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A FACULTĂŢII DE ŞTIINŢA ŞI
INGINERIA MATERIALELOR

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ŞTIINŢA ŞI INGINERIA MATERIALELOR

FILTEK Z250 DENTAL COMPOSITE MATERIAL BEHAVIOR ON ARTIFICIAL SALIVA IMMERSION

BY

ANCA ALUCULESEI* **and CONSTANTIN BACIU**

“Gheorghe Asachi” Technical University of Iaşi,
Faculty of Materials Science and Engineering

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Abstract. Dental composite resigns are highly used in restoration domain based on very good compatibility, mechanical and workability properties. Tests of corrosion resistance in artificial saliva help on usage and applications of these new and special materials. Scanning electrons micros copies and EDAX analyses were performed to analyze the material surface. The corrosion results, after a tough immersion test, recommend this material as a very good solution in biocompatibility applications even from the material surface under pitting influence material percentage pass in biological environment.

Key words: filtek z250, dental composite, artificial saliva.

1. Introduction

Since resin composite was introduced in the clinical practice (Leung & Darvell, 1997) many efforts have been made to improve the clinical behavior of this esthetic restorative material. One of the most important steps in this field was the introduction of visible light-cured resin composites (Gal *et al.,* 2001). The first light source used to start the polymerization reaction of dental resin composites was ultraviolet. However, this light source, produced

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*Corresponding author; *e-mail*: aluculesei_anca@yahoo.com

by plasma arcs, has shown a lower light penetration, limiting the depth of cure. In the last few years, quartz–tungsten–halogen lamps have been used, showing more satisfactory results (Duffo & Quezada Castillo*,* 2004; Fusayama *et al.,* 1963).

The filler type, shape and amount, as well as the efficient coupling of fillers and resin matrix, contribute to the material performance. Properties such as compressive or flexural strength, hardness and Young's modulus improve as the filler content increases. At the same time polymerization shrinkage decreases. Dental polymeric restorative materials are now incorporating nanofillers (5–100 nm) and/or organic–inorganic hybrids. The aim has been to improve mechanical properties, surface smoothness and gloss, polymerization shrinkage and biocompatibility (Gal *et al.,* 2001).

2. Experimental Details

Filtek Z250 light-curing dental materials, activated in the medical office, was immersed in different artificial saliva liquid mediums like Fusayama and Afnor type solutions and Ringer's solution, in an enclosed area and at room temperature for a period of 30 days.

In this study are presented the results after immersion in solution AFNOR. After maintaining these composite material areas of dental samples were investigated by electron microscopy and X-ray analysis EDAX to determine the state of material after prolonged contact with the artificial saliva. Natural saliva is a very complex and consists of inorganic compounds (0.2% - mainly salts) and organic compounds (0.4% - protein substances (proteins, enzymes, hormones) and non-proteinaceous (urea, KSCN, amino acids)), who's concentrations vary from base to the individual. Oral environment is very own to form corrosion products. The mouth is moist and continuously subjected to temperature fluctuations. Food and drink have pH values covering an entire area, from very acidic to alkaline. Since the most important fluid of the oral cavity is natural saliva is obvious that tests on dental alloys to be made in this environment. However, unstable and volatile nature of natural saliva makes it inappropriate for standardized in vitro studies. Then it is necessary to synthesize artificial saliva to react similarly to natural saliva. Over 60 formulations of artificial saliva were reported in the literature, a detailed presentation of the subject being made in the literature introduced a gas mixture to simulate the control of pH and redox buffering capacity through CO_2/HCO_3. In a recent study Quezada Duffo and (Duffo & Quezada Castillo, 2004) analyzed the behavior of Cu-Al alloys in 17 different artificial solutions cited in the literature compared with natural saliva and propose a new solution in the alloys studied behave as in saliva natural. In some studies, including the analysis of implantable materials were used to simulate fluid interstitial fluid (solution: Ringer, Cigada, Hank), these solutions are entirely inorganic. Chlorine concentration in the Ringer solution is about 7 times higher than in the saliva compositions. In Table 1 the compositions of several corrosion environments such as those used in this study are presented. Appear in literature and other solutions used to simulate the interstitial space (Fusayama *et al.*, 1963). They contain small amounts of additional ingredients such as glucose, magnesium chloride, lactic acid, amino acids and organic anions. (Leung & Darvell, 1997; Gal *et al.,* 2001). As shown by Gal and others, detailed examination of different types of saliva shows that in some cases they are combinations of substances which are more or less similar to those in human saliva. Some of these solutions better simulate human saliva, especially in the electrochemical behavior, and were widely used in corrosion studies. Some solutions containing only inorganic materials, while others include organic additives, consisting mainly in mucin, glucose, urea, sulfocianuri. Additional ingredients also include bicarbonates, sulphates, carbonates, organic acids, citrate and hydroxides. Some solutions to $CO_2/O_2/N_2$

Table 1

Chemical Composition of Some Biological Artificial Mediums

Solution	Compozition (g/l)		pH	Ref.
FUSAYAMA-MEYER	NaCl KCl $CaCl_2{\cdot}2H_2O$ $NaH_2PO_4{\cdot}H_2O$ $Na_2S{\cdot}9H_2O$ Uree (CH_4ON_2)	0.400 0.400 0.795 0.690 0.005 1.000	**5-5.5**	(Fusayama *et al.* 1963; Meyer, 1974; Meyer & Nally, 1975; Meyer, 1977; Holland, 1980; Holland, 1991; Holland,1992)
AFNOR Carter modify saliva	NaCl; $CaCl_2{\cdot}2H_2O$ KCl; $Na_2HPO_4\,.H_2O$ $NaHCO_3$ KSCN; Uree	0,700 1,200 0,26 1,500 0,330 1,330	**6,7-8**	(Ross *et al.* 1967; De Micheli & Riesgo, 1978; Carter-Brugirard AFNOR/NF 1999)
RONDELLI Modify saliva Tany-Zucchi	KCl $NaHCO_3$ KSCN $KH_2PO_4.H_2O$	1.470 1.250 0.520 0.190	**7.75**	(Angelini & Yucchi, 1984; Angelini *et al.* 1993; Rondelli 1996; Rondelli *et al.*1990)
DUFFO-QUEZADA (artificial saliva)	NaCl KCl $CaCl_2{\cdot}2H_2O$ KH_2PO_4 $Na_2HPO_4{\cdot}12H_2O$ KSCN $KHCO_3$ acid citric	0,600 0,720 0,220 0,680 0,856 0,060 1,500 0,030	**6,5**	(Duffo & Quezada Castillo, 2004)

Table 1

Continuation

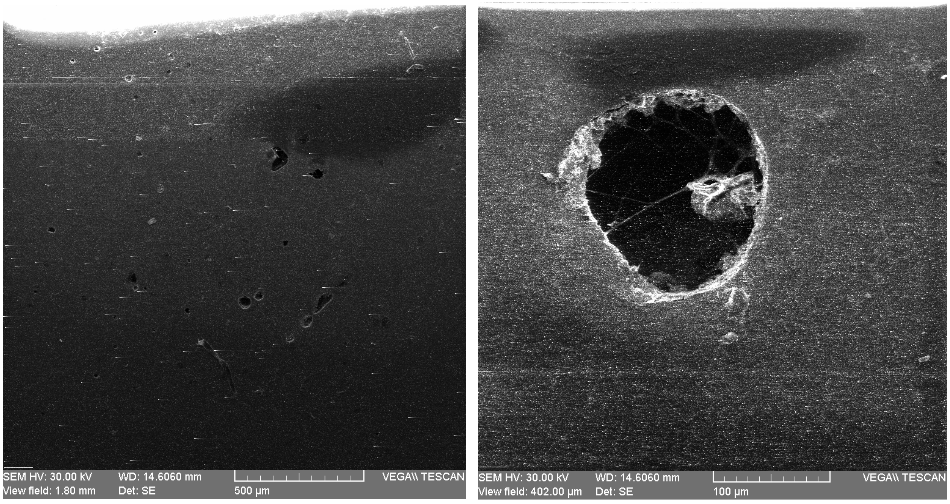
RINGER 1 (soluție fiziologica)	NaCl $NaHCO_3$ $CaCl_2 \cdot 6H_2O$ KCl	9,000 0,200 0,400 0,430	**6.8**	(Dobbs & Robertson, 1995; Sutow *et al.* 1985; Angelini *et al.* 1991)
RINGER 2	NaCl KCl $CaCl\ 2H_2O$	8,6 0,3 0,33	**7,4**	(Hoan & Mears, 1966)
HANKS (Phyziological solution)	NaCl KCl Na_2HPO_4 $NaHCO_3$ $CaCl_2$ KH_2PO_4 $MgCl_2 \cdot 6H_2O$ $MgSO_4 \cdot 7H_2O$	8.000 0.400 0.600 0.350 0.140 0.060 0.100 0.060	**6,8**	(Dobbs & Robertson 1995; Sutow & Jones 1985; Angelini *et al.* 1991; Mears, 1977)
CIGADA (Phyziological solution)	NaCl $NaHCO_3$ NaH_2PO_4 Na_2HPO_4	8,74 0,35 0,06 0,06	**7,1**	(Fraker)

Interactions of various salts in saliva are complex effects, various combinations of salts in saliva are not the sum of the effects of individual components. Chlorides produce a slight intercrystalline corrosion attack around places such as porosity or metal joints/bones. Add HPO_4^{2-} cause little effect, forming corrosion products in the areas of attack. Addition of HCO_3-system corrosion micro Cl-/HPO_4^{2-} increases. Conversely, addition of SCN-system corrosion microstructural Cl-/HPO_4^{2-} diminished. Hank solutions, CIGADA RINGER and are used both for testing of titanium surgical implants and for studying the behavior of dental alloys. Since the simulated solutions were used only for the study of chemical corrosion in their composition were not introduced organic compounds or lubricants that could reduce or inhibit some corrosion processes. Thus, it can be assumed that the corrosive effect of these artificial solutions is greatest in relation to real solutions. From this point but it neglects the effects of bacterial factors that may play an important role in the degradation of metallic materials. Artificial solutions are used to estimate the corrosion behavior but cannot simulate the influence of natural salivary components (proteins and enzymes that may inhibit or accelerators).

3. Experimental Results

Further analysis was performed on Filtek Z250 dental material behavior in artificial saliva Afnor corrosion environment. There have been tests on samples of composite Filtek Z250 immersed and kept 30 days continuously (without being a direct exchange with ambient air) in solution with chemical composition Afnor volley and properties shown in Table 1 is observed character of the acid solution.

Material surface condition is shown in Fig. 1 through S.E.M. microscopy at different power amplification of 100 and 700 times the detail of the pitting corrosion similar holes in Fig. 1 *b*.



a *b*

Fig. 1 – SEM microscopies of Filtek Z250 material surface after the immersion process in artificial solution Afnor: *a* – 100x; *b* – 700x.

In Fig. 1 is shown the material surface over an area of 1.8x1.8 mm^2 after he was kept in artificial saliva solution Afnor for 30 days. It is noted that the area was affected in 'pitting' type and the formation of holes in the material, such a surface condition is detailed in Fig. 1 *b*, with sizes between 10 and 100 µm with loss of composite material and the formation of compatible on the surface of composite material. From microscopy, Fig. 1 can be appreciated that the material has suffered different damage degrees to the surface at a rate of 20-30 % with a depth of pitting of the order of micrometers.

Fig. 2 shows the energy spectrum of chemical elements on the surface components of dental composite material Filtek Z250 after it was immersed for 30 days artficială Afnor saliva solution. Were identified qualitatively more different species of elements and energy fields of their involvement, for instance, zirconium participate in three different types of connections characterized by different energies in keV. Were identified as species of dental composite material such as carbon, silicon, zirconium and oxygen and artificial saliva elements such as chlorine, natriul, potassium or nitrogen.

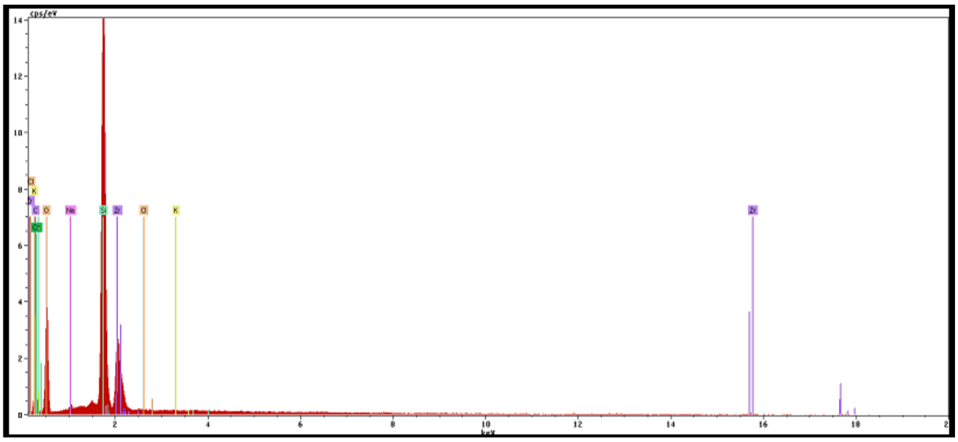
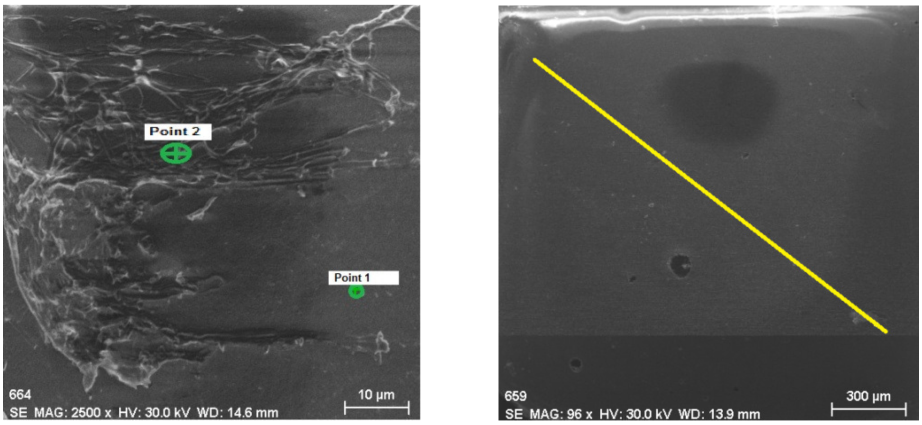


Fig. 2 – Energy spectrum of chemical from the Filtek Z250 surface material after an immersion period of 30 days in artificial saliva Afnor type.

Material surface analysis was carried further by selecting points for chemical composition that reflects the homogeneity of the attack made by the artificial solution, areas selected for analysis are shown in Fig. 3 and selecting a line to analyze the surface distribution of chemical elements investigated, selected area is presented in Fig. 3 *b*, which aims the chemical composite distribution material formed on the surface.



a *b*

Fig. 3 – Selecting points for chemical analysis; *a* – and a line distribution; *b* – the area affected by saliva solution Afnor.

Items selected for chemical analysis were first located in an area does not seem affected by the solution of artificial saliva and the second point in an area full of extra base material compounds that have appeared on the material by immersing it in saliva Z250. Chemical analysis results are presented in Table 2 for first selected point and in Table 3 for second point.

The material surface analyze shows a decrease in the percentage of zirconium to 6.322 % wt maintaining the oxygen and silicon percentages with high values to light-curing material and we attacked with artificial saliva solution. The low percentage is observed in saliva and the emergence of elements such as sodium, potassium or chlorine compounds that make up various surface materials is removed by washing compounds simple hydrogen peroxide, which become harmful material through involvement in dental composite surface reaction and the appearance of pitting holes in the base material.

Table 2

The Chemical Composition of Surface Material at the Point Selected Z250 1 in Fig. 3

Element	AN	Net	wt.%	norm. [wt.%]	norm. at.[%]	Error [%]
Oxygen	8	37319	60.173970	58.083220	68.184330	7.288356
Silicium	14	94085	24.191950	23.351400	15.615950	1.106298
Carbon	6	10188	7.183587	6.933993	10.842810	2.248051
Zirconium	40	144	6.550334	6.322742	1.301769	0.623410
Sodium	11	4816	3.724504	3.595096	2.937064	0.296023
Nitrogen	13	4349	1.394022	1.345586	0.936661	0.101849
Potasium	19	907	0.283566	0.273714	0.131485	0.039004
Chlorine	17	336	0.097641	0.094249	0.049930	0.032074
		Sum:	103.5996	100	100	

Table 3

The Chemical Composition of Surface Material at the Point Selected 2 of Fig. 3 on Z250 Surface

Element	AN	Net	wt.%	norm., [wt.%]	norm., [%]	Error, [%]
Oxygen	8	27961	69.68845	56.85496	61.232130	8.660875
Silicium	14	77752	18.18148	14.83326	9.100584	0.838324
Carbon	6	31063	10.82260	8.829562	12.667030	1.352884
Nitrogen	7	2248	9.495855	7.747144	9.530606	1.775725
Phosphorus	15	27374	7.558764	6.166779	3.430671	0.335129
Natrium	11	6487	4.599906	3.752809	2.812785	0.354617
Potasium	12	2726	1.163861	0.949530	0.673175	0.101001
Chlorine	13	3561	1.061413	0.865949	0.553019	0.084569
		Sum:	122.5723	100	100	

Looking at the second selected point in an area with compounds formed on the surface Z250 is observed an increase in percentages of nitrogen, phosphorus, potassium and chlorine in conjunction with decreased high rates of oxygen, silicon and zirconium composite material element undetected attributed to the disappearance of surface material and thickness of formed compounds. Increasing the percentage of carbon is attributed to lower percentage of silicon and zirconium chemical elements of the total 100% by mass or atomic.

In Fig. 4 are followed the main chemical elements on the surface of composite material Filtek Z250 appearing from the contact with artificial saliva Afnor during 30 days and signal strength of zirconium element on a line with a 1.6 mm length.

