development of new products with improved properties and innovative functionalities that can with stand aggressive environmental and high load conditions. Towards this need, the fabrication of materials composed of nanostructured ceramics and metals is a promising option, as they combine the high strength of ceramics with the crack deflection toughening attained by the nanostructure and the metallic phase. Within the above framework, Al<sub>2</sub>O<sub>2</sub>-(5-50) wt.% Ni composites have been manufactured by powder metallurgy processing of Al<sub>2</sub>O<sub>3</sub> and Ni nanopowders. The attained microstructure consists of a metallic network enclosing Al<sub>2</sub>O<sub>2</sub> grains. The latter are composed of Al<sub>2</sub>O<sub>2</sub> nanosized sub grains. Ni nanoparticles are dispersed in the Al<sub>2</sub>O<sub>3</sub> grains, whilst they are mostly located in pores. Nanostructured Ni-Al-O zones have been formed between Al<sub>2</sub>O<sub>2</sub> and Ni phases. Cyclic potentiodynamic polarization showed that the composites present passivation and high resistance to localised corrosion in 3.5 wt.% NaCl. Surface films are analysed by SEM/EDX and Raman spectroscopy. A mechanism of corrosion is proposed. Sliding wear testing (ball-on-disk) revealed that Ni improves the wear resistance of Al<sub>2</sub>O<sub>3</sub>. The maximum improvementis observed at 20 wt.% Ni addition. The roles of Ni on the corrosion and sliding wear performance of the composites are discussed and elucidated.

**Keywords:** Al<sub>2</sub>O<sub>3</sub>-Ni, Nanopowders, Sintering, Cyclic polarization, Sliding wear, Raman spectroscopy.

#### Introduction

Nowadays, in most engineering fields, there is a high need for the development of new products with improved properties and innovative functionalities that can withstand aggressive environmental and high load conditions. Towards this need, the fabrication of materials composed of nanostructured ceramics and metals is a promising option, as they combine the high strength of ceramics with the crack deflection toughening attained by the nanostructure and the metallic phase.

Nanostructured ceramics manifest remarkable properties, such as very high strength, good fatigue resistance, superplasticity, wear resistance, very low thermal conductivity, special electronic and optic properties (e.g. high transparency), as well as unusual magnetic properties (e.g. high magnetoresistance, superparamagnetic properties) [1-11].

The toughening mechanisms in nanocrystalline ceramic matrix composites comprise the conventional micromechanisms characteristic of microscale composites (fibre toughening, ductile phase toughening, microcrack toughening and transformation toughening) and the mechanisms characteristic of nanoscale ceramics. The latter are based on nanoscale plastic flow modes and includegrain boundary sliding/rotations/migration/diffusion, rotational deformation mode and cooperative grain boundary sliding [12]. However, to date, the fabrication of fully dense nanostructured components has encountered major difficulties particularly in nanopowder processing [10,13,14].

Alumina predominates in high technology areas due to its low cost and good properties, such as high strength and elastic modulus, excellent resistance to thermal and chemical environments, lightweight and high melting temperatures; however, its brittleness is a major drawback for applications to load bearing and thermal shock conditions [15]. Reportedly, incorporation of metal (Al, Ni, Cu, Cr, Zr, Ti, Mo,W, Ni-Co etc.) particles increases the fracture toughness and other mechanical properties of alumina ceramic [15-25]. Toughening is attributed to the bridging of ceramic grains with the metallic particulate. More specifically, the metallic phase forms (by plastic deformation) crack-bridging ligaments during crack growth under tensile stress. Hence, the energy that would be consumed for crack propagation is being absorbed for plastic deformation. Furthermore, the deformed particles can bridge the faces of the crack wake, thus reducing the stress intensity effect at the crack tip [26,27]. The toughness increase achieved is mainly affected by the mechanical properties of the metallic particle, the ligament diameter, the particle volume fraction, the interfacial properties and the reaction products of the constituents [28].