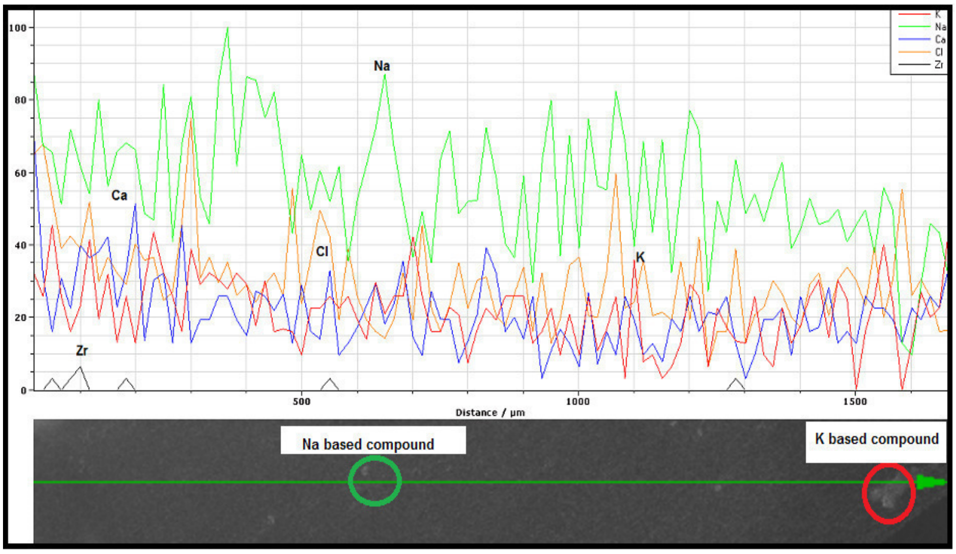
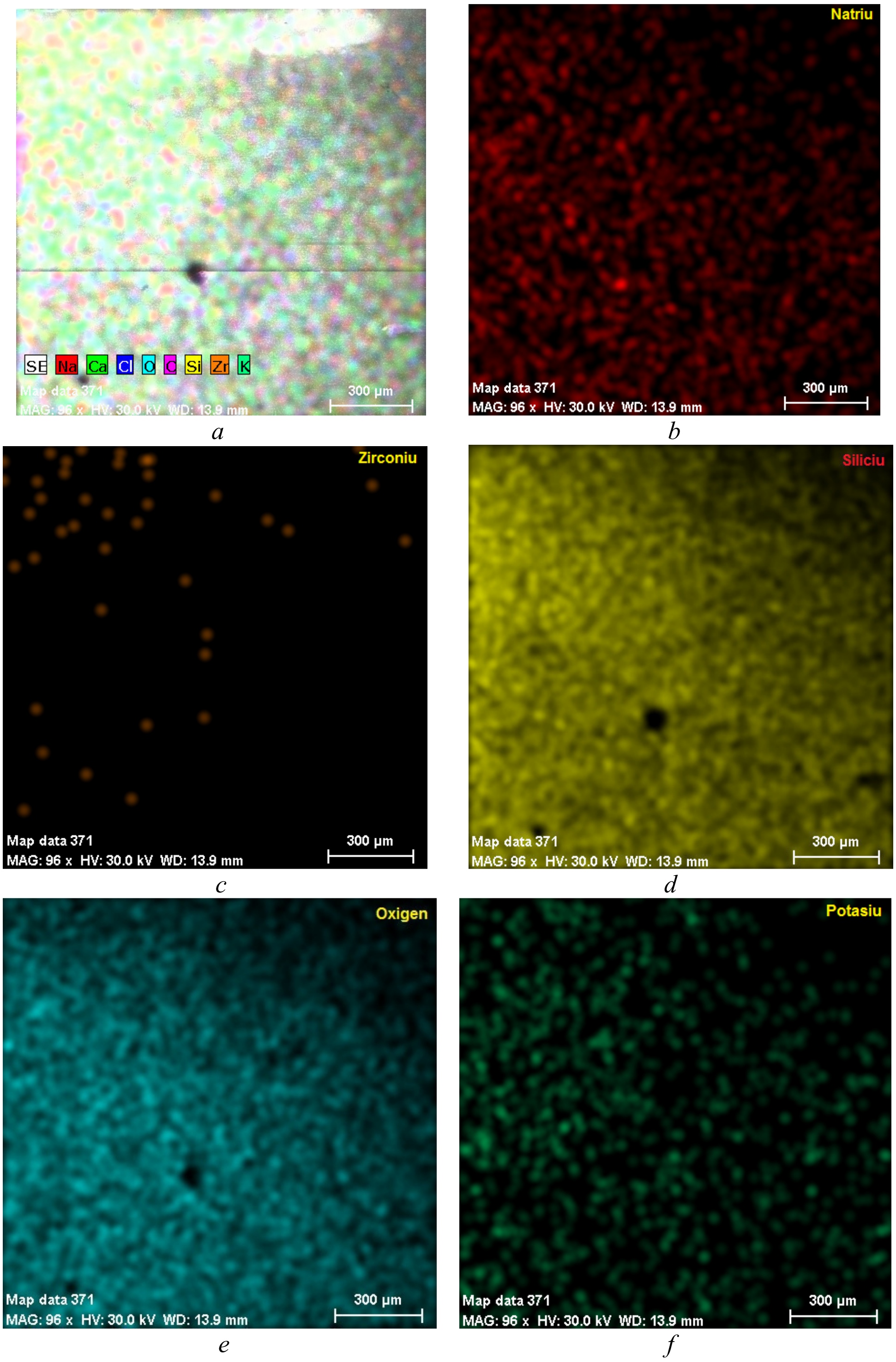


Fig. 4 – Distribution of elements K, Na, Ca, Cl and Zr on the material selected Z250 line in Fig. 3 *b*.

Formations shown in Fig. 4 are chlorine-based chemicals, sodium, potassium and calcium appeared on the surface after immersion Filtek Z250 and very large decrease of the signal element zirconium especially in areas covered with more pronounced reaction compounds.

Further selecting an area of 1.2x1.2 mm^2 an element distribution analysis was made concerning sodium, zirconium, silicon, oxygen, potassium, chlorine and carbon an dthe results of these distributions both separately and together are presented in Figs. 5 *b*,…,5 *h*. The analysis carried out is seems as pitting blush points and some different affected areas in artificial saliva solution.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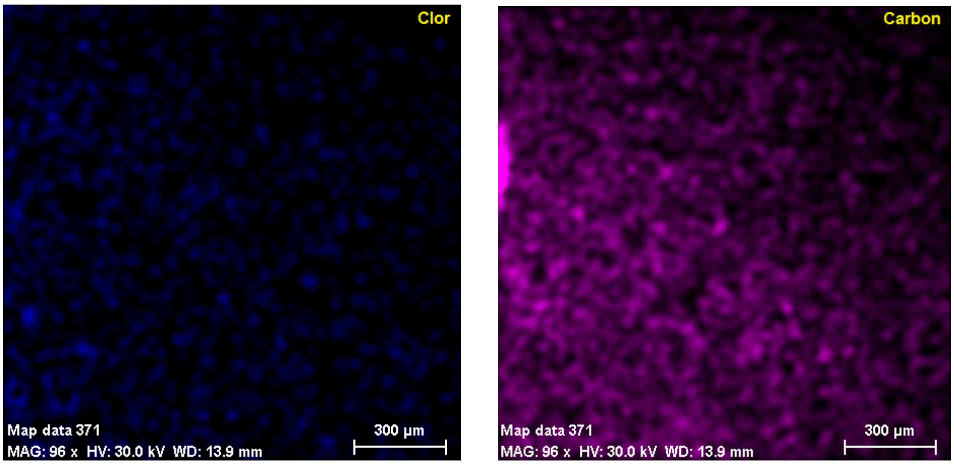

g *h*

Fig. 5 – Distribution of common chemical elements separate and together like Na, O, K, Zr, Si, Cl and C on an area of 1.2x1.2 mm^2 of material Filtek Z250 after being kept in artificial saliva solution for 30 Afnor days.

Composite dental material with a polymeric matrix and reinforced with micro and nano elements based on silica and zirconia present after immersion on artificial acid saliva few pitting points and also few compounds on the surface. After the chemical analyses and elements distributions on line or surface can be conclude that the compounds based on zirconium element are especially attacked and corroded missing from the contact surface of the material. Tough conditions applied on the material surface by corrosion resistance point of view partially can explain the material behavior.

4. Conclusions

The Z250 composite dental resign with a polymeric matrix and reinforced with micro and nano elements based on silica and zirconia present after immersion on artificial acid saliva few pitting points and also few compounds on the surface. After the chemical analyses and elements distributions on line or surface can be conclude that the compounds based on zirconium element are especially attacked and corroded missing from the contact surface of the material. Tough conditions applied on the material surface by corrosion resistance point of view partially can explain the material behavior.

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COMPORTAMENTUL MATERIALULUI COMPOZIT DENTAR FILTEK Z250 LA IMERSIA ÎN SALIVĂ ARTIFICIAL

(Rezumat)

Răşinile compozite dentare sunt des utilizate în domeniul restaurărilor datorită proprietăților deosebite mecanice, de compatibilitate şi prelucrare. Testele de rezistență la coroziune în salivă artificială îmbunătățesc utilizarea şi aplicabilitatea acestor materiale deosebite. Microscopii cu scanare electronică şi analize EDAX au fost realizate pentru analiza suprafeței materialului. Rezultatele coroziunii, după imersia prelungită a materialului, recomandă acest material ca fiind o soluție deosebită pentru aplicațiile biocompatibile chiar dacă suprafața materialului este supusă unui process de piting prin care procente din materialul compozit ajung în mediul biologic.

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CORROSION RESISTANCE OF A DENTAL COMPOSITE RESIGNS IN ARTIFICIAL SOLUTIONS

BY

ANCA ALUCULESEI* **and CONSTANTIN BACIU**

“Gheorghe Asachi” Technical University of Iaşi,
Faculty of Materials Science and Engineering

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Abstract. Surface mechanical workability of dental light curing resigns before and during photo-activation process represent an important parameter in this composite material resistance at corrosion especially in artificial saliva or Ringer solutions. Some roughness aspects of the dental composite material surface on corrosion resistance are followed in this article using scanning electrons microscopy (SEM) and X-ray (EDAX) analyses.

Key words: corrosion, dental composite.

1. Introduction

Because of aesthetic appearance, dentists are using composite materials in anterior and posterior dental restorations. However, wear is a frequent phenomenon present in the oral cavity and one of the biggest problems related to dental composites. For this reason, the wear of dental

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*Corresponding author; *e-mail*: aluculesei_anca@yahoo.com

resin composites has been extensively studied (Leinfelder & Suzuki, 1999; Condon & Ferracane, 1996; Kawai & Leinfelder, 1995; Bayne *et al.,* 1992; Peutzfeldt & Asmussen, 1992; Jörgensen & Asmussen, 1978; Mair (1992) researcher identified two main wear mechanisms in dental composites: abrasion and attrition. Abrasion occurs during the sliding action involving two teeth with a third body (layer of food) between them transmitting the forces. Attrition occurs during the direct contact of opposing teeth, producing wear. The microstructure and properties of the materials and the conditions used determine the mechanism of the wear process and, consequently, the materials wear rate (Ferracane, 1995).

Some authors have studied the effects of some features of filler particles like arrangement, size and geometry and volume fraction in the wear resistance and hardness of particulate resin composites (Bayne *et al*., 1992; Turssi *et al*., 2005; Braem *et al.,* 1989). According to some studies, the wear resistance of the composites in the oral cavity depends on the space available between filler particles providing protection against food bolus. The presence of smaller filler particles reduces inter-particle spacing in the composite, improving its wear resistance (Bayne *et al*., 1992; Jörgensen & Asmussen, 1978; Soderholm & Richards, 1998). The use of particles in nano-size range as fillers in polymeric composites is increasing.

The presence of nano-particles improves mechanical and tribological properties of the materials, because of their high specific surface area to volume ratio. The use of nanoparticles can give rise to a material with a new behaviour, due to interfacial interactions, resulting in exceptional properties (Shi *et al*., 2004; Wang *et al.,* 1996).

Saliva is a liquid with a complex composition, which involves organic and inorganic groups and micro-organisms. Dental composite materials must resist to the oral cavity environment in contact with saliva. Some authors have studied the effects of fluids (artificial saliva, deionized water) on the mechanical properties of resin-based composites (Martin *et al.,* 2003; Concha *et al.,* 1996). Kanchanavasita (1998) observed that excess water acts as a plasticizer in resin-based materials. Moreover, Soderholm *et al.* (1996), Soderholm *et al.* (1984) detected particle removal from composites stored either in artificial saliva or distilled water. In this study we investigated the resistance in saliva of commercial dental composites containing nanoparticles as reinforcement elements.

The main objective was to identify the effect of storage in artificial saliva on dental composites properties. So, samples were tested without any treatment (control) to compare with samples stored in artificial saliva. The microstructure and surface of the materials were studied by scanning electron microscopy (SEM) and EDAX in order to characterize the surface wear mechanism.

2. Experimental Results

Dental composite material, Filtek Z250, was subjected to immersion for 30 days under artificial saliva solution Fusayama. In Fig. 1 are two representative SEM microscopy material surface conditions Filtek Z250 after immersion in artificial saliva Fusayama these two powers of magnification are of 100x and 1000x.

There is an area affected by the artificial environment in which the material was introduced by exclusion of material (similar to pitting holes) and the emergence of many compounds on the surface of dental composites. In microscopy from Fig. 1) can be seen a selection in the lower right, framed by colored lines, hitting an area that coincides with a material such material arising from operation of mechanical stretching and fastening the composite material.

On the material appeared after prolonged contact with artificial saliva solution Fusayama and numerous holes pitting size from 1 to 5 µm. Micron size and is observed in many compounds the reaction whose nature will be determined by EDAX analysis of the surface material.

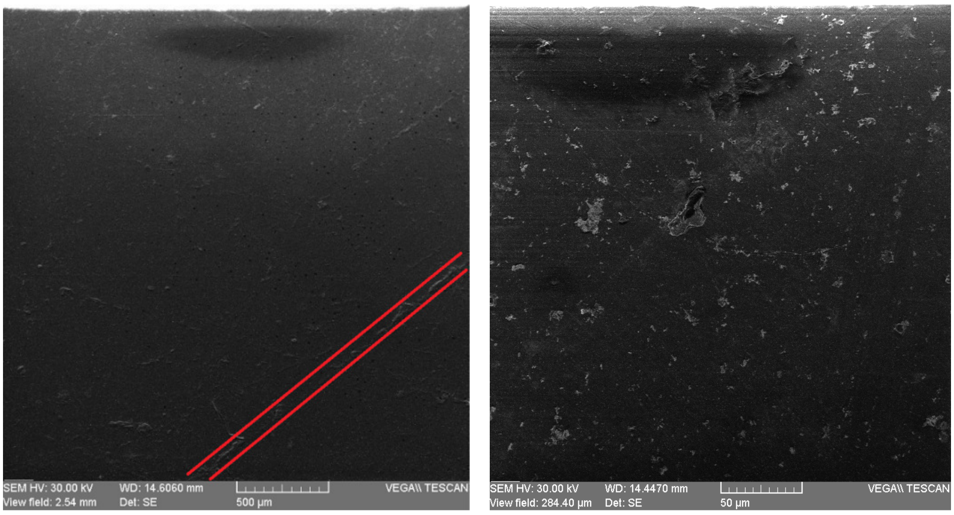


Fig. 1 – SEM microscopy of the surface material Filtek Z250 after immersion in saliva solution Fusayama; *a* – 100x; *b* – 1000x.

Chemical analysis of material on a surface determine the qualitative presence of 1.2x.12 mm^2 elements more chemical energy of their corresponding links as shown in Fig. 2, all common elements dental composite material, carbon, oxygen, silicon and zirconium, and the solution Fusayama artificial saliva, sodium, chlorine, potassium, phosphorus and calcium with 3 (Zr) 2 (Cl, Ca, K) and 1 (remaining elements) activation energy and participating in chemical bonds.

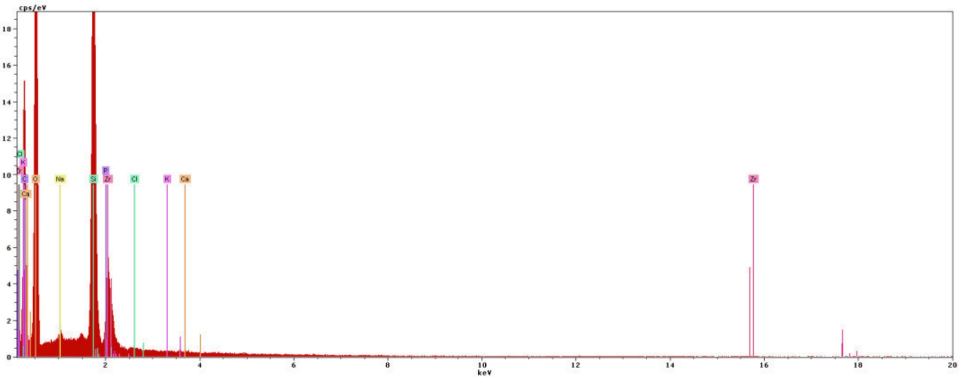


Fig. 2 – Energy spectrum of chemical elements on the material surface Filtek Z250 over a period of 30 days immersion in artificial saliva solution Fusayama

Table 1 shows the chemical composition of composite material on a surface area of 2.25 mm^2 material after immersion in artificial saliva solution for 30 days Fusayama. From the results of chemical analysis on the surface, Table 1, there is an oxidized state of the material represented through many oxygen compounds (74.4% and 78.84% by mass atomic percent) resulting in a drop in the percentage of silicon (at 7.89% percent atoms) and zirconium as well (from 0.59% atomic percent).

Table 1

Chemical Composition of Surface Material Filtek Z250 Over an Area of 2.25 mm^2 Material After Immersion in Fusayama Artificial Saliva Solution for 30 Days

Element	AN	Net	wt.%	norm. [wt.%]	norm.[%]	Error [%]
Oxygen	8	21108	74.405730	74.407220	78.838550	24.221760
Silicon	14	102207	13.074250	13.074510	7.891702	0.609075
Carbon	6	6557	8.757519	8.757694	12.360550	5.225150
Zirconium	40	432	3.150578	3.150641	0.585487	0.206998
Calcium	20	762	0.214220	0.214224	0.090613	0.035856
Sodium	11	502	0.168245	0.168249	0.124064	0.041327
Potassium	19	454	0.113371	0.113374	0.049157	0.031991
Phosphorus	15	455	0.076933	0.076934	0.042107	0.072010
Chlorine	17	166	0.037151	0.037152	0.017765	0.003513
		Sum:	99.998	100	100	

Compounds that appear on the surface based on artificial saliva solution are small, with small percentages of chemical elements components, and without stability on the composite surface are easily removed by washing with hydrogen peroxide.

Fig. 3 shows distributions of chemical elements are Na, Ca, K, Cl and Zr on a line of 130 µm from the surface of this material Filtek Z250 after immersion in artificial saliva Fusayama test.

Observing the formation of compounds on the surface based of NaCl, KCl or $CaCl_2$ and many other oxides. Element zirconium signal is weak and heavily masked compounds on the surface.

Filtek Z250 composite material behavior analysis continued by determining its behavior immersed in a Ringer type 1 solution for 30 days in similar conditions above the other two tests.

Using a supply voltage of the filament electron gun scanning electron microscope with 30 kV were carried out with a secondary electron detector surface electron microscopy Z250 material after 30 days of immersion in Ringer's solution to two power amplification 100 and 1000 times respectively. The images obtained are shown in Fig. 4 and shows a relative state affected by corrosion Ringer solution of the dental composite material by the formation of pitting holes (resulting in a significant loss of material depending on the size of corrosion holes) and by the emergence of compounds reaction on the surface Z250.

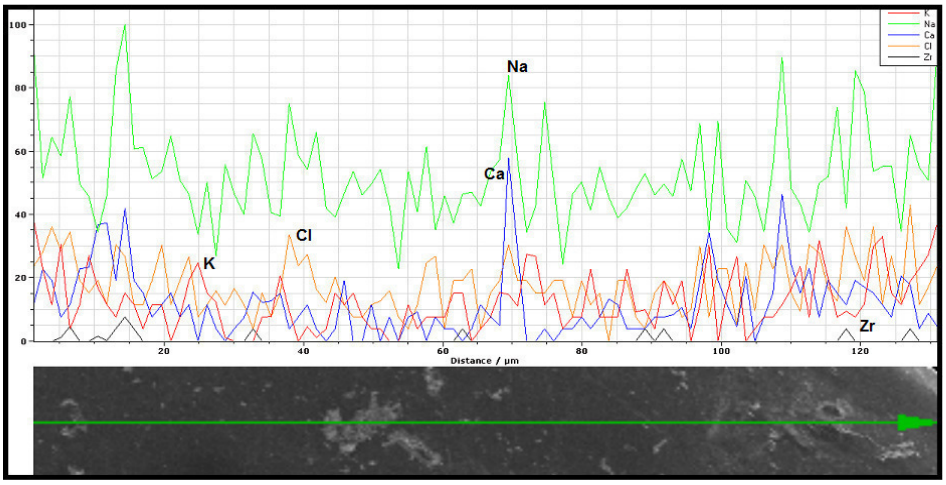


Fig. 3 – Distribution of chemical elements Na, Ca, K, Cl and Zr on a line of 130 µm from the surface of this material Filtek Z250 after immersion in artificial saliva Fusayama.