Further improvement of the mechanical properties of alumina could be achieved by the fabrication of nanocomposites, which combine the very good properties of conventional composites with the unique mechanical and physical attributes of nanostructured materials, as aforementioned. For example, the strength of alumina-spinel-nickel composites was found to primarily be enhanced by grain size reduction to a range of tens up to one hundred nanometres [21]. However, alumina transforms at relatively low temperatures (~1200 °C) to a-Al<sub>2</sub>O<sub>3</sub> of a vermicular morphology, entrapping a network of large and elongated pores [29]. Therefore, very high temperatures are required to attain full densification, leading to significant grain growth and destruction of the nanostructure. Moreover, nanoparticles have the tendency to agglomerate due to their high specific surface; agglomeration is enhanced exponentially with particle size reduction. Major repercussions of agglomeration during the fabrication of ceramics from nanopowders may be low relative green density during consolidation, high sintering temperature and time and an inhomogeneous microstructure[30].

Within the above framework, the present work is part of a wider effort with the objectives: (a) to attain a satisfactory packing of nanoparticles into green compacts whilst retaining the nanostructure; (b) to achieve fast sintering processes or low sintering temperatures (below 1300 °C), thus leading to accountable energy/cost savings in comparison with conventional materials; (c) to assess performance of the final products in aggressive environments so as to achieve comparable material performance under critical service conditions. The present effort is orientated towards objective (c), namely: a systematic study of the electrochemical performance in an aggressive electrolyte (3.5 wt.% NaCl) and the sliding wear behaviour of  $Al_2O_3$ -Ni composites prepared from nanopowders via a simple powder metallurgy route.

## **Materials andmethods**

Nano-powders of  $Al_2O_3$  (<50 nm) and Ni (<100 nm) were homogenized in a medium energy ball mill. After a study of optimization of the processing parameters with respect to the minimization of porosity and micro-cracking that depended on the type of binding agent, dry or wet milling, sintering time and temperature, briquettes (1 g, 1 cm diameter, 5 mm thickness) of  $Al_2O_3$ -(0-50)wt.% Ni were manufactured under the following conditions: wet milling (6 h, 50 ml isopropanol, 0.15 g H<sub>2</sub>O, 150 rpm, 1wt.% bentonite as a binding agent)  $\Rightarrow$  drying (80 °C, 18 h)  $\Rightarrow$ dry milling  $\Rightarrow$  green compacting (uniaxial press, 3.5 t)  $\Rightarrow$  sintering (1300 °C, 4 h, Ar+5% H<sub>2</sub>). The prepared materials were subjected to:

a) Potentiodynamic polarization in 3.5 wt.% NaCl at room temperature (r.t.) using the ACM Gill AC potentiostat(standard three electrode cell, reference electrode: Ag/AgCl (3.5 M KCl), counter electrode: platinum gauze). The corrosion rate was determined by Tafel extrapolation as in detail described in previous work [31]).The resistance to localised corrosion was studied by cyclic polarization. The main concept of this technique is that pitting would occur if the current density of the forward scan for the same anodicpotential [32]. This type of hysteresis is labelled as "negative hysteresis" (More details can be foundin [33]).

b) Dry sliding wear testing at r.t. using the CSM ball-on-disc tribometer (normal load: 2 N, sliding speed: 10 cm/s, acquisition rate: 20 Hz, total sliding distance: 1000 m, $Al_2O_3$  counter ball of 6.0 mm diameter). Each run was interrupted every 200 m, for measuring the mass loss of the sample. Before each weighing, the specimen was ultrasonically cleaned by acetone.

The microstructure inspection of all samples was performed by SEM/EDX at the JEOL JSM 6510LV SEM (secondary electron (SE) and back-scattered electron composition image (BEC) modes) equipped with an Oxford Instruments X-Act EDX analyser. The nature of the corrosion products was studied by Raman Spectroscopy (RS) immediately after cyclic polarization using the Labram HR Horiba Scientific spectrometer (laser excitation wavelength: 514 nm, laser power: 12 mW, power incident on the sample surface: 2 mW, focused spot diameter:  $\sim 1 \mu$ m).