Electron microscopy shows the occurrence of pitting holes of different sizes implies a significant loss of passing the composite corrosion environment.

In this respect a 1x1 mm^2 area were observed an average of 5-7 holes corrosion size of circumference between 100 and 250 µm and a total of 55-60 holes between 1 and 100 µm as circumference.

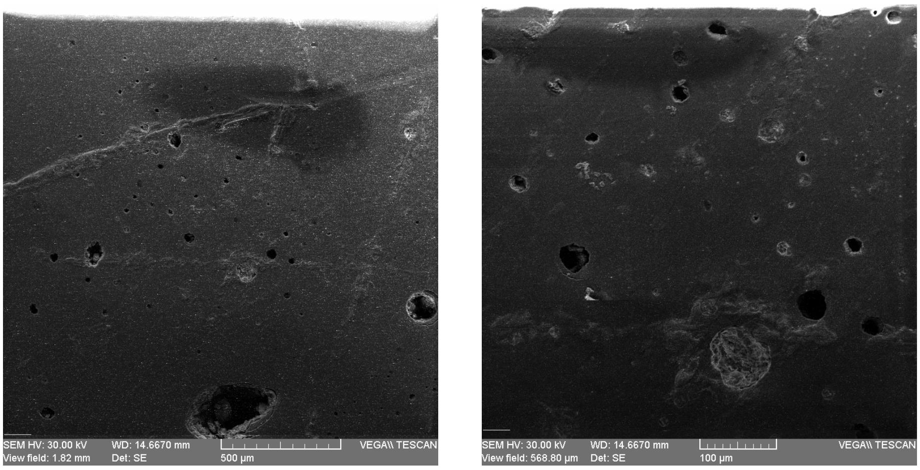


Fig. 4 – SEM microscopy of the surface material Filtek Z250 after immersion in Ringer's solution for different power amplification) 100x and b) 1000x.

Selecting the formation of reaction compounds is achieved in this case the directions imposed mechanical training material for photo-polymerization. Fig. 5 presents the energy spectrum of chemical elements in the material after immersion in Ringer's Z250.

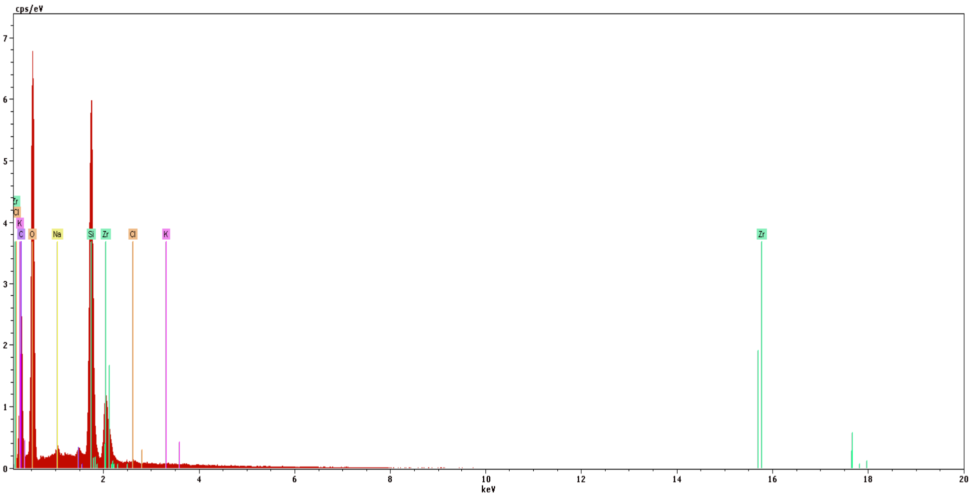


Fig. 5 – Energy spectrum of chemical elements in the material Filtek Z250 over a period of 30 days immersion in Ringer's solution.

Samples immersed in biological solutions had a circular diameter of 1 cm and a thickness of 10 mm with LED light-curing in the medical office. Since the preferential corrosion was observed on the surface of a material based on physical form of the material by spreading it with a spatula and the emergence of cute naked eye but the direction of stretching characterize jurisdictions to analyze the material is the material in the center of sample surface condition and test on its side to observe any differences in surface condition data clearly more disordered and rough edge. Chemical analysis were made on areas of 2.25 mm^2 in the central and marginal area of the material after its immersion in Ringer solution for 30 days and the results presented in Tables 2 and 3.

Table 2

The Chemical Composition of Surface Material Filtek Z250 over an Area of 2.25 mm^2 in the Central Area of the Material After Immersion in Ringer Solution for 30 Days

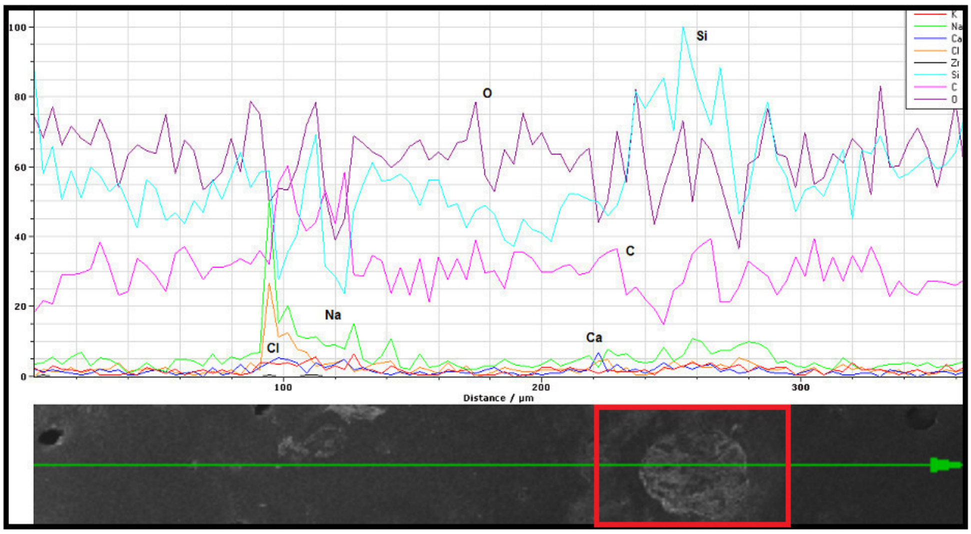
Element	AN	Net	wt.%	norm. [wt.%]	norm. [%]	Error, [%]
Oxygen	8	23662	49.99631	55.73542	66.62576	6.324707
Silicon	14	106416	26.95466	30.04881	20.46255	1.228897
Carbon	6	4309	5.024156	5.600883	8.918501	2.280675
Zirconium	40	447	4.188367	4.669153	0.978912	0.263891
Sodium	11	2796	2.129077	2.373475	1.974534	0.186050
Calcium	13	3466	1.080993	1.205081	0.854209	0.085826
Potassium	19	788	0.223671	0.249346	0.121972	0.036514
Chlorine	17	347	0.105695	0.117828	0.063564	0.032572
		Sum:	89.70293	100	100	

There is a difference mainly between the elements silicon (from 30.04 to 20.49 percent by weight) and sodium (from 2.37 to 7.23 percent by weight) for two selected areas illustrating the nature of the surface elements that characterize a more intense corrosion on the sample. In this extreme material Filtek Z250 applied as part of the restoration can become the most dangerous areas in terms of material corrosion and destruction of chemical compounds but may be considered a creative area points of failure, cracking and deterioration of the material resulting in further mechanical shocks. They observed an increase in the percentage of oxygen enrichment attributed to surface oxides.

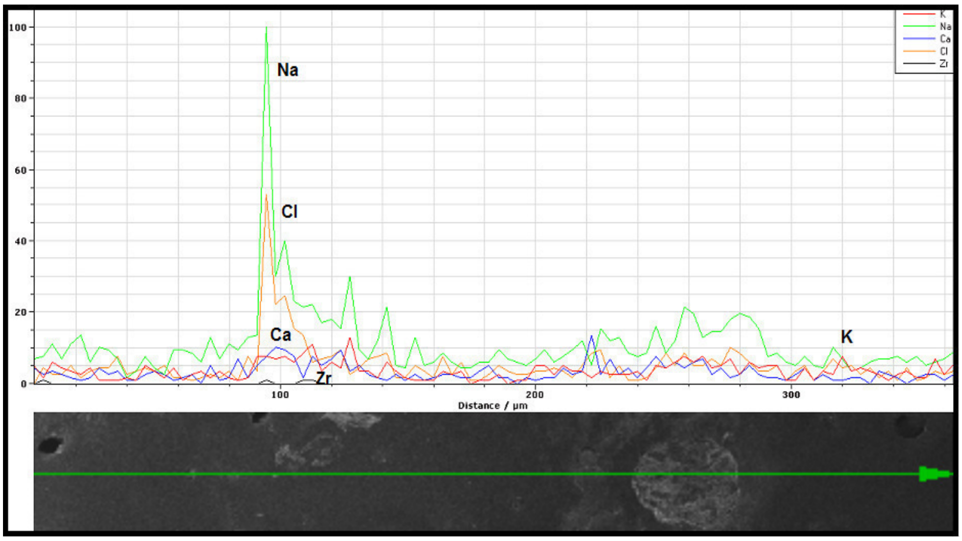
Table 3
The Chemical Composition of Surface Material Filtek Z250 over an Area of 2.25 mm^2 in a Marginal Area of the Sample Material After Immersion in Ringer for 30 Days

Element	AN	Net	wt.%	norm. [wt.%]	norm. [%]	Error, [%]
Oxygen	8	61078	69.811580	57.965320	67.453410	8.136067
Silicon	14	72846	24.685450	20.49660	13.587490	1.130367
Natrium	11	7435	8.717527	7.238259	5.861906	0.646002
Carbon	6	15061	8.085343	6.713349	10.406370	2.260222
Zirconium	40	137	6.142426	5.100124	1.040905	0.598897
Calcium	13	5890	2.586061	2.147235	1.481672	0.164387
Potassium	19	743	0.241941	0.200887	0.095660	0.037677
Chlorine	17	567	0.166466	0.138219	0.072587	0.035127
		Sum:	120.4368	100	100	

In Fig. 6 is shown the distribution of key chemical elements on the surface of dental composite material as the material and corrosion compounds formed. There are a characterized surface oxides and compounds of chlorine, sodium, potassium and calcium.



a



b

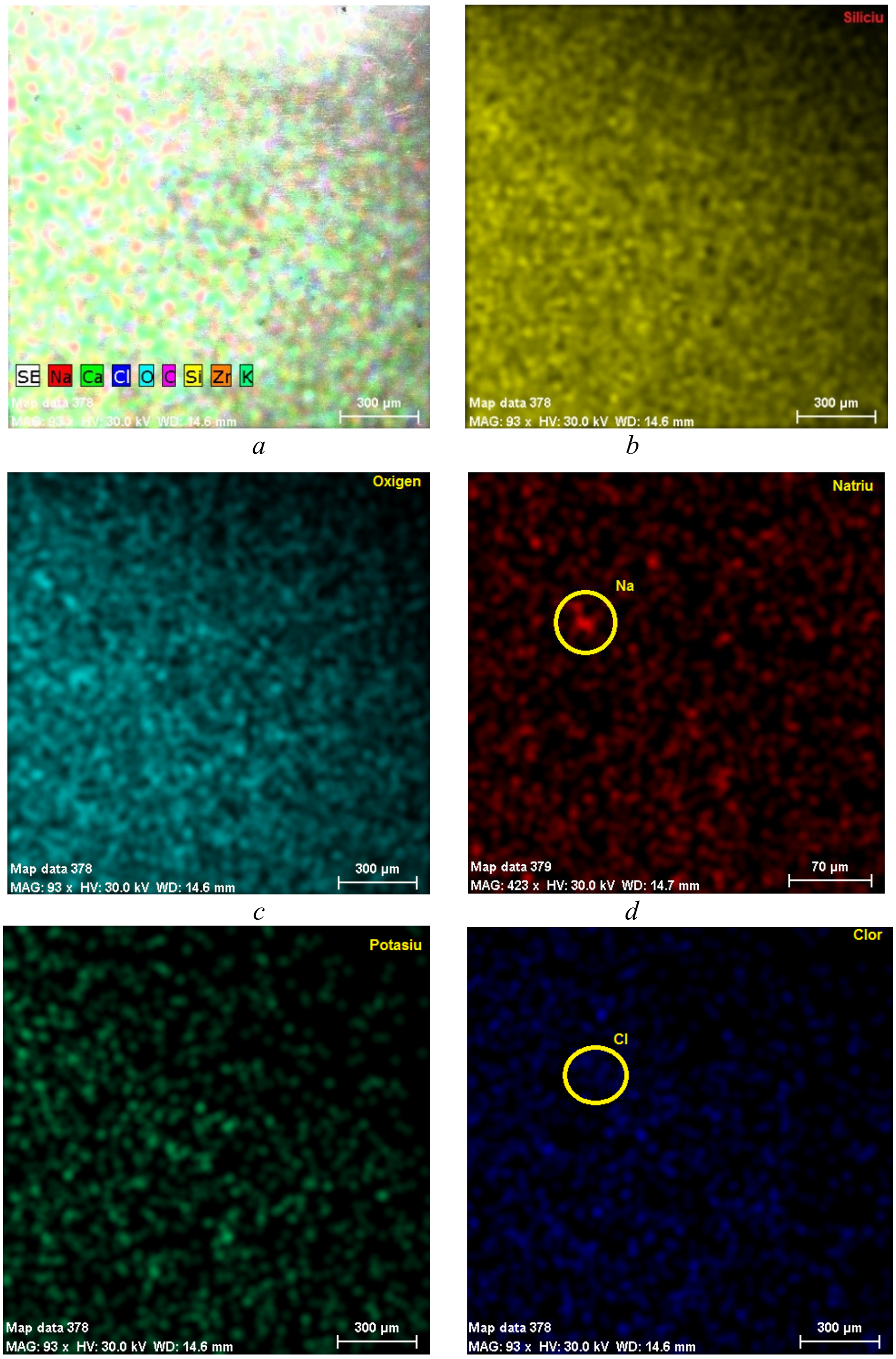
Fig. 6 – Distribution of elements on the material Filtek Z250 surface over a line of 350 µm material after immersion in Ringer solution for 30 days.

The area affected by corrosion is selected and an increase in the percentage of sodium and calcium and silicon oxide which makes the conclusion that the polymer matrix composite material has deteriorated especially in this case. Strong signals eliminating silicon, carbon and oxygen in the diagram from Fig. 6 can be seen more easily agglomerate chemical formations on the surface in Fig. 6 *b*.

The whole area has a very low signal zirconium and compounds formation is predominantly NaCl, KCl or $CaCl_3$.In figure 8 are presented separately and combined distributions of chemical elements like Na, O, K, Zr, Si, Cl and C an area of 1.2x1.2 mm^2 of material Filtek Z250 after being kept in Ringer solution for 30 days.

Fig. 7 shows a mapping of all chemical elements on the surface selected using different colors. In Fig. 7 *b* and *c* there is a cluster direction of SiO_2 composite material processing and in Fig. 7 *d* and *f* identifying compounds NaCl surface formation material. Following chemical and structural results obtained on the surface of composite material can be considered that they have changed both at micro and macro chemically and structurally.

Although the material formed after 30 days of immersion many chemicals compounds on the surface they were wash away easily by not being chemically bound to the composite based material.



a *b*

c *d*

e *f*

Fig. 7 – Distribution of the separate and combined chemical elements
Na, O, K, Zr, Si, Cl and C an area of 1.2x1.2 mm^2 of material Filtek Z250
after being kept in Ringer solution for 30 days.

Risks of prolonged exposure to this material in artificial solutions mentioned above is given by pitting holes that have appeared on the material they released different percentages of zirconium in the solution of saliva and directly affecting the material structure and its behavior after the various chemical applications and individuals.

2. Conclusions

A dental composite resign win nano to micro sized reinforcement particles as SiO_2 and ZrO_2 was tested by corrosion resistance point of view in artificial saliva and Ringer solution after an immersion period of 30 days. Corrosion effects type pitting holes or compounds were observed on the material surface after both immersions with not stable chemical compounds and a preferential distribution of affected areas on the mechanical made lines from the surface.

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REZISTENŢA LA COROZIUNE A UNOR RĂŞINE COMPOSITE DENTARE ÎN SOLUŢII ARTIFICIALE

(Rezumat)

Prelucrabilitatea mecanică a suprafeţei răşinilor dentare foto activabile înainte şi în timpul procesului de activarea reprezintă un parametru important în privinţa rezistenţei acestui material la coroziune în mod special în soluţii de salivă artificial şi soluţii Ringer. Câteva aspecte ale rugozităţii suprafeţei materialului compozit dentar din punct de vedere al rezistenţei la coroziune sunt urmărite în acest articol utilizând metode de analiză prin microscopie cu scanare de electroni (SEM) şi de raze X (EDAX).

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CHEMICAL PROCEDURES FOR METALLIC SURFACE PREPARATION FOR THIN COATINGS DEPOSITION PROCESS
PART II

BY

RAMONA HANU CIMPOEŞU[*] **and CONSTANTIN BACIU**

“Gheorghe Asachi” Technical University of Iaşi,
Faculty of Materials Science and Engineering

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Abstract. Continuing the work start on thin polymeric coatings deposition on metallic substrates as an improvement method of metallic materials, especially those used in the medical field as in contact body applications some few new chemical engraving methods were used to prepare the shape memory alloy wire surface for further thin metallic or non metallic films deposition.

Key words: shape memory alloy, polymer thin layer.

1. Introduction

Based on the number of published papers on Nitinol surfaces, especially recently, one might conclude that this issue indeed deserves serious attention. Various techniques and protocols have been used for surface treatments; among them mechanical and electrochemical treatments, chemical etching, heat treatments, conventional and plasma ion immersion implantation, laser and

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[*] Corresponding author; *e-mail*: ramonahanu@yahoo.com

electron-beam irradiation, design of bioactive surfaces, and a proper technique can easily be lost in that jungle of publications. Some of the procedures that were developed originally for pure Ti and their application to NiTi not only may not bring any improvement but, rather, can cause surface damage because of inevitable Ni involvement.

Surface modification and coating of Nitinol (an acronym for NiTi Naval Ordnance Laboratory), a family of nearly equiatomic NiTi alloys with shape memory and superelastic properties, is a subject of numerous recent studies directed at improving the material's corrosion resistance as well as its biocompatibility through elimination of Ni from the surface. This chemical element is known to be allergenic and toxic, though essential for the human body. Although it has been shown that the amount of Ni recovered in biological studies in vitro may be either very low from the beginning or drop to undetectable levels after a brief exposure to biological environments (Wever *et al.* 1998; Cui *et al.* 2005), 'the nickel case' keeps reappearing. Thus, the recent results obtained on commercial ready-to-use orthodontic wires showed that the Ni release varied in a wide range from 0.2 to 71 g cm^2 (Arndt *et al.* 2005). Moreover, it has been reported that the Ni release can actually significantly increase with time (Sui & Cai 2006; Kobayashi *et al.* 2005; Bogdanski 2005; Clarke *et al.*), maintaining a high level up to 8 weeks and even for a few months (Bogdanski, 2005; Clarke *et al.*), indicating the need for better understanding of the material/surface interface.

The electrochemistry of Nitinol is poorly explored. Until recently, there have been no studies on electro-polishing and anodizing of this material. This situation is gradually improving with the publications of papers on electro-polishing processes in various electrolytes (Pohl *et al.*, 2004), and anodizing in various solutions and voltage regimes (Shi *et al.*, 2007). The effect of chemical etching (passivation) in HF+HNO_3 aqueous solutions on Nitinol surface chemistry has also been studied (Shabalovskaya *et al.*, 2003).