## **Results and discussion**

## Microstructure of the prepared materials

Figures 1 and Figure 2 illustrate the microstructures of the fabricated materials. Figure 1 shows that a metallic network of Ni agglomerates is enclosing Al<sub>2</sub>O<sub>3</sub> grains. The fineness of the metallic network and grain size of alumina decrease with Ni content increasing. A zone of Ni-Al-O nanoparticles has formed between the Al<sub>2</sub>O<sub>2</sub> and Ni phases surrounding the Ni particles (Figure 1f). Although, EDX analysis showed varied compositions of Ni-Al-O, a specific stoichiometry was quite often encountered, that of NiAl<sub>6</sub>O<sub>10</sub> or NiO.3Al<sub>2</sub>O<sub>3</sub> (5.8 $\pm$ 0.3 at% Ni, 34.4 $\pm$ 0.9 at% Al, 59.8±0.4 at% O), a phase included in the sub-solidus region of the NiO-Al<sub>2</sub>O<sub>3</sub> phase diagram [21]. The formation of NiAl<sub>2</sub>O<sub>4</sub> spinel at the solid Ni/aAl<sub>2</sub>O<sub>3</sub> interface has long been established [34,35]. It should be noted that  $NiAl_2O_4$  presents notable solubility for Al<sub>2</sub>O<sub>3</sub>, whilst almost none for NiO. Hence, Nialuminate can generally be represented as NiO  $(y=1+x)Al_2O_3$ , where x varies from nil (NiAl<sub>2</sub>O<sub>4</sub>) to  $x_{max}$  (the Al<sub>2</sub>O<sub>3</sub> saturated composition) [35]. Trumble and Rühle [35] showed that the threshold oxygen level required for spinel formation at the Ni/ Al<sub>2</sub>O<sub>3</sub> interface is just ~200 at. ppm. (A NiO intermediate is not thermodynamically necessary for the reaction to proceed.)



Figure 1: SEM micrographs of the Al<sub>2</sub>O<sub>2</sub>-Ni composites (sintering at 1300 °C, 4 h). f) Phases identified by EDX (Ni contents: wt.%)

Larger magnifications (Figure 2) show that each alumina grain consists of  $Al_2O_3$  nanoparticles among which nano to submicron particles of Ni are dispersed. In Al-10 wt.% Ni, the interior of the  $Al_2O_3$  grains contains very few submicron Ni particles in dispersion. The porosity of  $Al_2O_3$  is high (Figures 2a, 2b). With Ni content increasing, the dispersed Ni nanoparticles have increased whilst they are mostly located in pores, as shown in Figure 2d (in circles). Hence, the microstructure of Al-10 wt.% Ni (compare Figure 2a with Figure 2c). In Figures 2e, 2f, the layer of NiAl<sub>6</sub>O<sub>10</sub> nanoparticles that has grown between  $Al_2O_3$  and Ni is arrow pointed. In conclusion, the microstructure inspection suggests that the nanostructure of  $Al_2O_3$  has largely been retained, despite

the sintering process.

#### **Corrosion performance**

**Potentiodynamic polarization:** Figure 3 demonstrates the potentiodynamic polarization behaviour of the  $Al_2O_3$ -Ni materials including that of nano  $Al_2O_3$  sintered at 1300 °C for 4 h. Critical electrochemical values drawn from the polarization curves are listed in Table 1. Figure 3a includes the forward voltammograms of all tested compositions and the cyclic voltammogram of Al-50 wt.% Ni. Figure 3b includes the cyclic voltammograms of two compositions (Al-10 wt.% Ni and Al-40 wt.% Ni). Critical potential values are also presented in Figure 3b.