In this study few chemical surface modification methods are analyzed to improve the adhesion on Nitinol with further superficial thin layers that can be deposited on them.

2. Experimental Details

A superelastic echiatomic NiTi shape memory alloy (http://www. saesgetters. com) acquisitioned from Saes Getters Group was prepared through different engraving solution for thin layers deposition operation. The shape memory alloy has 50.5% Ni and 49.5% Ti mass percentages and an oxide layer on the wire surface. The material was "attack" with different solutions like 34% H_2SO_4 + 12% HCl, 48% H_2SO_4 + 18% HCl and HF40% + HNO360%. Microstructure of alloy surface before and after chemical treatments were analyzed using SEM equipment with a SE detector and 30 KV alimentation tension of the gun lamp. Using an EDAX equipment chemical analysis were performed on 2.5 mm^2 surfaces following especially the Ni and Ti percentage evolution and also the other elements from the surface like oxygen, fluorine, sodium or carbon.

3. Experimental Results

Various techniques and protocols to have been used for surface treatments; among them mechanical and electrochemical treatments, chemical etching, heat treatments, conventional and plasma ion immersion implantation, laser and electron-beam irradiation, design of bioactive surfaces, and a proper technique can easily be lost in that jungle of publications. Some of the procedures that were developed originally for pure Ti and their application to NiTi not only may not bring any improvement but, rather, can cause surface damage because of inevitable Ni involvement.

The surface state of shape memory alloy NiTi is presented in Fig. 1 at a 250x power amplification of the image and a 50 µm scale. Can be observing a smooth surface of the material obtained from the element manufacturing that had a preparation necessity for better adhesion of the superficial layers ready for deposition.

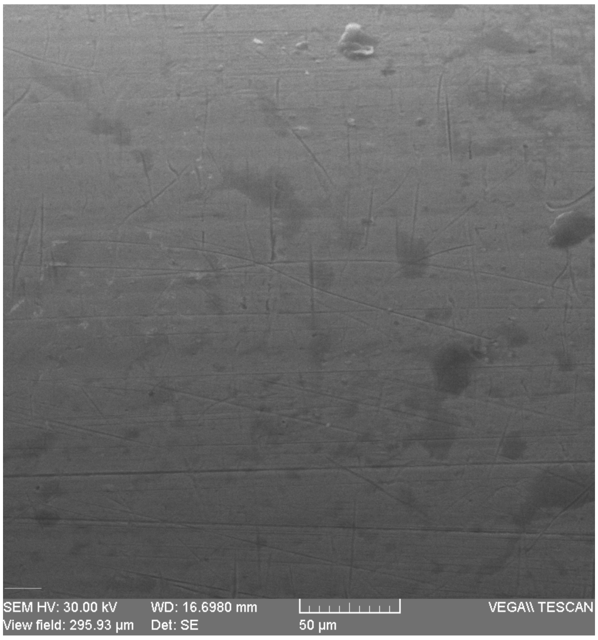
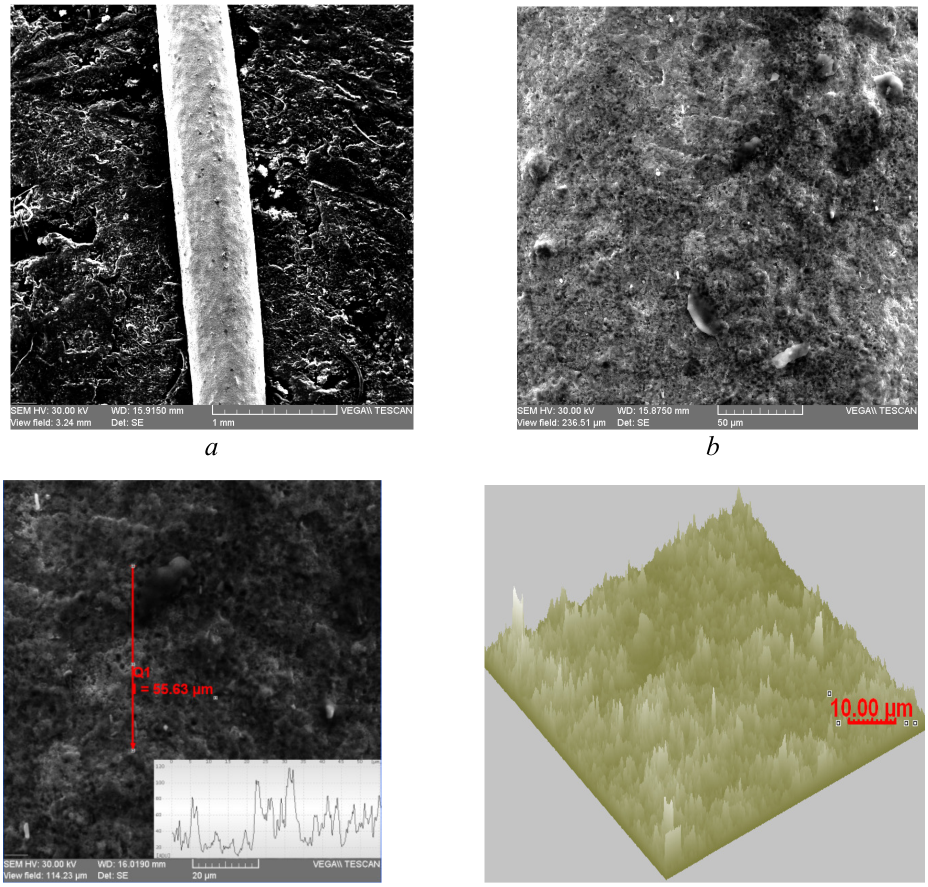


Fig. 1 – SEM microscopy of NiTi surface as taken at a 250x power amplification.

Further the chemical etching was made using the same engraving method to process the material surface in a more concentrated solution of 48% H2SO4 18% HCl, and the results are shown in Fig. 1 through electron microscopy, changes in light intensity and 3D surface analysis. As shown in Fig. 2 *a* and *b* the attack on this solution of the surface material was manifested more violent on the smart material surface affecting at least the surface of the alloy more intensively.



a *b*

c *d*

Fig. 2 – NiTi shape memory alloy surface with electron microscopy at different amplification powers; *a*) 100 x; *b*) 1000 x variation a in light intensity on the surface and a length of 55 µm; *d*) 3D analysis of the surface material chemically etched.

Change in light intensity variations was performed on the same distance as the first case (55 µm) showing a larger variation between 20 and 120 ADU field describes this area as more affected than if the surface of the diluted solution in and out of the variation original surface, Fig. 2 *c*, well. This is confirmed by the 3D surface analysis, Fig. 2 *d*, where the same scale of 10 µm of the surface is unchanged larger and deeper than the first case, the surface changes that cause material loss and destruction of property surface of the substrate before the deposition operation.

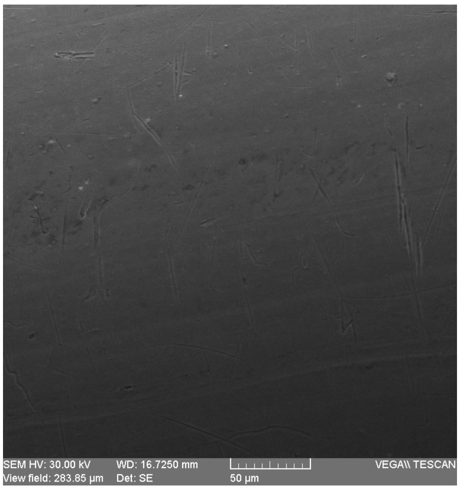
Table 1 is presenting the chemical composition of surface material by chemical etching were seen in a percentage loss of titanium, an element that has passed the acid solution.

Tabel 1

Chemical Composition of the Shape Memory Alloy Surface After his Immersion in Solution of 48% H_2SO_4*+18% HCl*

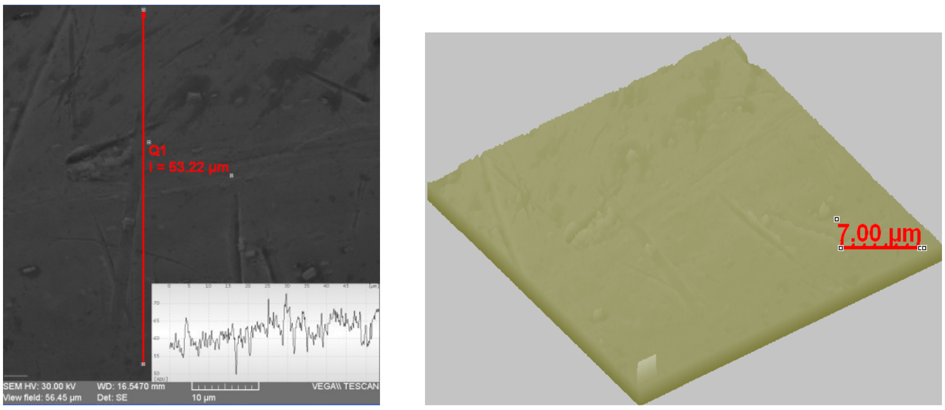
Element	AN	Net	wt. %	norm. wt. [%]	norm. [%]	Error [%]
Nickel	28	59001	48.56184	51.5174	43.61972	1.242112
Titanium	22	89438	43.85844	46.52775	48.2921	1.236405
Carbon	6	1438	1.842694	1.954844	8.088184	0.403659
		Sum:	94.26297	100	100	

Attempts of NiTinol engraving continue with processing the material surface in $HClO_4$ solution at a temperature of 65ºC for 60 minutes. Surface conditions are represented in Fig. 3 by electrons microscopy, *a*) 100x and *b*) 5000x, light intensity distribution in *c*) and 3D surface analysis.



a

b



c *d*

Fig. 3 – SEM electron microscopy of NiTi superelastic alloy surface at various power amplifier; *a*) 1000 x and *b*) 5000 x after immersing it in $HClO_4$ solution at a temperature of 65°C for 60 minutes maintaining time.

Changes in light intensity falling in 55-70 ADU range relatively different from the initial state of the surface material, fact that does not recommend this surface for deposition because the initial fall in the surface is properly etched, Fig. 3*d*. Table 2 present the chemical composition of surface material that is observed as a high percentage of oxygen due to surface oxidation, especially of titanium, which decreased in weight percentage.

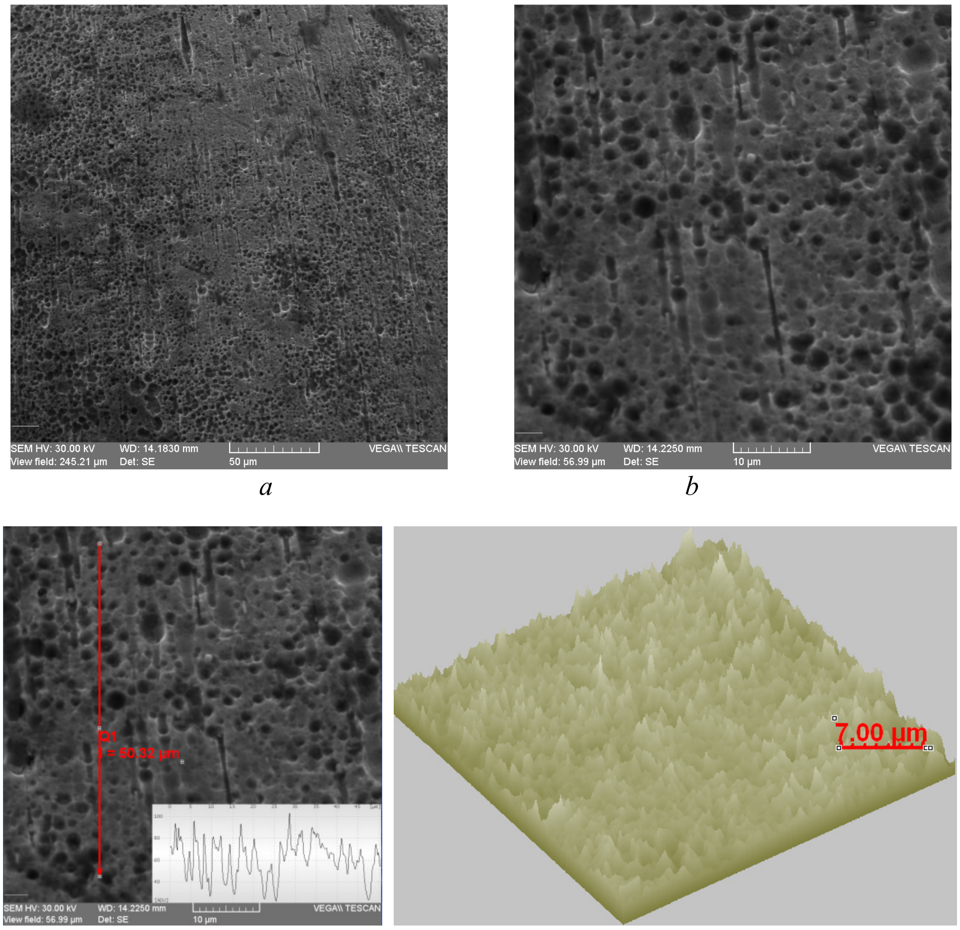
Table 2

Chemical Composition of the Alloy Surface After Immersion of NiTi in $HClO_4$ Solution at a Temperature of 65°C for 60 Minutes Maintaining Time

Element	AN	Net	wt.%	norm.[wt.%]	norm. [%]	Error [%]
Nickel	28	59001	48.56184	51.5174	43.61972	1.242112
Titanium	22	89438	43.85844	46.52775	48.2921	1.236405
Oxygen	8	1438	1.842694	1.954844	8.088184	0.403659
		Sum:	94.26297	100	100	

Finally we used an acid-HF40% + HNO360% solution and also the temperature of 65ºC time of 60 minutes. The material is presented in Fig. 4 by electrons microscopy technique at different amplification powers *a*) 1000x and *b*) 5000x and size effects are observed in this acidic solution like craters between 0.1 and 5 µm on the entire surface.

Light intensity falling on initial domain and have a very close variation to the original surface of shape memory alloy wire even though now the material is now heavily engraved. The 3D microscopy of the material, Fig. 4 *d* shows a uniform surface engraved with deep craters on average, Fig. 4 *c*, which can hold an average proper polymeric material suitable immersion method.



a *b*

c *d*

Fig. 4 – Electron microscopy analysis - SEM of surface of the shape memory material after immersion in solution HF40% + 60% HNO3 at 65°C for 60 minutes at two amplification powers; *a*) 1000x and *b*) 5000 x.

Given respect for shape, size and uniformity of surface material effects on the shape memory material surface the HF40% + HNO_3 60% solution is most proper of the acid solutions for etching the surface of superelastic nitinol material. The chemical composition shows an intense surface material fluoridation, fluoride element being beneficial for medical applications of metallic and nonmetallic materials (Sui & Cai, 2006), but whose influence on subsequent deposit of shallow surface layers is not sufficiently investigated.

Table 3

Chemical Composition on the Surface of Titanium Alloy After its Activation Process in Solution HF40% + 66% HNO_3 at 6°C for 60 Minutes

Element	AN	Net	wt.%	norm. [wt.%]	norm. [%]	Error [%]
Nichel	28	59995	49.25716	48.37716	34.41047	1.259201
Titan	22	85391	38.52161	37.8334	32.98836	1.0895
Fluor	9	400	11.15141	10.95219	24.06708	3.495825
Oxigen	8	1939	2.074414	2.037354	7.081523	0.420884
Clor	17	276	0.814443	0.799893	1.452569	0.115832
		Sum:	101.819	100	100	

Atomic percentages of titanium and nickel are still keeping a close proportion of properties suitable for shape memory alloys even if it is only the surface of this material. Chemical etching and electro-polishing of NiTi can be used for surface structuring as well.

The research on the surface of nitinol material preparation by chemical methods continued in a further article using other attack solutions also observing the microstructural surface aspect and chemical behavior in the same time with observing the variation of TiO thin layer.

4. Conclusions

Trying to improve the surface properties of these materials for depositions of superficial thin layers is considered a solution among the increase and evolves of TiO thin layer. Different engraving solution was used to improve the surface of material for adhesion with thin deposited layers the results being based on micrographic analyze (macro and micro areas analyzed) and chemical composition observation at the surface as well. Nitinol materials are widely used in the medical field, many applications being in direct contact with the human body.

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PROCEDURI CHIMICE PENTRU PREGĂTIREA SUPRAFEȚELOR METALICE ÎN VEDEREA DEPUNERII DE STRATURI SUBȚIRI

Partea a II a

(Rezumat)

Continuând o muncă începută privind depunerile subțiri polimerice pe substraturi metalice ca metodă de îmbunătățire a materialelor mecanice, în special cele utilizate în domeniul medical sub formă de aplicații în direct contact cu corpul uman, câteva metode chimice noi de gravare au fost utilizate pentru pregătirea suprafeței firului din aliaj cu memoria formei în vederea acoperirii acestora cu filme subțiri metalice sau nemetalice.

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INVESTIGATION OF NITINOL WIRES UNDER ELECTRO-CORROSION SOLICITATIONS IN ARTIFICIAL SALIVA

BY

RAMONA HANU CIMPOEŞU* **and CONSTANTIN BACIU**

“Gheorghe Asachi” Technical University of Iaşi,
Faculty of Materials Science and Engineering

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Abstract: Even the mouth behavior as a function is very complex and hard to reproduce we can extract some information from electro-corrosion tests of biomedical materials like nitinol used in saliva mediums like Afnor. Special materials, like nitinol, have many applications in different fields like medical. In this work, using potentiostat equipment and a SEM (scanning electron microscope), we analyze the alloy Ni-Ti behavior in solution of artificial saliva type Afnor.

Key words: nitinol, electro-corrosion.

1. Introduction

As will be shown in this paper superelasticity can even be considered part of the shape memory effect (EMS) (Duerig T.W. *et al*., 1990). The shape memory and superelaslicity effect are particularly pronounced in Ni-Ti alloys named usually nitinol (most used s.m.a. in medical applications). While the shape memory effect in Ni-Ti alloys has been described many times (Hodgson

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*Corresponding author; *e-mail*: ramonahanu@yahoo.com

DE, Wu M.H. & Biermann R.J., 1990) every few papers can be found describing superelasticity and its applications. Superelasticity is an isothermal event (Duerig *et al.*, 1996; Birman, 1997), therefore, applications with a controlled temperature environment are especially successful. As body temperature is extremely well controlled, superelastic elements have been used for medical applications first.

Even today, most applications of superelastic Ni-Ti wires are related to the human body in one way or another. The term "superelasticity" is used to describe the property of certain alloys to return to their original shape upon unloading after a substantial deformation. Superelastic alloys can be strained ten times more than ordinary spring materials without being plastically deformed. This unusually large elasticity is also called pseudoelasticity, because the mechanism is nonconventional in nature, or transformational superelasticity because it is caused by a stress induced phase transformation.

The first superelastic application was as orthodontic arch-wire (Fig. 1). The biggest advantages that Ni-Ti provides over conventional materials obviously are the increased elastic range and a nearly constant stress during unloading (Wu & Lin, 2000). The first reduces the need to retighten and adjust the wire and provides the clinician with a greater working range. The second tends to decrease treatment time and increase patient comfort. Temperature changes induced during the ingestion of cold or hot food change the stress level of the wire, which apparently can accelerate tooth motion. Another successful superelastic application is the Mammalok needle wire localizer, used to locate and mark breast tumors so that subsequent surgery can be more exact and less invasive. A hook shaped Ni-Ti wire straightens when it is pulled into a hollow needle (Mantovani, 2000). The needle is then inserted into the breast using a mammogram as a guide to the location of the lesion.

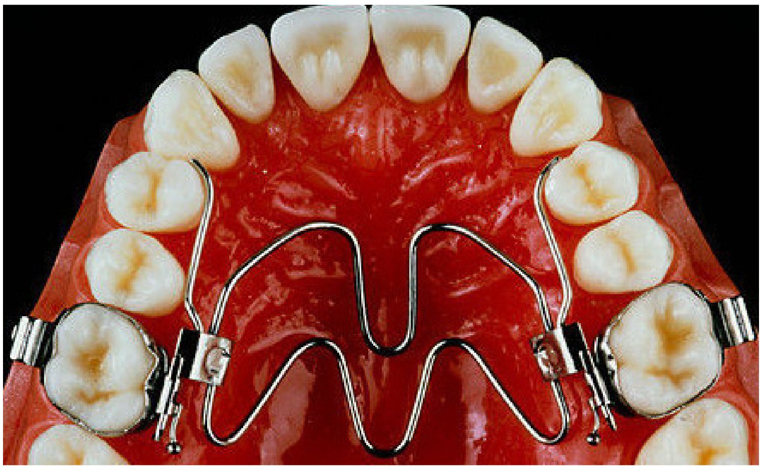

Fig. 1 – Application of superelastic Ni-Ti wires for orthodontics.

At the right location the wire is pushed out (the needle, thereby deploying itself around the lesion. If the mammogram after placement shows that the needle was improperly positioned, the superelastic hook can be pulled back into the needle and repositioned. This is done in radiology. The patient is then taken to the operating room for surgery. A third successful medical application is the guide wire, which is passed through blood vessels and used as a guide or catheters (Pelton *et al.,* 2000; Van Humbeeck, 1997).

Eyeglass frames using temples and bridges made from superelastic Ni-Ti wires are getting increasingly popular, particularly for sports and children's glasses. For the temples, the pieces that set over the ear and along the side of the head to connect to the front of the frame, material with sufficient stiffness at temperatures down to –20°C (*e.g.* for skiers) is desirable (Shabalovskaya, 1995). The bridge, the part that connects the two glass rims, on the other hand should show maximum elasticity to prevent permanent distortion of the frame when accidentally deformed. As conclusion, superelasticity in Ni-Ti wires caused by the formation of stress induced martensite. This transformational superelasticity is about ten times higher than the elasticity in ordinary materials. It is strongly temperature dependent. Therefore, the most successful applications of superelastic wires are medical or other applications that work in a narrow temperature range.

In this study we analyzed the corrosion resistance of a superelastic material nitinol under wire shape in an artificial saliva environment. The investigations take place with potentiostat equipment and a scanning electrons microscope.

2. Experimental Procedures

The investigated material is a wire, 700 μm in diameter produce by Saes brand with technical properties presented in Table 1.

Table 1

Superelastic NiTi Wire Properties (http://www.memry.com)

As (Fully annealed)	-15
Nominal Loading plateau stress@3% strain, in Austenite	500 MPa, 72,500 psi
Nominal Ultimate Tensile Strength in Austenite	1250 MPa, 181,000 psi
Min. elongation to failure in Austenite [%]	10

Corrosion behavior was made through fast electro-chemical tests and by dynamic potentiometry. Potential measurement in open circuit and potentiodynamic polarizations was realized with a potentiostat Volta Lab 21 (Radiometer, Copenhagen) presented in next figure (Fig. 2)). Data processing and acquisition was realized with Volta Master 4 software. A three electrodes cell equipped with agitation system was used with specification that the electrodes, made with cylindrical shape, was put in a Teflon holder which permit connection to spinning electrode of electro-chemical system.

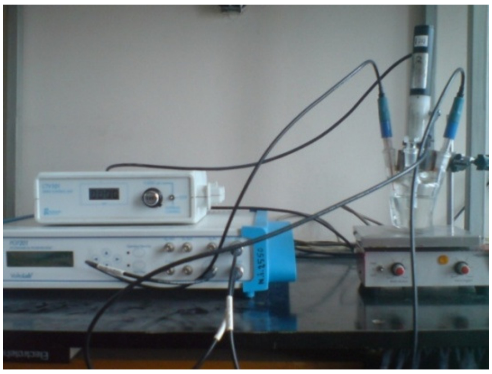

Fig. 2 – Potentiostat equipment used in electro corrosion tests.

As auxiliary electrode was used a platinum electrode and as reference electrode a satiated calomel. Measurements take place at 28°C, and the electrolyte was naturally aerated, the linear polarization curves was registered at a scanning rate of electrode potential of 1 mV/s, in a potential domain of ± 150 mV round of open circuit potential. Cyclic polarization curves was registered with a 10 mV/s rate in potential domain (–700 …+1500 mV) (Hanu Cimpoesu *et al*, 2009).

As corrosion medium an aerated solution of Afnor artificial saliva (Normalization 591-141) (http://ljs.academicdirect.org) was used, having the composition presented in table 2 and pH = 8.5.

Table 2

Electrolytic Solution of Artificial Saliva for Electro-Corrosion Test

Artificial saliva/ Compounds	NaCl g/l	KCl g/l	Na_2HPO_4/ 2 H_2O g/L	$NaHCO_3$ g/L	KSCN g/L	Urea g/L	$CaCl_2$ g/L	NaH_2PO_4 H_2O g/L	Na_2S g/L
Afnor	0.4	0.4	-	0.69	-	1	0.65	0.69	0.05

After the electrochemical treatments, a study of the modifications of the alloys surface was performed on a VEGA-TESCAN Scanning Electron Microscope equipped with QUANTAX Bruker AXS Microanalysis system, find on the SIM Faculty laboratories Iasi. The microscopy's was realized using a Secondary Electrons detector at different scales to present the corrosion effects at 30 kV power supply of the tungsten filament. The images were taken from a

10 mm distance of samples, for SEM results and by 16 mm distance between samples and AXS detector for chemical analysis, producer best performance recommendations.

3. Results and Discussions

To realize this test a special sample holder, describe above, was use. After the electro-corrosion test the wires sample was investigated with a scanning electrons microscope to analyze the material surface and the effects of corrosion. Material behave normally in solution having a high resistance at corrosion in time but at reduce current values passing through the alloy exhibit a pitting corrosion phenomena which can be observed from microstructures realized with SEM in Figs. 3 *a* for ensemble 3 *b* and 3 *c* for pitting holes details.

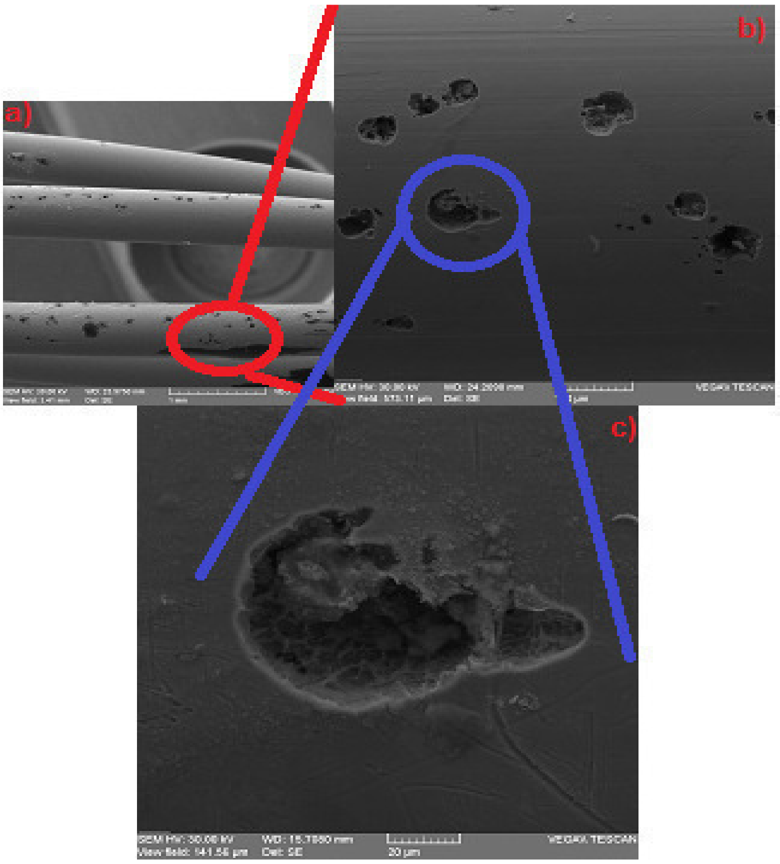

Fig. 3 – SEM microcopies at: *a*) 100x; *b*) 1000x and *c*) 5000x magnified power of a superelastic nitinol after corrosion in artificial saliva.

After the corrosion tests using specialized software we obtain the Tafel diagram, presented in Fig. 4, and cyclic diagram, presented in Fig. 4, that characterize the superelastic nitinol investigated corrosion behavior.

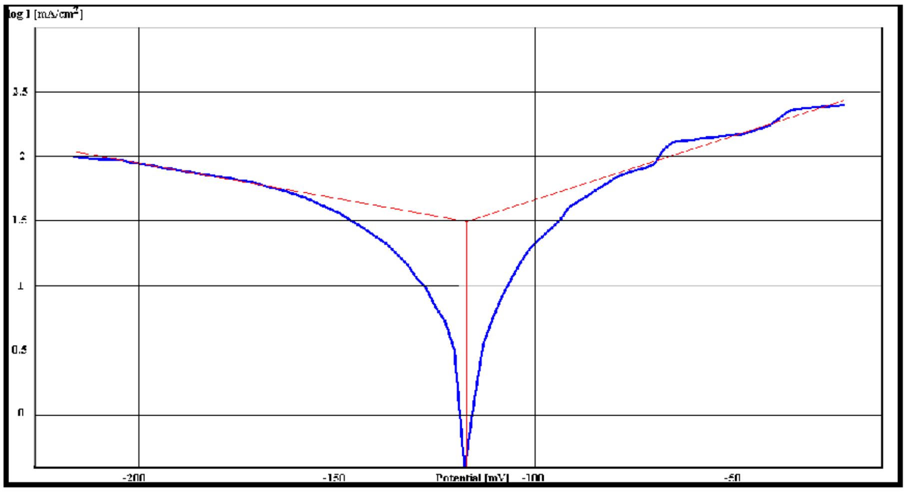

Fig. 4 – Tafel diagram of nitinol wire behavior in artificial saliva.

The registered results present a proper corrosion resistance in this medium with a tension of –117,3 mV for a current by 0 A, the corrosion current has 31,58 μA/cm^2 value, polarization resistance Rp=866,22 Kohm.cm^2, and the anodic and cathode branches Ba=101,7 mV respectively Bc= –184,5 mV.

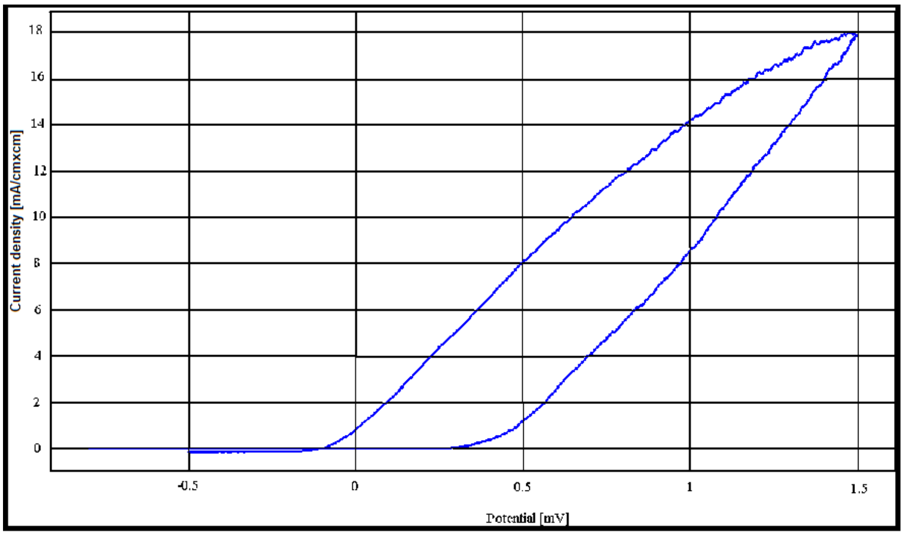

Fig. 5 – Cyclic diagram of analyzed alloy in artificial saliva.

Corrosion rate registered is 0,57 μm/year, a small corrosion rate, but dangerous for an alloy propose for medical applications. Analyzing the cyclic diagram can be observed the pitting character of corrosion having a hysteresis type diagram with the comeback on the left top of the diagram. Pitting corrosion represent a dangerous type of materials behavior causing big amounts of material loss in environment, in our case artificial saliva, decreasing the biocompatibility functions of the nitinol.

4. Conclusions

A superelastic nitinol wire was investigated by electro-chemical point of view in artificial saliva solution. Pitting holes are numerously and presenting material loss, especially nickel, fact that can reduce the biocompatibility property of the alloy. Further investigation is necessary to establish the real quantity of nickel that passes through in solution. Corrosion resistance of this alloy is appreciable as very good in artificial saliva solution with reduce amounts of loss per year (nanometer sizes) in the immersion case but became dangerous, with a pitting character, at current passing through.

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ANALIZA FIRELOR DE NITINOL LA SOLICITĂRI ELECTRO-COROZIVE ÎN SALIVĂ ARTIFICIALĂ

(Rezumat)

Chiar dacă comportamentul cavităţii bucale luat ca o funcţie este foarte complex şi dificil de reprodus se pot extrage informaţii importante din testele de electrocoroziune a materialelor biomedicale cum ar fi nitinolul testate în medii de tip salivă cum ar fi cea Afnor. Materialele cu proprietăţi speciale cum ar fi nitinolul îţi găsesc numeroase aplicaţii în diferite domenii cum ar fi şi cel medical. În această lucrare folosind un echipament Potenţiostat şi un SEM (microscope cu scanare de electroni) a fost analizat comportamentul aliajului NiTi în soluţie artificial tip Afnor.

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THERMAL CONDUCTIVITY OF A Ti- BASED ALLOY

BY

ALINA COSTAN * **and ADRIAN DIMA**

“Gheorghe Asachi” Technical University of Iaşi,
Faculty of Materials Science and Engineering

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Abstract. Heating on room temperature to 150°C temperature range the material $TiAl_6V_4$ exhibit a proper manifestation through reduce thermal conductivity, small dilatation or depth penetration. A titan grade five material for dental implants behavior was analyzed by thermal conductivity point of view. The thermal properties were analyzed by differential dilatometry and thermal conductivity at room temperature and under heating process during time. The results are comparing with properties of other dental materials like enamel, dentin, amalgam, gold, porcelain, glass, PMMA polymer or $ZnPO_4$ cited from the specialty literature.

Key words: dilatometry, dental alloys, thermal conductivity.

1. Introduction

First of all the used alloys materials have to be biocompatible defined as the ‘‘ability of a material to perform with an appropriate host response in a specific application” (Hauman & Love, 2003) and there are always some sort of interaction between the physiological environment and the foreign body – the response being strongly influenced by the surface properties of the implant

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*Corresponding author; *e-mail*: alina0384@yahoo.com

material. Over the last decade titanium based implants have become more important in all areas of modern medicine especially implant logy.

Commercially pure Ti and its titanium– aluminum–vanadium alloy $TiAl_6V_4$, titan grade 5, have been used as implants due to their excellent biocompatibility and ability to allow bone-implant integration. $TiAl_6V_4$ has been also used preferentially in orthopedic- prosthetic replacement due to its added mechanical strength, while commercial pure Titanium has been employed for some dental implants (Ask *et al.*, 1988). Chemical element Ti forms a biocompatible surface oxide layer capable of interacting with surrounding biological fluids and cells when implanted in situ (Kasemo & Lausmaa, 1986; Ratner *et al.*1990). This layer, composed primarily of TiO_2, is found superficially on both commercial pure Ti and $TiAl_6V_4$ metals (Milossev *et al.* 2000).

Generally the thermal properties of implants and implant materials are characterized under strongly simplified heating and environmental conditions. Thermal fatigue loading and the resulting microstructural changes on the implant surface may strongly affect the interface with the living tissue.

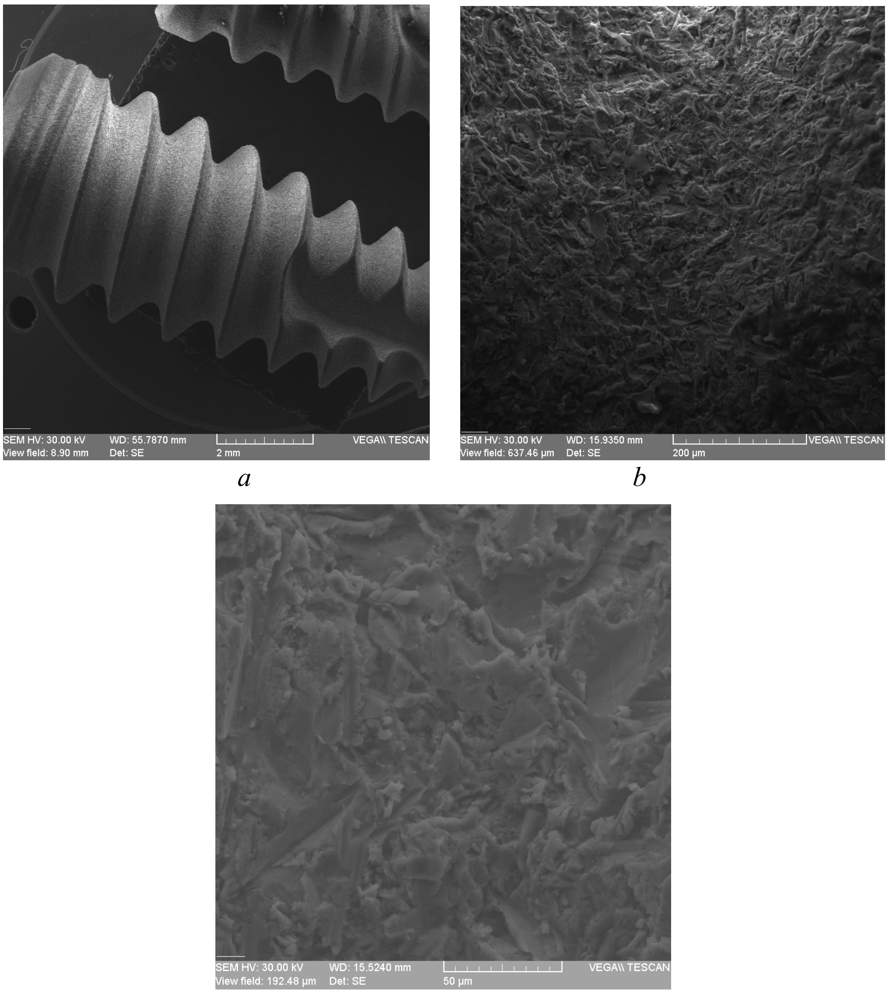
A multiplicity of implant surface forms exist, engineered with mechanical features that physically interlock the implant with bone. Various strategies have been utilized to improve bone integration of titanium-based implants. However, the effects of chemical modifications (Pettit et al. 1992; Sittig *et al.* 1999; Wen *et al.* 1998) of the surface oxide of Ti-alloys on their physical, chemical and biological properties have not been extensively studied. The objective of this investigation was to examine the effects of different heating rates apply on $TiAl_6V_4$ to analyze the material thermal conductivity property.