All compositions present passivation over large ranges of anodic



**Figure 2:** Nanostructure retention indications. In circles: submicron dispersed Ni particles close porosity in  $Al_2O_3$ . Arrow pointed: a layer of Ni-Al-O nanoparticles has grown between  $Al_3O_3$  and Ni (Ni contents: wt.%)

potentials; however, the high values of passive currents (>0.1 mA/ cm<sup>2</sup>) indicate pseudopassivity. All compositions present regimes of negative hysteresis loops (i.e.  $i_{reverse} > i_{forward}$  in the ( $E_r E_{rep}$ ) potential range) indicating localised degradation. Nevertheless, repassivation during reverse polarization at  $E_{rep}$  occurs. As a result, the anodic-to-cathodic transition potentials ( $E_{a/c}$  tr) are several hundred mV higher than the corrosion potentials ( $E_{corr}$ ), indicating nobler surfaces at  $E_{a/c}$  tr than those at  $E_{corr}$ . The above behaviour suggests high resistance to localised corrosion.

Increase in the Ni content leads to a shift of the curves to higher current densities suggesting faster corrosion kinetics. Indeed Table 1 shows that the rate of general corrosion  $(i_{corr})$  and the passive current density  $(i_p)$  generally increase with Ni content.

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This increase is attributed to the increase in the surface area of the metallic network with Ni content increasing, as seen in Figure 1.

Two groups of polarization curves are observed in Figure 3a: (i) Curves corresponding to Ni contents of 0-30 wt.% with very similar  $E_{corr}$ ,  $E_{cp}$ ,  $E_b$ ,  $i_{cor}$ ,  $i_p$  and  $(E_b-E_{cp1})$  values; and (ii) curves corresponding to Ni contents of 40-50 wt.% that present smaller ranges of passive potentials and are shifted to nobler potentials and higher current densities. This differentiation is compatible with the differentiation in the microstructures of the 40 and 50 wt. % Ni composites, which are characterized by extensive networks of metallic agglomerates. At 0-30 wt.% Ni, the electrochemical performance of the composites is very similar to



Current density (mA/cm<sup>2</sup>)

**Figure 3:** Potentiodynamic polarization curves of the  $Al_2O_3$ -Ni nanocomposites in 3.5 wt.% NaCl, r.t. **a**) Forward polarization curves of all compositions and cyclic polarization curve of  $Al_2O_3$ -50 wt.% Ni; **b**) Cyclic polarization curves of  $Al_2O_3$ -10 wt.% Ni and  $Al_2O_3$ -40 wt.% Ni

**Table 1:** Electrochemical values of the  $Al_2O_3$ -Ni materials immersed in 3.5 wt.% NaCl, at r.t.  $E_{corr}$ : corrosion potential,  $E_{cp1}$ : critical "passivation" potential,  $E_b$ : breakaway potential,  $E_{a/c tr}$ : anodic-to-cathodic transition potential,  $E_{rep}$ : repassivation potential,  $i_{corr}$ : corrosion current density,  $i_p$ : current density in the middle of passive stage ( $E_b-E_{cp1}$ ). (All values reported are the mean of three responses)

Al <sub>2</sub> O <sub>3</sub> -x wt.% Ni	E <sub>.orr</sub> (mV vs. Ag/AgCl))	E <sub>cp1</sub> (mV vs. Ag/AgCl)	E <sub>b</sub> (mV vs. Ag/AgCl)	E <sub>a/c tr</sub> (mV vs. Ag/AgCl)	E <sub>rep</sub> (mV vs. Ag/AgCl)	i <sub>corr</sub> (mA/cm²)	i <sub>p</sub> (mA/cm²)
0%Ni	-1302±1	-1118±36	-199±12	-738±5	-652±17	0.89±0.01	0.30±0.003
5%Ni	-1313±13	-1133±38	-180±18	-734±4	-608±34	0.87±0.01	0.45±0.07
10%Ni	-1288±23	-1106±49	-161±8	-731±4	-659±39	0.77±0.05	0.41±0.15
20%Ni	-1327±30	-1185±45	-154±18	-745±7	-548±63	0.74±0.07	0.49±0.15
30%Ni	-1274±5	-1003±8	-158±11	-727±10	-541±7	1.07±0.16	0.58±0.18
40%Ni	-1029±15	-863±4	-91±12	-694±1	-317±64	2.52±0.41	1.45±0.07
50%Ni	-983±12	-828±110	-235±8	-676±20	-583±83	2.44±0.3	1.77±0.03