In this paper some thermal conductivity characteristics of $TiAl_6V_4$ dental alloy are presented and comment to establish thermal behavior of these materials used in medical applications.

2. Experimental Procedures

Thermal analyses of a $TiAl_6V_4$ alloy were carried out by dilatometry (using Linseis L75 equipment) and thermal conductivity at room temperature (with TCi device and typical test preparation (Perju *et al.* 2010; Achitei *et al.* 2010)) point of view using differential equipments. Chemical composition of the titanium based alloy was obtained on a spectrometer Foundry Master showing a Titan 5 type composition (Perju *et al.* 2010). The test temperatures were from room to 150°C concerning calorimetry and dilatometry properties and at room temperature for thermal conductivity. Samples of 46 mm length and 5 mm diameter were used for dilatometry tests, in thermal conductivity case samples of 50 mm diameter and 10 mm height also round shape were used. For differential calorimeter experiment sample of 25 mg was used from the same bar material.

Samples were obtain from AL Technology implants, made of the titanium alloy $TiAl_6V_4$ ELI, in accordance with ASTM F136-02 (http://www. ab-dent.com). In Fig. 1*a* general view of a dental implant is presented with details of geometrical shape and physical dimensions as thread pitch, thread dimension characteristics that influence the implant evolution in time.



a *b*

c

Fig. 1 – Scanning Electrons Microscope micrographs of a dental implant made from Ti6Al4V alloy: *a* – general view; *b* – microstructure of surface at 500 x power amplification; *c* – detail of surface at 2000 x image amplification.

In Fig. 1*b* and *c* the implant surface is analyzed by scanning electrons microscopy at different amplification scales, 100 and respectively 10 µm showing TiO_2 specific microstructures (Tomaszeka 2007). In this study thermal properties of $TiAl_6V_4$ alloy are analyzed in a room to 150°C temperature range.

3. Experimental Results

Dilatometry tests show a different behavior of $TiAl_6V_4$ at heat modifications by heating rate modifications, in this case 2 and 5 k/min as is graphically represented in Fig. 2. Following the results represented in Fig. 2 can be observe a loop difference in 60 to 105°C temperature range in 2K/min case, the superior represented line, marking an increase of material dilatation in a reduce temperature case impact with the implant material similar in opposed to shape memory alloys behavior at temperature exchange in martensitic transformations range (Bujoreanu *et al.,* 2010; Cimpoeşu *et al.,* 2010).

In this study case of thermal interesting behavior of $TiAl_6V_4$ was obtained a dilatation of 7.4 µm in heating regime of material with 5 K/min and 14.48 µm, almost double, for 2K/min heating regime. At a maximum temperature of 150°C the material dilatation measure 17.26 µm in 5K/min heating case and 22.33 µm in 2K/min case presenting a smaller deployment in faster heating case.

The material behavior as environment temperature modification influence was analyzed by collaboration of the medium temperature and sample temperature evaluation in time, property connected straight to thermal conductivity properties of the material.

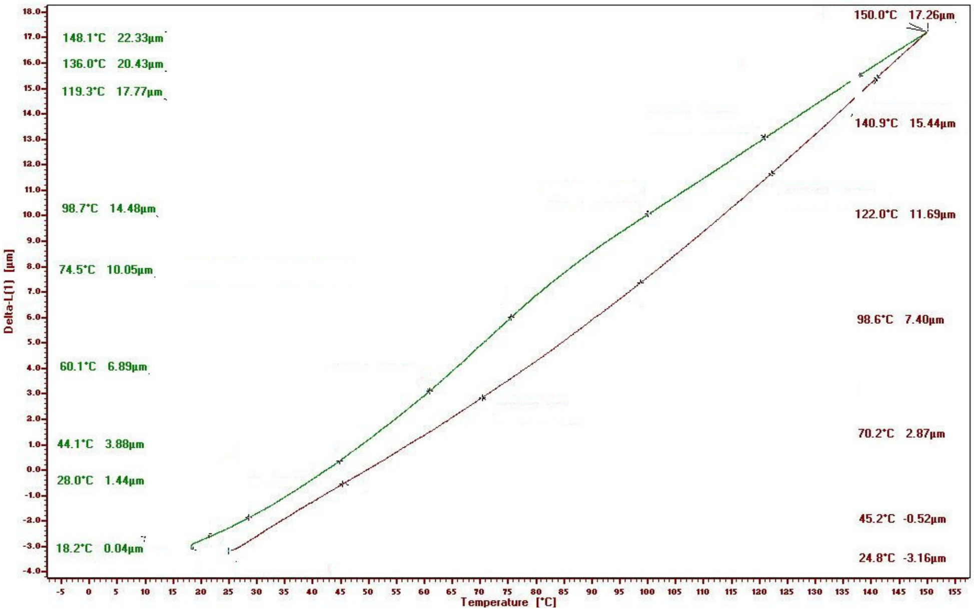
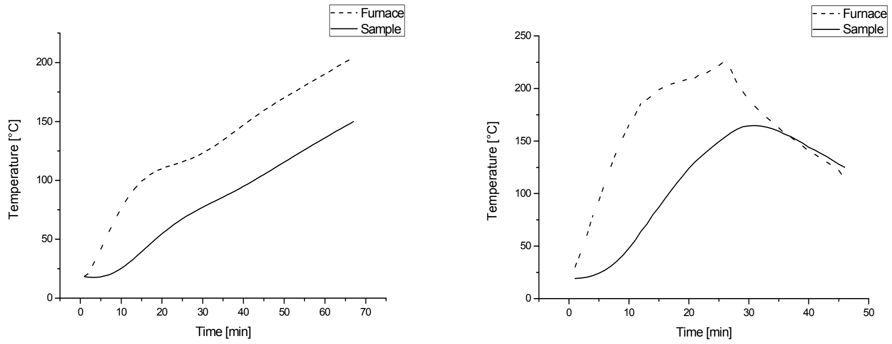


Fig. 2 – Thermal behavior of a$TiAl_6V_4$ dental alloy at different heating rates respectively 2 and 5 K/min.



a *b*

Fig. 3 – Furnace and sample temperatures behavior during heating cycle for dilatometry test: *a* – heating rate of 2K/min; *b* – heating rate of 5K/min.

Starting from the same from variations of temperature with time presented in Fig. 3, the material behavior at heating can be appreciate that $TiAl_6V_4$ is a low thermal conductive material kipping a 50°C degrees difference between furnace and sample temperature. Using a higher heating rate, 5K/min, and a loop on 50 to 105°C range is observe for both thermal conditions. The low thermal conductivity is observed on cooling branch as well for the second regime, in Fig. 3*b*.

Thermal conductivity tests of dental material based on Ti were obtained at room temperature in conditions presented in Table 1. Ten tests were carried out to determine the thermal conductivity and other thermal properties of the investigated alloy. Most important properties concerning a thermal behavior of a material like thermal conductivity, effusively, diffusivity, heat capacity, depth penetration and R value (thermal resistance) are given also for ten tests and as average in Table 2.

Comparing with other materials, $TiAl_6V_4$ alloy, have a reduce thermal conductivity with a value ranged of 6.516347 W/ (m K) (Table 2) much smaller than steel or cobalt based materials and them alloys conductivity (Achiţei et al. 2010) but bigger than cements, epoxy, resigns or polymers (http://www.thermal.com).

Concerning other dental materials like enamel with 0.9, dentin with 0.6, amalgam with 23, gold with 300, porcelain with 1.0, glass with 0.6 to 1.4, PMMA (Poly(methyl metacrylate) acid) with 0.2 to 0.3 and $ZnPO_4$ with 1.2, $TiAl_6V_4$ have a medium experimental value of thermal conductivity.

Thermal resistance (R-value) present a very small value of 2.15043 x 10^{-6} m^2K/W comparing to other materials like dental cements based on CoCr, glass, foams or polymers (http://www.thermal.com) .

Table 1

Thermal Conductivity of $TiAl_6V_4$ Alloy Results Obtained on TCi Equipment

Nr. crt.	Sensor	V0 mV	VMax mV	DeltaV mV	Ambient °C	T0 °C	DeltaT °C
1	TC92	2741.007	2744.543	3.535986	22.13577	20.60594	0.377501
2	TC92	2740.391	2744.001	3.610611	22.13577	20.54014	0.385468
3	TC92	2738.951	2742.547	3.595591	22.13577	20.38643	0.383864
4	TC92	2740.034	2743.647	3.613949	22.13577	20.50201	0.385823
5	TC92	2739.559	2743.181	3.621578	22.13577	20.45136	0.386639
6	TC92	2738.907	2742.509	3.602266	22.13577	20.38172	0.384577
7	TC92	2739.69	2743.318	3.627539	22.13577	20.46536	0.387275
8	TC92	2738.997	2742.603	3.606081	22.13577	20.39129	0.384984
9	TC92	2738.534	2742.134	3.599405	22.13577	20.34196	0.38427
10	TC92	2739.683	2743.299	3.615379	22.13577	20.4646	0.385976
Average	TC92	2739.575	2743.178	3.602839	22.13577	20.45308	0.384638

Depth penetration measures the distance or thickness of thermal energy propagating into the surface through conduction. In most heat transfer textbooks and literatures, penetration depth is only dealt with qualitatively for the simple surface boundary condition- a prescribed surface temperature (*i.e.* boundary condition). In this study, the concept of penetration depth is presented by TCi evaluation software as a medium value of 6.716426 mm lower than the value registered on a aluminum alloy type 6061 of 37.1 mm or even of a stainless steel 304L with a value of 8.9 mm (Yang & Green 2005).

Thermal diffusivity with a range value of 0.509512 x10^{-6} m^2/s has an eight times smaller value comparing with a 304A stainless steel thermal diffusivity of 4.2 x 10^{-6} m^2/s or three times smaller than a quartz material with a 1.4x10^{-6} value (Yang & Green 2005), materials also used in corrosion resistance fields. Comparing with values obtained for other dental materials the $TiAl_6V_4$ thermal diffusivity has a medium value near to enamel material characterized by a 0.5 values or porcelain 0.4 and ZnPO4 with 0.3, bigger than dentin and PMMA and much smaller than gold, amalgam or glass (http://www.thermal.com).

Table 2
Thermal Properties of $TiAl_6V_4$ Dental Alloy at Room Temperature

Nr. crt.	Effusivity (Ws½/m^{2}K) x10^{-3}	Thermal conductivity k (W/mK)	Diffusivity (m^2/s)x10^{-12}	Heat Capacity (J/kgK) x10^6	Depth Penetration (m) x 10^{-6}	R-Value ((m^{2}K)/W)	1/m
1	4756.934	6.840227	483629.9	0.0022	6543.858	2.10219E-06	183.1499
2	4636.99	6.475201	512821.1	0.002023	6738.453	2.15657E-06	178.64
3	4631.187	6.457651	514322.3	0.002014	6748.309	2.15927E-06	178.4226
4	4637.739	6.477464	512628.3	0.002024	6737.187	2.15622E-06	178.668
5	4644.989	6.499405	510766.3	0.002034	6724.94	2.15286E-06	178.9398
6	4643.066	6.493584	511258.9	0.002032	6728.182	2.15375E-06	178.8677
7	4642.693	6.492456	511354.4	0.002031	6728.81	2.15392E-06	178.8537
8	4651.271	6.518424	509164.3	0.002044	6714.385	2.14995E-06	179.1753
9	4630.446	6.455412	514514.5	0.002013	6749.57	2.15962E-06	178.3949
10	4629.863	6.453650	514665.9	0.002012	6750.563	2.15989E-06	178.373
Average	4650.518	6.516347	509512.6	0.002043	6716.426	2.15043E-06	179.1485

The heat capacity is typically for titanium alloys having a reduce thermal conductivity with a value averaged of 2.043 J g^{-1} K^{-1} higher than chrome, copper, tin, tungsten or other dental materials like enamel with 0.75, dentin – 1.26, amalgam – 0.210, gold – 0.126, porcelain – 1.1, glass – 0.8, PMMA 1.46 or ZnPO$_4$ with 0.5 J g^{-1} K^{-1} (http://www.thermal.com).

4. Conclusions

Thermal behavior of dental material based on Ti was analyzed in 23 to 150°C temperature range. Dilatometry present a reduce dilatation until 150°C evidencing a loop in 50 to 105°C temperature range. The material behavior, as heat conductivity, under constant heating was analyzed registering a similar loop in thermal transfer from the environment to material in the same temperature range. The material present a poor thermal conductivity comparing with other metallic alloys used in dentistry but bigger than materials as cements, rubbers, polymers or epoxy. A comparison with other dental materials (enamel, dentin, amalgam, porcelain and glass, PMMA or ZnPO$_4$) thermal properties is realized.

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CONDUCTIVITATEA TERMICĂ A UNUI ALIAJ PE BAZĂ DE Ti

(Rezumat)

Încălzind în domeniul de temperaturi de la cea a camerei la 150°C materialul $TiAl_6V_4$ prezintă o manifestare propie printr-o conductivitate termică scăzută, dilatare şi adâncime de pătrundere deasemenea reduse. Un material pe bază de Titan de gradul 5 pentru aplicații medicale a fost analizat din punctul de vedere al conductivității sale termice. Proprietățile termice au fost determinate prin dilatometrie diferențială şi conductivitate termică la temperatura camerei dar şi sub influența în timp a procesului de încălzire. Rezultatele obținute au fost comparate şi cu cele obținute pe alte materiale dentare cum ar fi enamelul, dentinul, amalgamul, porțelanul, sticla, polimerul PMMA sau $ZnPO_4$ şi citate din literatura de specialitate.

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IMPROVEMENT OF Ti-6Al-4V ALLOY DENTAL IMPLANT MATERIAL THROUGH THIN LAYERS DEPOSITION

BY

ALINA COSTAN[*] and ADRIAN DIMA

“Gheorghe Asachi” Technical University of Iaşi,
Faculty of Materials Science and Engineering

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Abstract. Titanium based dental alloy, $TiAl_6V_4$, was improved by covering his surface with a thin hydroxyapatite (HA) layer using a sol gel method. The research follows some coating properties and analyzes the thermal conductive behavior of the substrate and the substrate-layer materials. The substrate was prepared through chemical etching procedures to increase the substrate – layer adhesion. Scanning electrons microscopy and X-ray analyses was used to characterize some layer properties and thermal conductivity was determined with TCi equipment. Having a continuous and smooth character the coating presents some affected areas and few micrometer exfoliations that are analyzed as well.

Key words: $TiAl_6V_4$, dental implant, hydroxyapatite.

1. Introduction

Materials used for tissue engineering applications must be designed to stimulate specific cell response at molecular or atomic level. They should elicit specific interactions with cell and thereby direct cell attachment, proliferation,

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[*] Corresponding author; *e-mail*: alina0384@yahoo.com

differentiation, and extracellular matrix production and organization. The selection of biomaterials constitutes a key for the success of tissue engineering practice (Hauman & Love 2003; Cimpoeşu *et al.* 2010).

The fundamental requirements of the biomaterials used in the tissue regeneration are biocompatible surfaces and favorable mechanical properties. Conventional single-component polymer materials cannot satisfy these requirements. In fact, although various polymeric materials are available and have been investigated for tissue engineering, no single biodegradable polymer can meet all the requirements for biomedical scaffolds. Hydroxyapatite (HA) has been widely used as a biocompatible ceramic material in many areas of medicine, but mainly for contact with bone tissue, due to its resemblance to mineral bone (Ratner, *et al.* 1990).

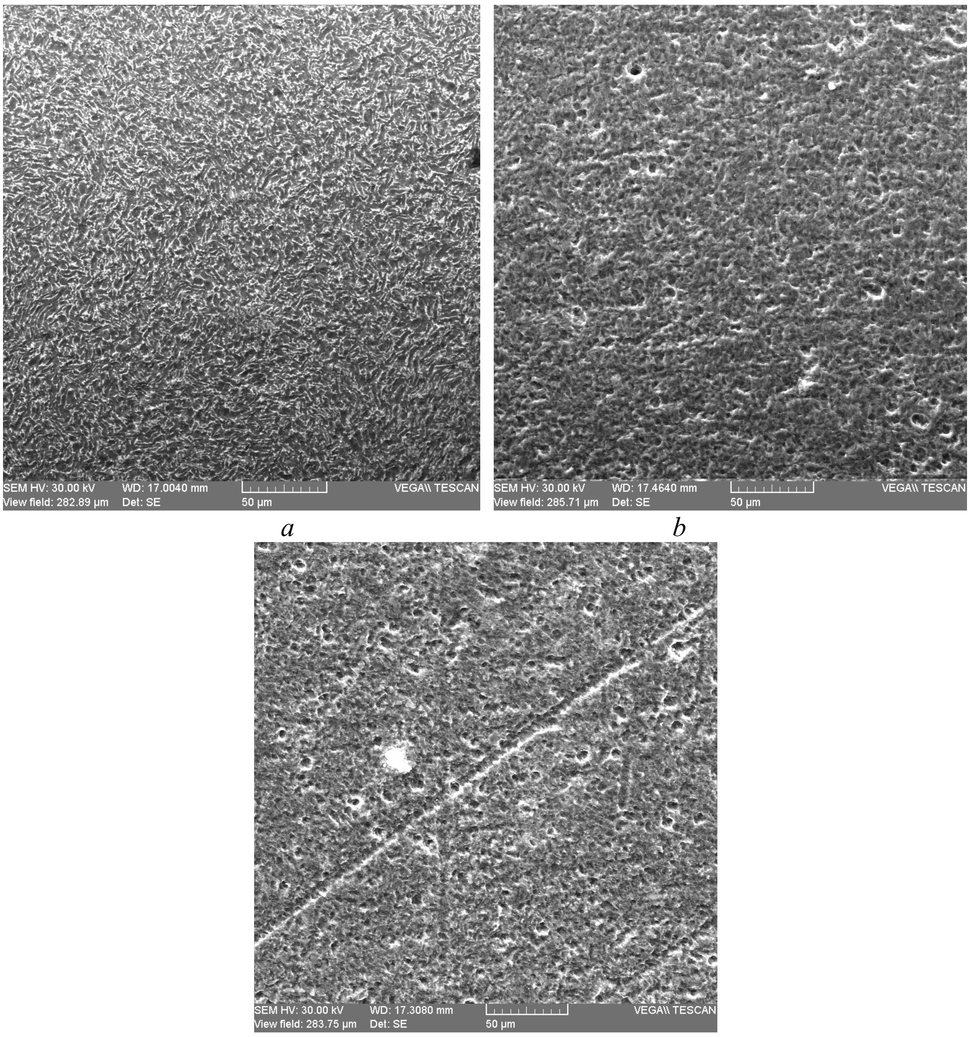
Hydroxyapatite is chemically similar to the mineral component of bones and hard tissues in mammals. It is one of few materials that are classed as bioactive, meaning that it will support bone in growth and osseointegration when used in orthopedic, dental and maxillofacial applications. Hydroxyapatite may be employed in forms such as powders, porous blocks or beads to fill bone defects or voids. These may arise when large sections of bone have had to be removed (*e.g.* bone cancers) or when bone augmentations are required (*e.g.* maxillofacial reconstructions or dental applications).

In this work a thin HA layer was obtained by sol-gel deposition method, after the substrate surface preparation through chemical methods, and characterize through SEM and EDAX techniques especially on the cover problems like micro cracks and exfoliations. Thermal conductivity of the substrate and separately the substrate covered was analyzed to establish the thin layer influence on the thermal properties.

2. Experimental Details and Results

Coatings of hydroxyapatite are often applied to metallic implants (most commonly titanium/titanium alloys and stainless steels) to alter the surface properties. In this manner the body sees hydroxyapatite-type material which it is happy to accept. Without the coating the body would see a foreign body and work in such a way as to isolate it from surrounding tissues. To date, the only commercially accepted method of applying hydroxyapatite coatings to metallic implants is plasma spraying. For a better adhesion between substrate and thin layer deposited the material $TiAl_6V_4$ surface were improved by chemical attack conditions the resulted surface states being presented in Fig. 1.

As can be see immersing the material in a (2 ml HF+4 ml HNO_3) solution at a 70°C bath temperature and during a 65 minutes period. Engraving surface was 4.40 cm^2 and doesn't affect more than a classic chemical attack the material surface, see Fig. 1 *a*).



a *b*

c

Fig. 1 – SEM images of attacked surface of$TiAl_6V_4$ alloy on different conditions a) immersion in (2 ml HF+4 ml HNO_3) solution b) immersion in (H_2SO_4 48% + HCl 18%) solution for a 30 minutes period at a 65°C temperature c) immersion in (H_2SO_4 48% + HCl 18%) solution for a 60 minutes period at a 75°C temperature.

Using a concentrate solution of (H_2SO_4 48% + HCl 18%) for a 30 minutes period at a 65°C temperature, in Fig. 1*b*, and for 60 minutes at 75°C in Fig. 1*c* can be observe an affected surface with many pores and suitable surface for polymeric or biodegradable materials.

Using a material with surface prepared as in Fig. 1*b* case a thin HA layer was obtained through sol-gel deposition method. HA material is biocompatible and it is widely employed for hard tissue repair in orthopedic surgery and dentistry (Milossev *et al.,* 2000; Pettit *et al.,* 1992). Inorganic/organic composites aiming to mimic the composite nature of real bone combine the toughness of the polymer phase with the compressive strength of an inorganic one to generate bioactive materials with improved mechanical properties and degradation profiles.

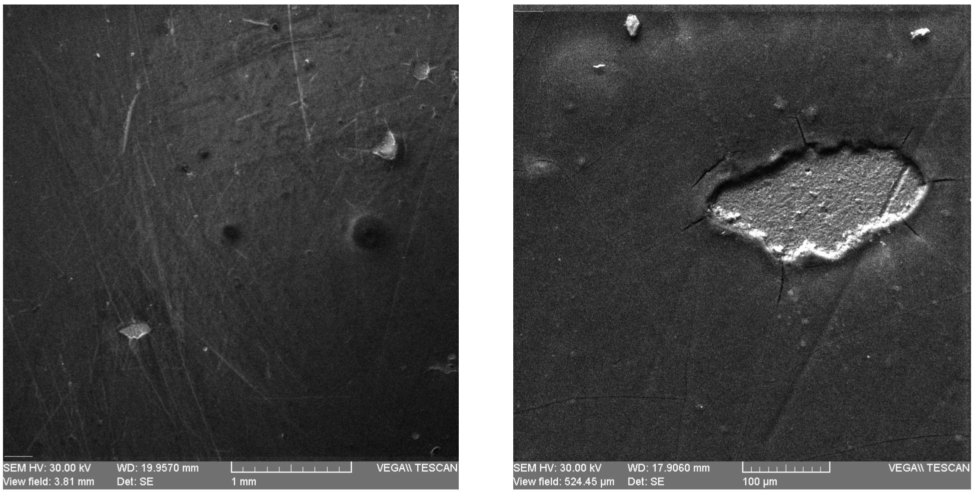
The sol-gel process, also known as chemical solution deposition, is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution (or *sol*) that acts as the precursor for an integrated network (or *gel*) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal chlorides, which undergo various forms of hydrolysis and poly-condensation reactions.

In this study was used a gel based on phosphorus acid/calcium acetate that have a molar rate of Ca:P of 1.69. The colloidal solution for covering was obtained by mixing 50 mL solution of $Ca(CH_3COO)_2$, containing 1.7 10^{-2} molar acetate in ethylene glycol, with 10 mL H_3PO_4, containing 10^{-2} molar H_3PO_4. The concentrations in the mixture were: c(acetate) = 0,283 molar/L, respectively c(H_3PO_4) = 0,167 molar/L. The mixture was kept at ultrasound during 30 minutes and let on rest for 70 hours before experimental using (Weng & Baptista, 1998; Liu *et al.,* 2002; Vijayalakshmi & Rajeswari, 2006; Guzman Vazquez *et al.,* 2005).

For covering operation the samples were vertically introduced in the phosphorous – calcium gel and pull out very slowly with a reduce rate to avoid gel accumulations in the bottom part of the sample, in this case the rate was of 2,5 mm/minute. After the pulling out operation the samples were dry in an oven to 130°C temperature and maintaining time of 15 minutes. In this case were growth 5 layers in similar conditions and the final drying was by calcinations at 800°C for 2.5 hours (Ben-Nissan *et al.* 1997; Kim *et al.* 2004; Bujoreanu *et al.*, 2011).

In Fig. 2 SEM microscopies is presented of the HA superficial layer deposited on a titanium based alloy. In Fig. 2*a* a general aspect is presented evidencing an affected area detailed in figure 2*b* and on this image another area and characterized by micro cracks is enlarge and presented in Fig. 2*b*. The film obtained is relatively smooth and homogeneous but is also presenting some defects as cracks and exfoliations. On the layer surface can be observe a defects line and an area marked with 1 selected on it that seems to appear based on a substrate surface modification like the line appeared in Fig.1 *b*.

From Fig. 2 *b* can be observe that an exfoliation point create some collateral cracks with 1-2 μm thicknesses and 200-300 μm long that affect the layer stability.



a *b*

Fig. 2 – Scanning electrons microscopy of the superficial HA coating on dental $TiAl_6V_4$ alloy: *a* – surface state at 250x; *b* – detail of area 1 from a) at 1000x.

Chemical analyze of the covering is presented in Table 1 checking the Ca:P rate which is 1.58, a value close to usual HA rate modification, caused by the deposition transfer method, HA transformation behavior during depositing and surface – covering interactions. The titanium, vanadium and aluminum elements signals are poor based on the deposited layer thickness.

Table 1

Chemical Composition of thin Superficial HA Film on a $TiAl_6V_4$ Substrate

Element	AN	series	Net	wt.%	norm. wt.%	norm. at.%	Error %
Oxygen	8	K-series	6903	78.90181	62.09898	78.35819	127.3719
Calcium	20	K-series	74216	18.84735	14.83364	7.567504	0.583386
Titanium	22	K-series	47476	18.58123	14.62419	6.244947	0.852254
Phosphorus	15	K-series	29078	7.267406	5.719748	4.775669	0.322802
Carbon	6	K-series	3331	1.75212	1.378991	2.347433	0.335828
Vanadium	23	K-series	2640	1.114167	0.876896	0.351955	0.760787
Aluminum	13	K-series	1573	0.59407	0.467558	0.354307	0.061957
			Sum:	127.0581	100	100	

Choosing an affected by exfoliation area the chemical variations of most important chemical elements is analyzed to present the elements variation. In Fig. 3 a result of elements variation is presented, on a 300 µm length, with respect for the substrate elements like titanium, aluminum and vanadium and the superficial layer components like calcium, phosphorus and oxygen.

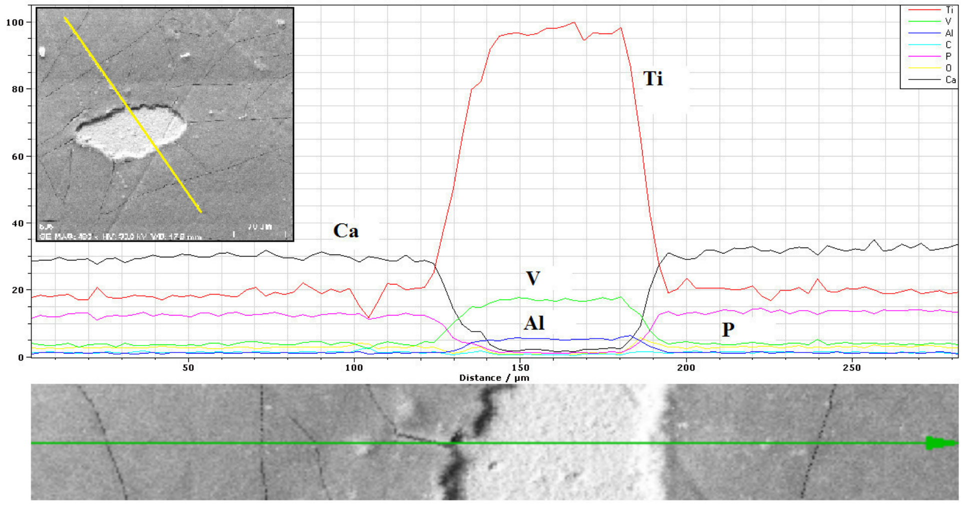


Fig. 3 – Chemical elements distribution on a 250 µm line marking a HA superficial layer defect.

Analyzing the target area, which has an exfoliation zone, presented in detail from Fig. 3 can be identify the obtained layer homogenization with nice Ca:P rates and the increasing of the substrate chemical elements signals on the exfoliation area. The entire substrate morphology was kept by the superficial layer form through sol-gel technique and with a 500-1000 nm thickness. The substrate signals (titanium, aluminum and vanadium) vary on the covered areas as the deposited layer is smoother, cracked or non-homogeneous especially near to the exfoliated area (Paun *et al.,* 2010; Paun *et al.* 2010; Cimpoeşu *et al.,* 2010).

Table 2

Thermal Conductivity of Dental Material $TiAl_6V_4$ *as Cast and Improved with a thin Superficial Layer of Hydroxyapatite* ($Ca_{10}(PO_4)_6(OH)_2$)

Ti6Al4V alloy	Effusivity (Ws½/m²K) x10^{-3}	Thermal Conductivity k (W/mK)	Diffusivity (m²/s)x10^{-12}	Heat Capacity (J/kgK) x10^{6}	Depth Penetration (m) x 10^{-6}	R-Value (m²K)/ W
Un covered	4650,518	6,516347	509512,6	0,002043	6716,426	2,15043
Covered 1 layer	4650,510	6,516340	509515,3	0,001935	6716,410	2,15920
Covered 5 layers	4617,279	6,415733	518033,4	0,001994	6397,854	2,17012
Covered 10 layers	4617,179	6,405733	518283,4	0,001908	6357,854	2,17327

Having samples with 1, 5 and 10 HA layers deposited on a $TiAl_6V_4$ substrate by sol-gel method them thermal conductivity was analyzed with results that confirm the role of the superficial layer as a thermal barrier decreasing with a small percentage the thermal conductivity of the new material. Thermal properties of the samples deposited with superficial HA material and the substrate are presented in Table 2. The thermal barrier created by HA superficial layer decrease thermal conductivity of the material from 6.51 to 6.41 W/mK.

Recent research suggested that better properties would be achieved if synthetic HA could resemble bone minerals in composition, morphology and size. Thermal properties suffer reduce modifications for more than 2 layers deposited on dental material $TiAl_6V_4$, like five or ten layers, but with big modifications comparing to a single or none deposited substrate. Depth penetration of thermal effect decrease with number of layers deposited and off course with the thickness of the layer but also with the adhesion properties at the substrate.

Conclusions

Using a sol-gel chemical deposition method a superficial HA layer with nanometric thickness was obtained on a dental material type $TiAl_6V_4$. The cover is smooth and continuous except some areas characterized by exfoliations and micro-cracks influence by the metallic alloy surface preparation. The hydroxyapatite layer respects a 1.59 rate between Ca and P with generally good adhesion to substrate and a reduced thermal influence on material properties.

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ÎMBUNĂTĂȚIREA UNUI ALIAJ DENTAR Ti-6Al-4V PENTRU IMPLANTURI PRIN DEPUNEREA DE STRATURI SUBȚIRI

(Rezumat)

Aliajul dentar pe bază de titan, $TiAl_6V_4$, a fost îmbunătățit prin acoperirea suprafeței acestuia cu un strat subțire de hidroxiapatită (HA) folosind o metodă de depunere tip sol-gel. Cercetarea urmăreşte analiza unor proprietăți a stratului depus şi comportamentul de conducție termică a substratului şi a substratului acoperit. Substratul a fost preliminar pregătit prin proceduri de gravare chimice pentru creşterea adeziunii dintre substrat şi stratul depus. Analize prin microscopie electronică şi de raze X au fost realizate pentru caracterizarea unor proprietăți de strat iar conductivitatea termică a fost determinată cu un echipament tip TCi. Cu un carater continuu şi puțin rogos stratul depus prezintă şi câteva zone afectate şi câteva exfolieri ce au fost deasemenea analizate.

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SINGLE-PULSE DEPOSITION COMPARATIVE MORPHOLOGY FOR NICKEL AND TITANIUM ELECTRODES ON STEEL SUPPORT USING ESD METHOD

BY

ANCA ELENA LĂRGEANU * **and DAN-GELU GĂLUŞCĂ**

“Gheorghe Asachi” Technical University of Iaşi,
Faculty of Materials Science and Engineering

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Abstract. The paper presents surface analysis obtained by nickel and titanium electrodes deposition with ESD method. The study was done on single-pulse coatings of low alloyed steel. Pictures and EDX analysis on electronic scanning microscope were made to highlight the chemical composition.

Key words: single-pulse deposition, nickel, titanium, SEM.

1. Introduction

ESD method (electrospark deposition) is used for thin metallic layers deposition and can be performed only on support materials with good electrical conductivity. Electrodes material is significantly influencing the

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*Corresponding author; *e-mail*: pufankapuf@yahoo.com

alloying process with electric sparks, the influence develops by the difficulty of the coating or it's facility, but also the quality of the coating (quality means adherence, roughness, layer thickness, oxide presence etc.).

The products analysis of erosion coating, obtained in the electric spark alloying result, of the same material sample coated using different electrodes, demonstrated that the particles from the layer that were developed after the deposition are different by means of shape and size. The report of different shapes and sizes for same processing conditions are established by the alloying electrode material nature.

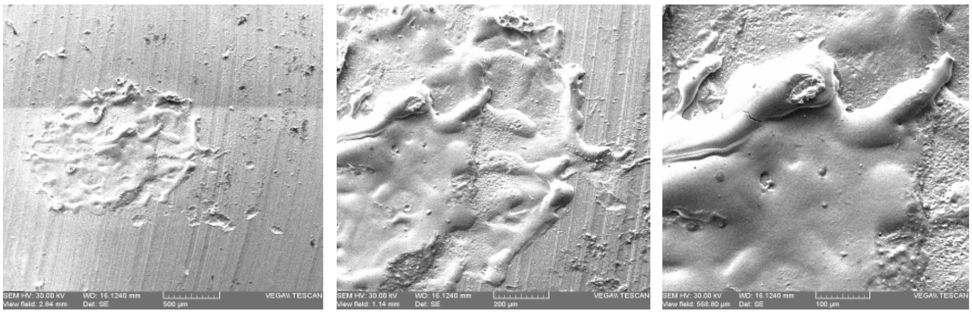
Single-pulse coating was analysed by the name of "drop". The coating drop shape, on the support, depends on the discharge process parameters (amplitude, regime etc.) but also on support and coating material (nature of the electrode) thermo-physical characteristics, (Jun Liu *et al.*, 2005; Wang *et al.*, 2005).

2. Experimental Results

Single-pulse depositions were made bi electric impulse discharge method on low alloyed steel support with Ni and Ti electrodes. For "drops" analysis electronic scanning microscope was used (Perju, 2010).

2.1. "Drop" Analysis Obtained by Ni Electrode Deposition on Steel Support

Analysing the single-pulse deposition using Ni electrode on low alloyed steel support we can see a "drop" with ovoid shape, compact, with small bumps, no cracks and no splash or adherences.



a *b* *c*

Fig. 1 – Ni "drop" micrographs at different magnification power:
a) 500 µm; *b*) 200 µm; *c*) 100 µm.

In line analysis was performed to highlight the chemical composition of the “drop” observing Ni presence between 5÷50%, Fe presence between 5÷100% and C presence <1%.

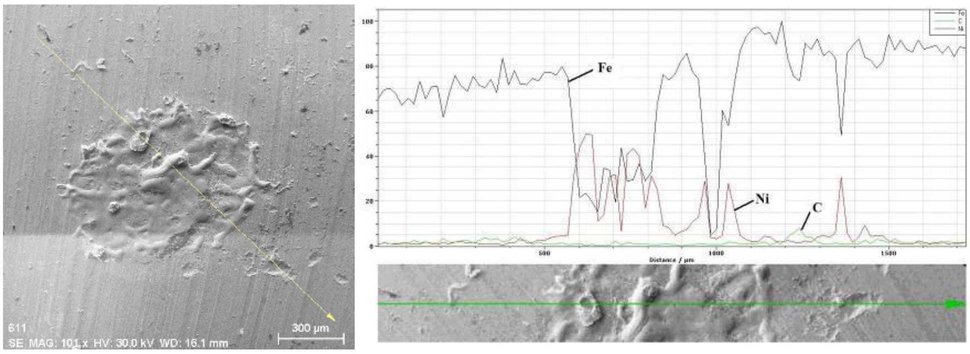
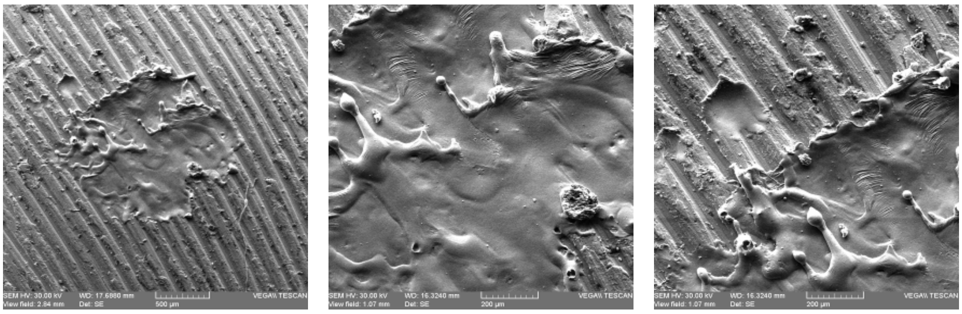


Fig. 2 – In line analysis for single-pulse coating with Ni electrode.

2.2. ”Drop” Analysis Obtained by Ti Electrode Deposition on Steel Support

One titanium electrode melting “drop” on low alloyed sub-layer was analysed with electronic scanning microscope. Relatively compact shape is observed, with a slightly concave meniscus in the centre caused by the splashing impact. Beads from the contour of the “drop” are caused by the dynamics of the deposition. Due to the expanding coefficients difference, substrate – coating thin cracks appear.



a *b* *c*

Fig. 3 – Ti “Drop” micrographs at different magnification power:
a) 500 µm; *b*) 200 µm; *c*) 250 µm.

The avulsion area is caused by the deposition technology by stopping the oscillation motion which is specific for coating, from a slightly adhesion of the electrode.

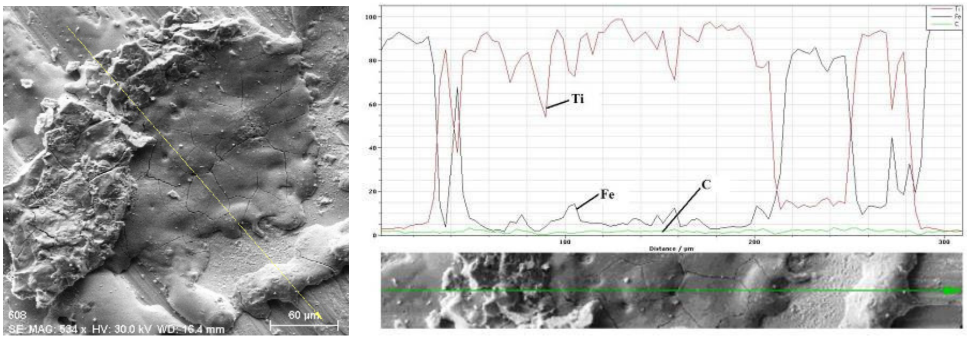


Fig. 4 – In line analysis for single-pulse deposition using Ti electrode.