that of sintered nano- $Al_2O_3$ , suggesting that the electrochemical behaviour of all materials in the 0-30 wt.% Ni range is controlled by the electrochemical behaviour of alumina. (The paradox of the conductive behaviour of nano- $Al_2O_3$ , observed in Figure 3a, can be justified by two likely reasons: (a) reduction of  $Al_2O_3$  in the reducing atmosphere of sintering; (b) adsorption of water as undissociated molecules bonded with strong hydrogen bonds [36]). In the 0-30 wt.% Ni compositions, dispersion of Ni nanoparticles within the alumina grains is so occasional that does not significantly affect the polarization behaviour of alumina. The main electrochemical role of Ni is passivity inducing for a high range of potentials, sincethe fine metallic networks uniformly distributed around alumina grains as well as the ultra-fine Ni dispersoids within the alumina grains lead to uniform surface

films (of relatively low conductivity though).

On the other hand, at 40 and 50 wt.% Ni, the agglomeration of Ni nanoparticles is so high that the electrochemical behaviour of the composite is controlled by the metallic constituent-due features of the composite, namely: extended and compact metallic zones composed of Ni agglomerates, increased grain boundaries, increased number of interfaces (Al<sub>2</sub>O<sub>2</sub>/Ni, Al<sub>2</sub>O<sub>2</sub>/Ni-Al-O, Ni-Al-O/Ni, etc.). The relatively noble corrosion potentials of the 40 wt.% and 50 wt.% Ni compositions can be explained by the: (i) lower amount of residual stresses due to the ductile Ni dispersion in the alumina grains that closes stress concentration points, such as pores, and dissipates stresses by plastic deformation. (It has long beenknown that stresses -either by applied loads or residual ones- may increase the internal energy level of a metal system and cause a shift of the electrochemical potential to a more active direction [37]). Also, the intermediate zone of Ni-Al-O is expected to induce stress relief due to a smoother transition from the Al<sub>2</sub>O<sub>3</sub> to the Ni phase; and (ii)extensive presence of the (nobler to Ni) Ni-Al-O phase due to the interaction of Al<sub>2</sub>O<sub>3</sub> with Ni.

**Corrosion products:** Figure 4 presents the surface state of the  $Al_2O_3$ -Ni composites after cyclic polarisation. The absence of any signs of pitting confirms the high resistance to localised corrosion suggested by the polarization behaviour in Figure 3. Figures 4a-d reveal an extensive deposition of thick films partly composed of salt crystallites, most likely responsible for the very high current values at potentials higher than  $E_{cp2}$  (final pseudopassive stage,

see Figure 3b). Hence, the sharp increase in the current density at potentials higher than E<sub>b</sub> (Figure 3b) is attributed to: (a) The formation of thick heavily hydrated surface films with high conductivity (hydrated Cl<sup>-</sup> containing salts, shown in Figure 4a,b). Cl<sup>-</sup> concentration is very high at potentials higher than  $E_{L}$ , since it is well established that  $Cl^{-}$  concentration on the free surface increases as anodic overpotential increases [38]. As such, some localised attack may also occur at potentials higher than  $E_{rep}$  and up to  $E_r$ , as suggested by the negative hysteresis loop in the potential range  $E_{rep} \rightarrow E_r$  ( $E_{rep} \rightarrow E_b$ : localised attack initiates and occurs along with pseudopassivity). (b) To the transpassive dissolution of the passive film at he potentials  $E_{h} \rightarrow E_{cp2}(E_{h} \rightarrow E_{c})$ transpassive dissolution takes place simultaneously with localised degradation.) In the range of  $E_b \rightarrow E_{,}$  localised attack is the governing process as indicated by the negative hysteresis loop. In the range of  $E_r \rightarrow E_{cp2}$ , the transpassive dissolution of the passive film becomes the governing process as suggested by the positive hysteresis loop.

The formation of Ni-Al mixed oxidised structures on the surface of the Ni phase enhances the postulation that  $Al_2O_3$  reduction has taken place during sintering. The Ni phase appears oxidised, whilst always containing Al in minor amounts or traces; it seems that oxidation of Ni (primarily) and Al in the active stage has led to the passive stageduring polarization at potentials higher than  $E_{cp1}$  (Figure 3). Figure 4d includes indications of galvanic corrosion of Ni in the NiO·yAl<sub>2</sub>O<sub>3</sub> /Ni couple (in yellow outlined ellipse). Nevertheless, at high Ni contents, galvanic corrosion is



**Figure 4:** Surface state of the composites after cyclic polarization (3.5 % NaCl, r. t.). **a) & b)**  $Al_2O_3$ -20 wt.% Ni and EDX map, respectively; **c)**  $Al_2O_3$ -40 wt.% Ni; **d)**  $Al_2O_3$ -50 wt.% Ni; tr: traces. (yellow outlined ellipse: galvanic corrosion of Ni indications)

not intensive owing to the high ratio of the anode area (Ni) to the cathode area (O-Al-Ni).

The paradox of high localised corrosion resistance despite pseudopassivity can be explained by the nature of the surface films. Raman spectroscopy on the surface of Al<sub>2</sub>O<sub>2</sub>-Ni specimens after cyclic polarization revealed the presence of alumina hydrates, Ni-oxide based structures, Ni-aluminate spinel and carbonates. Typical Raman spectra are presented in Figure 5. The Raman spectra of aAl<sub>2</sub>O<sub>3</sub>and NiO commercial powders are also included in Figure 5 for reference purposes. The jagged morphology of the spectra and the humpy morphology of groups of numerous bands coexist with strong, complex peaks of large surface area; numerous small peaks are standing out from the jagged background. The above features indicate a complex structure containing both amorphous and crystalline phases. Numerous bands corresponding to the Al-O,  $\gamma$ (OH) and  $\delta(OH)$  vibrations of the alumina hydrates are observed. A more detailed information on the Raman manifestations of the alumina hydrates is out of the scope of this paper, however it can be found in previous works [31,39]. Strong complex Raman modes with overlapping bands are observed to peak at ~1050, 1070 and 1088 cm<sup>-1</sup>. They are assigned to the stretch vibration mode of CO32-. The observation of multiple bands peaking at three different wavenumbers suggests the presence of nonequivalent carbonate units [40]. The intense stretch vibrations of  $CO_3^{2-}$  are due to the easy penetration of the hydroxide films by carbonate ions and subsequent formation of carbonate salts. The latter are readily accommodated in the alumina hydrates. At 962-964 cm<sup>-1</sup>, strong bands ascribed to deformation modes of (OH ) groups are observed [41]. The bands peaking at 537-542 cm<sup>-1</sup> are due to the Ni-O stretch vibrations of NiO [42]. The bands peaking at 550-557 cm<sup>-1</sup> and 481-485 cm<sup>-1</sup> are assigned to the formation of higher valence nickel oxides from its divalent oxide (HOFN), such as NiOOH [43]. The likely presence of  $\beta$ Ni(OH),

is also indicated by the bands corresponding to 511-515 and 311-313 cm<sup>-1</sup> [43]. The presence of spinel NiAl<sub>2</sub>O<sub>4</sub> is suggested by the formation of bands corresponding to the A<sub>1g</sub> (300-304, 334-336, 600, 786-792, 871-876 cm<sup>-1</sup>), E<sub>g</sub> (325-333 cm<sup>-1</sup>) and T<sub>2g</sub> (615-616 cm<sup>-1</sup>) Raman active vibrations [44]. The Raman active modes of aAl<sub>2</sub>O<sub>3</sub> have an abundant presence especially at the spectrum of Al<sub>2</sub>O<sub>3</sub>-20 wt.% Ni.

Based on the RS findings, one can justify the protection efficiency of the surface films despite the relatively high passive (i.e. pseudopassive) currents. It has long been known that the passive film on Alisbi-layered: The inner layer is a compact amorphous layer, while the outer layer is a permeable hydrated oxide layer [45]. The inner layer is responsible for the barrier effect, whereas the outer layer is responsible for the high passive current values. Also, NiO, as a p-type semiconductor, should have a barrier character [46,47].

In conclusion, the following mechanism may account for the anodic polarization behaviour of the Al<sub>2</sub>O<sub>3</sub>-Ni materials in 3.5% NaCl at r. t.: During the active stage, Ni dissolution occurs induced by galvanic coupling with the surrounding Ni-Al-O phase. Dissolution of Al (resulting from reduction of Al<sub>2</sub>O<sub>3</sub> during sintering) also occurs at pores and cracks of Al<sub>2</sub>O<sub>3</sub>. Above  $E_{col}$ , passivation of Al and Ni occurs that protects from pitting up to  $E_{rep}$  (positive hysteresis loop). Above  $E_{rep}$ , (Cl<sup>-</sup> adsorption-due) thick soluble salt films are formed allowing access of Cl to the subsurface and pitting initiates (negative hysteresis loop). Above E<sub>b</sub>, breakdown of the passive film occurs. Thick hydrated salts are continuing to form rapidly rising the current. Above  $E_{cn2}$ , salt layers have grown so thick that obstruct Cl<sup>-</sup> penetration to the uncorroded surface, resulting in a positive hysteresis loop upon reverse polarization. Below  $E_{rep}$ , hysteresis turns to positive showing the reversibility of pitting, that eventually leads to nobler surfaces at E<sub>a/c tr</sub> compared to those at E<sub>corr</sub>.



**Figure 5:** Raman spectra of surfaces after cyclic polarization in 3.5 % NaCl, r. t.;  $\alpha$ :  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>;  $\beta$ :  $\beta$ -Ni(OH)<sub>2</sub>; sp: NiAl<sub>2</sub>O<sub>4</sub>; HOFN: Higher oxide forms of Ni (e.g. NiOOH); Al-O,  $\gamma$ (OH),  $\delta$ (OH): Raman active modes of alumina hydrates:  $\alpha$ -Al(OH)<sub>3</sub>,  $\gamma$ -Al(OH)<sub>3</sub>,  $\alpha$ -AlOOH,  $\gamma$ -AlOOH



Figure 6: a) Mass loss versus sliding distance; b) extracted wear rates of the examined materials

**Sliding wear performance:** Figure 6a shows the mass loss of the different materials as a function of the sliding distance. In all cases, as the sliding distance increases the mass loss also increases. Figure 6b shows that Ni addition benefits the wear resistance of alumina. However, the wear rate presents a minimum at 20 wt.% Ni, increasing thereafter with Ni content. The wear track morphologies are illustrated in Figure 7. The typical morphology of a brittle material, namely long cracks and flat areas after material detachment, characterizes the wear track morphology of compositions up to 20 wt.% Ni (Figure 7a-c). At higher Ni contents, relief becomes higher due to the plastic deformation of the ductile Ni agglomerates (Fig. 7d-e). In Figure 7f, large areas of material removal are noticed.

The two different modes of material detachment are more clearly manifested in Figure 8. In the case of alumina (Figure 8a), crack formation along grain boundaries and elongated or interconnected porosity lead to brittle fracture. In the case of  $Al_2O_3$ -20 wt.%Ni (Figures 8b, 8c), cracks are not associated with the presence of Ni; on the contrary, cracks propagate in  $Al_2O_3$ , circumferentially to the Ni network. On the other hand, in the case of  $Al_2O_3$ -50 wt.%Ni (Figure 8d), large areas of material removal are associated with the extensive presence of Ni agglomerates. It is thus suggested, that at the high Ni contents, the intensive plastic deformation of Ni exerts stresses to the adjacent brittle NiO.yAl\_2O\_3 / Al\_2O\_3 phases, eventually leading to material fracture and removal of large areas; the latter include ceramic phases together with engulfing metallic agglomerates.

Based on the microstructural observations of Figures 7 and Figure 8, different explanations are postulated for the increasing mass loss with sliding distance in Figure 6a, depending on the brittle (low Ni contents) or ductile (high Ni contents) character of the composites. The increase in the mass loss with sliding distance for the materials containing up to 20 wt.% Ni is attributed to the increasing crack propagation in the brittle matrix. Regarding the Ni-rich compositions (30-50 wt.%), the increase in the mass loss with sliding distance is attributed to the increase in he contact area between the friction pairs, owing to deformation of asperities; the latter are formed by plastic deformation of the Ni agglomerates. Furthermore, at larger sliding distances, the increase in the temperature of the sliding surfaces leads to softening of the extended metallic network and, thus, more severe deformation. A complementary reason for the increasing mass loss as the accumulative distance increasesis the wear fatigue enhanced by thermal fatigue. The latter is owing to the interruption of the test every 200 m of sliding distance for mass loss measurements. Considering the poor thermal shock resistance of the Al oxide-based phases, such thermal cycling stimulates a "thermal fatigue" mechanism that causes formation of cracks.

The microstructural observations of Figures 7 and 8 also lead to the following explanations for the varying trends in the wear rate with Ni content in Figure 6b. Plain alumina presents high wear rate due to the presence of porosity that enhances crack initiation and propagation. The addition of Ni (up to 20 wt.%) closes the porosity causing crack deflection; moreover, the fine metallic network also deflects cracks directing them to a circumferential propagation. Higher contents, however, increase the ductile character of the composites and lower their hardness and brittleness. Consequently, large coagulates of Ni are subjected to severe plastic deformation. Not only is their shear strength reduced but they also exert increased stresses to the adjacent brittle ceramic phases; thus, wear rates increasing with Ni content (higher than 20 wt.%) result.

## Conclusions

The microstructure of  $Al_2O_3$ -(5-50 wt. %)Ni materials prepared by sintering of nanopowders (1300 °C, 4 h) consists of a uniform metallic network of Ni agglomerates around  $Al_2O_3$  grains. Each grain is composed of agglomerated nanoparticles, whilst it presents a dispersion of Ni nanoparticles mostly located in pores. Nanostructured Ni-Al-O zones often composed of NiAl<sub>6</sub>O<sub>10</sub> have been formed between  $Al_2O_3$  and Ni phases.

The polarization behaviour in 3.5 wt.% NaCl is characterized by passivation of Ni<sup>2+</sup> and possibly Al<sup>3+</sup>, lack of pitting indications and galvanic coupling of Ni with NiO·yAl<sub>2</sub>O<sub>3</sub>. High corrosion rates are noted for 40 and 50 wt.% Ni.

Surface films after cyclic polarization have complex mixed structures. They are composed of alumina hydrates, Ni-aluminate spinel and Ni-oxide (NiO,  $\beta$ Ni(OH)<sub>2</sub>, possibly NiOOH) based



Figure 7: Panoramic views of the wear track morphologies of alumina and the different Al<sub>2</sub>O<sub>3</sub>-x wt.% Ni composites prepared from nanopowders



**Figure 8:** Worn surfaces showing: **a**) cracks along grain boundaries of  $Al_2O_3$ ; **b**) **& c**) cracks in  $Al_2O_3$ , circumferentially to the Ni phase; **d**) large areas of material removal, associated with the presence of Ni(Ni contents: wt.%)

structures. Thick salt compositions (carbonates, chlorates etc.) are also constituents most likely deposited at high overpotentials.

Ni addition decreases the wear rate of alumina. The sliding wear performance is optimized at 20 wt.% Ni. At Ni contents lower than 20 wt.%, the wear performance is improved with Ni increasing due to the crack deflection role of Ni sub-micron/ nano dispersions and Ni fine intergranular (i.e. around ceramic grains) network. At higher Ni contents (30-50 wt.%), the wear performance deteriorates with Ni increasing due to the plastic deformation of the Ni agglomerates.

## Acknowledgement

The financial support of the National Strategic Reference Framework (NSRF) Research Funding Program Thales"MIS 380143" is acknowledged. The authors would like to acknowledge Prof. S. Makridis for applying part of the arc-melting apparatus

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system under his patent: https://www.researchgate.net/ publication/200664162\_Multiapparatus\_Arc\_Melting\_for\_ Rapid\_Solidification\_Processes?ev=prf\_pub.

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