Single-pulse coating is not always characterized by significant quantity from electrode material that adhere to the surface in specific conditions, which depend of deposition parameters and the operator; beads and cracks can occur which are formed, mainly, from melted and alloyed substrate with a small quantity of electrode. One characteristic of this coating "drop" is the smoothness of the waved shape relief or burns and oxides developed at the surface. Also micro-bubbles formed due to gasses adsorbed at the surface at the part are missing.

3. Conclusion

The study of single-pulse drop and its morphology shows important details for nickel coating quality on steel we study. Nickel has a good adherence on the steel face, without cracks. Studying the element distribution we see that nickel coating is relatively compact, because the high temperature from the contact area it creates a superficial micro-alloying. An advantage of the melting dynamics and solidification, specific for Ti drop, is the fact that these visible cracks are not large, and the layer is relatively compact. Titanium has good adhesion to the surface of steel without the cracks. Comparing the SEM photographs of the single-pulse drops Ni and Ti is observed that both have a high spattering dynamic and a very high voltage in the micro-alloying metal bath, which leads to uncovering the graphite sheets.

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ANALIZA COMPARATIVĂ A DEPUNERII UNIPULS CU ELECTROZI DE TITAN ŞI NICHEL FOLOSIND METODA ESD

(Rezumat)

Lucrarea prezintă analiza suprafeţei obţinute prin depunerea cu electrozi de nichel şi titan prin metoda ESD. Studiul a fost realizat pe depuneri unipuls pe suport de oţel slab aliat. Au fost realizate fotografii la microscopul cu scanare de electroni şi s-a făcut şi analiza EDX a depunerii pentru evidenţierea compoziţiei chimice.

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TITANIUM SUPERFICIAL LAYER ON CAST-IRON SUPPORT ANALYSIS FOR PLD METHOD

BY

ANCA ELENA LĂRGEANU* **and DAN-GELU GĂLUŞCĂ**

“Gheorghe Asachi” Technical University of Iaşi,
Faculty of Materials Science and Engineering

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Abstract. The paper presents analysis for the obtained surface with laser ablation Ti deposition. The support on which the coating was done is cast-iron previously heated at 400°C. For structure analysis, pictures with electronic scanning microscope were made.

Key words: laser ablation, superficial layer, titanium, SEM.

1. Introduction

Laser ablation represents the process of removing matter from a solid part (or occasionally liquid) by irradiation with laser beam. For low intensity laser beams, material is heating up due to laser energy absorption and it’s vaporizing or sublimates.

For high intensity laser beams treated material is passing into plasma stage. For most of applications, to obtain ablation pulsed laser is used.

To be able to cause a lasting effect on the treated material first condition for the laser beam is to be absorbed.

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*Corresponding author; *e-mail*: pufankapuf@yahoo.com

Although it seems peddling, absorption is a critical parameter very important in laser processing. Absorption process can be observed as a secondary source of energy from inside the material. Although it is determined by the incident beam, it has a tendency to develop it's own dynamics an can have a behavior that can divert from the known laws of optics. This secondary source is responsibly of what happens with the irradiated material more than the laser beam itself.

Main mechanisms involved in the forming process of laser inducted plasma are multi-photonic ionization and electronic collisions, leading to cascade piercing and material ablation. It was demonstrated that during the nanoseconds irradiation only a part from laser pulse interacts directly with the target while, depending on the pulse duration, most of the energy is consumed for free expelled electrons heating and photo-ionization introduction of the ablated material.

Furthermore plasma is expanding with a supersonic speed (10^5 - 10^7cmm/s), is cooling and induces in the environment mechanical effects (shock waves in gases and cavities in liquids).

Laser inducted plasma are used for a vast scale of technological applications, from material science to analytical applications.

Most usual techniques that are using this type of plasma are: PLD (Pulsed Laser Deposition), where plasma developed by the laser acts like a material source that must be deposited on the surface of the sub layers in the process of thin film growth and nano-particles creation for carbon or other materials nano-tubes production, (Willmot, 2004; Musil *et al.*, 2005; Brinker *et al.*, 1992; Kakihana & Yoshiura 1999; Afonso & Gonzalo, 1996; Weber *et al.*, 2005; Douglas *et al.*, 1994; Ohnishi *et al.*, 2008; Ferguson *et al.*, 2009; Koster Gertjan *et al.*, 1998).

2. Experimental Results

Titanium deposition was realized using PLD methode(pulsed laser deposition) to increase the electro-corrosion resistance of metalic materials. For the experiment gray cast-iron was used as under-layer which chemical composition is presented in Table 1 and was obtained with Foundry Master spectrometer. The cast-iron suport was heated to 400°C.

Table 1

Gray Cast-Iron Chemical Composition, %

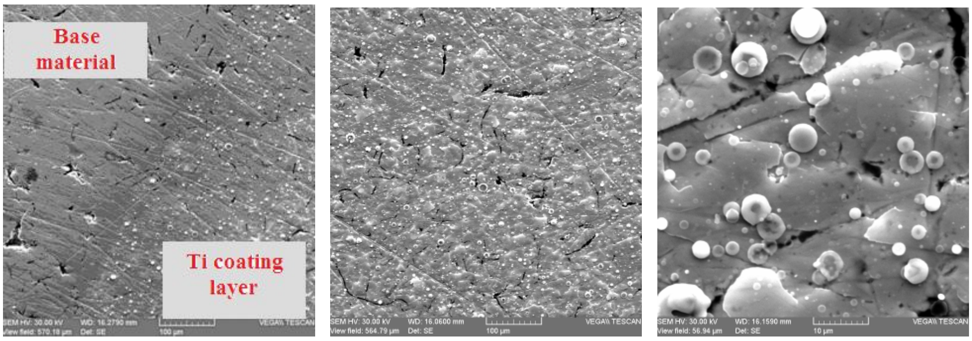
Material	Fe	C	Si	Mn	P	S	Cr	Ni	Cu
Gray Cast-iron	91.8	4.50	1.54	1.03	0.620	0.140	0.096	0.057	0.148

2.1. Electronic Microscopy Analysis of Titanium Superficial Layer on Cast-Iron Metallic Support Heated at 400°C

Experimental technique is based on a device mainly used in analytic purpose. The experiments were developed inside a chamber maid of stainless steel. Whit a turbo-molecular pump, of 450 l/s, vacuum is obtained to a base pressure less than <10^{-6} Torr. A pulsed laser Nd:YAG of 10 ns (λ=266nm) was focused with lens f=25cm onto a Ti metallic target. Estimated diameter of the support in the impact point was 700µm.

The energy of the laser beam was continuously monitored by a joule-meter OPHIR. Usually the energy used was 40mJ/puls.

Material surface electronic microscopy after coating is presented in Fig. 1, highlighting the border area between Ti layer and under-layer (Fig.1 *a*), coating layer characterization (Fig.1 *b*) and superficial layer detail (Fig.1 *c*).



a *b* *c*

Fig. 1 – SEM microstructures for cast-iron samples coated with Ti using laser ablation at various image magnification power and different analysis area: *a*) 500x with border highlighting between under-layer and coating, *b*) 500x; *c*) 5000x.

We can see beside main characteristics of deposited layer, the morphology of titanium particles and titanium oxides compounds, the cast-iron under-layer structure highlighting by phase transformation which occurred by heating the metallic material.

In Fig. 2 is presented energies spectrum of main chemical elements from the surface of the coated cast-iron with the superficial layer of titanium by laser ablation, for “in point” analysis from Fig. 3.

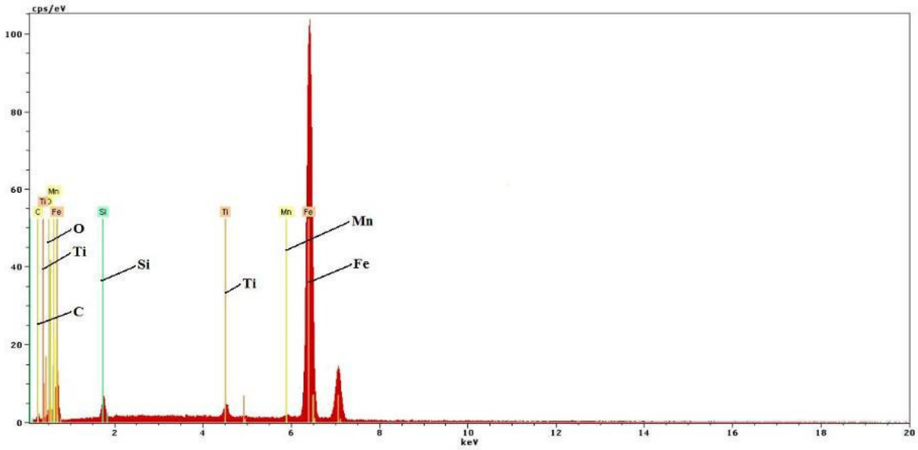


Fig. 2 – Energetic spectrum for chemical elements obtained with "in point" analysis.

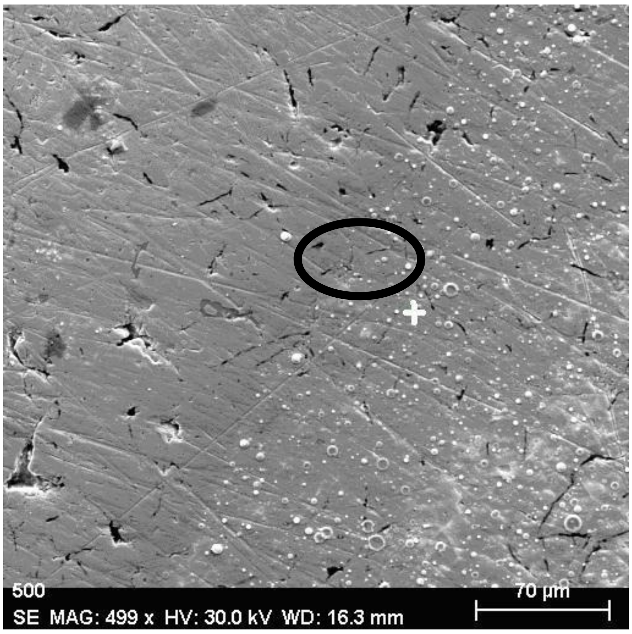


Fig. 3 – In point analysis for Ti coating using PLD method.

Chemical composition for "in point" analysis of the material is presented in Table 2 highlighting the mass and atomic percent of main elements on the surface.

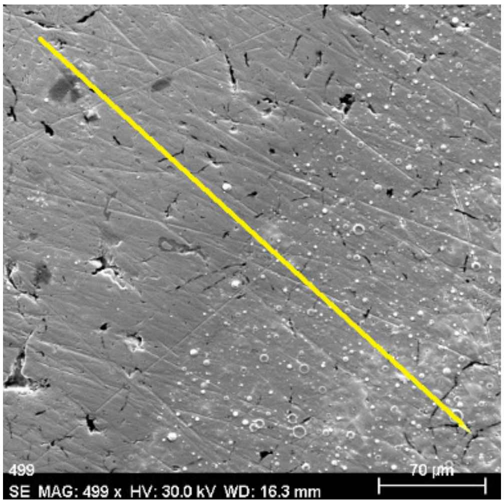
Table 2
Chemical Composition of in Point Analysis Material.

Chemical elements	Mass percent %	Atomic percent %
Iron	87.57661	71.4928
Oxygen	3.913114	11.15046
Silicon	3.58463	5.818837
Carbon	2.441764	9.268265
Titanium	1.703449	1.621993
Manganese	0.780438	0.647649

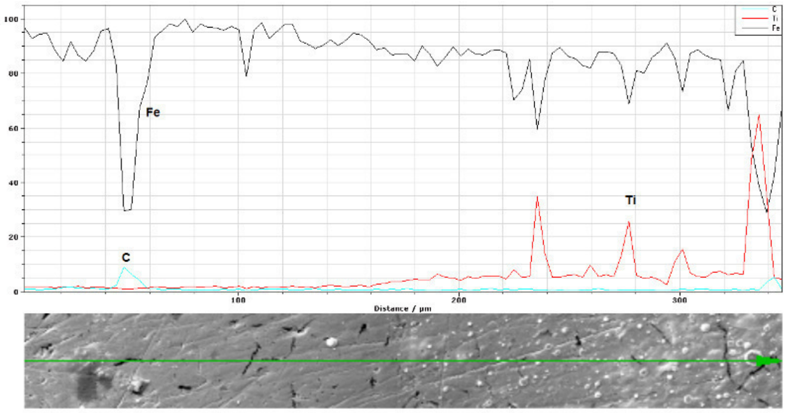
The point selected for chemical analysis shows a low energetic titanium contribution of 1.7%; mass percent which characterize a part of Ti layer obtained by PLD with nano-metric dimensions. Other signals are received given by chemical elements from the under-layer, coating layer having a thickness under one micron.

In Fig. 4 *a* is selected a border area between layer and under-layer were the chemical elements, iron, titanium and carbon, is analyzed (Fig. 4 *b*)), highlighting the titanium layer obtained by laser ablation coating.

Large titanium and titanium oxide particles are observed by high signal on the element distribution from Fig. 4 *b* we can observed the high signal level for titanium element on all deposited area.



a



b

Fig. 4 – In line analysis for Ti deposition using PLD method.

Although the under-layer heating effects are not obvious this operation helps the titanium layer developing and homogenizing increasing the necessary energetic contribution.

The deposited layer depends on some process parameters of the PLD method and also the under-layer condition.

3. Conclusion

1. Atomic species transport by laser ablation represents a deep studied and extensively publicized technique in the last decade thanks to the special proprieties of the layers and also the control that can be applied to the process to obtain a specific superficial layer quality.

2. The layers obtained by laser ablation are homogeneous, small dimensions and compact, improving the base material for corrosion resistance mainly due to titanium oxide layer formation at the cast-iron under-layer surface.

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ANALIZA STRATULUI SUPERFICIAL DE TITAN PE SUPORT DE FONTĂ PRIN METODA PLD

(Rezumat)

Lucrarea prezintă analiza suprafeţei obţinute prin depunere cu Ti prin ablaţie laser. Suportul pe care a fost făcută depunerea este fontă cenuşie, care în prealabil a fost încălzit la 400°C. Pentru analiza structurii au fost realizate fotografii obţinute cu ajutorul microscopului cu scanare de electroni.

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DIFFERENTIAL CALORIMETRY OF POLYMER MATRIX COMPOSITE REINFORCED WITH CARBON NANOTUBES

BY

RĂZVAN IULIAN LIŢOIU* **and DAN-GELU GĂLUŞCĂ**

“Gheorghe Asachi” Technical University of Iaşi,
Faculty of Materials Science and Engineering

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Abstract. Behavior of materials in any circumstance suffers modification when the environment is changing and influences the material properties. By this point of view a material thermal properties manifest modifications with temperature modification and differential thermal conductivity manifest similar. Using two temperature sensors, one for furnace and the other one for sample, two increasing temperatures were analyze for different polymer or composite polymers materials. The influence of reinforcement elements percentages was follow to determine the differential thermal conductivity of few polymer composites reinforced whit carbon nanotubes.

Key words: differential calorimetry, composite, carbon nanotubes.

1. Introduction

The use of carbon nanotubes (CNTs) as filler material of thermosetting plastics has already been the object of numerous research efforts (Coleman *et al.*, 2006; Thostenson *et al.*, 2005; Andrews & Weisenberger, 2004). Due to their fibrous shape, outstanding thermal and mechanical properties and a large

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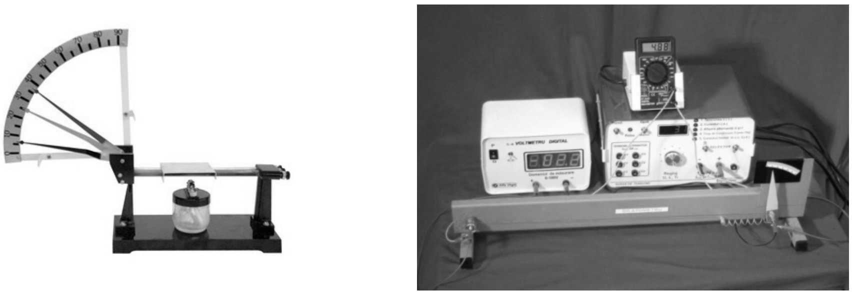
*Corresponding author; *e-mail*: razvan_cel_cam_bun@yahoo.com

specific surface area, CNT-based nanocomposites can be expected to show significantly improved characteristics as compared to the pure matrix material. This requires successfully performing the critical issues of dispersing as well as surface functionalization. The complete break-up of the agglomerates, the homogenous distribution of the exfoliated nanotubes and their integration into the molecular structure of the matrix are requirements for manufacturing of high quality nano-composites and the development of their potential (Fiedler *et al.*, 2006). Being relatively cost-intensive, the use of CNTs needs to be justified by a higher efficiency than that of conventional fillers. This would be the case, for example, if an exceptional improvement of the thermal or mechanical properties arise, based on the mechanisms of short fiber reinforcement. In the literature, this feature has been demonstrated for various functionalized CNTs (Zhu *et al.*, 2003; Kim *et al.*, 2006). Especially amine derivatives have been used for the surface functionalisation of the CNTs (Shen *et al.*, 2007; Zhu *et. al.*, 2004; Gojny *et al.*, 2005; Liu & Wagner 2005), which typically reacts with defects in the carbon structure introduced by acid treatment.

Many of these results present improved thermal properties as a result of optimized interaction between the nano-scale reinforcement fibers, dispersion quality and variation and surface functionalisation. As these substances are used to interfere in the curing reaction of the epoxy resins, thus enabling the covalent integration of the CNTs into the molecular network of the matrix, a chemical influence of the substances is also conceivable in this context. This paper focuses on the thermal improvements of the nano-composites based on the desired short fibre reinforcement by the CNTs, marking out the influences of surface functionalisation and dispersing.

2. Experimental Procedures

Dilatometer represents an equipment make to measure the geometrical modifications of a body based on temperature modification. In Fig. 1 are presented few examples of such equipment and are based on a very good temperature control.



a *b*

c

Fig. 1 – Different experimental dilatometer types:
a – dilatometer with scale; *b* – electrical dilatometer; *c* – classic dilatometer.

The test were registered on a laboratory equipment, presented in Fig. 2, from Materials Science Faculty from Iasi horizontal type L75HS that can register the thermal modification (irreversible and reversible) step by step, mass phase transformations and crystallization properties (Fiedler *et al.*, 2006). The main system is based on a furnace with a good temperature control system connected to a computer device for capturing and work with experimental data. Different kinds of sample can be analyze on this equipment like solid, liquid, fibers, powders of thin films which necessity a mechanical preparation based on the standard holder of the equipment (Zhu *et al.,* 2003).

Samples can be heated or cooled, by case, with a linear regime the sample temperature being registered with a thermocouple until 2050°C and the test atmosphere can be controlled in air, vacuum or inert gas.

Fig. 2 – Horizontal Linseis L75HS dilatometer.

Using the equipment presented in Fig. 2 a few measurements can be done like:

a) Relative length modification or change of a sample under heating – cooling cycles;

b) Dilatation linear coefficient;

c) Transformation points;

d) Density modification;
e) Contraction;
f) Penetration;
g) Thermal dilatation.

To achieve an experiment with the equipment it is necessary for the user to know the settings and parameters which will use in programming, which is done by computer, and that after loading the desired program will automatically lead the experiment. Like other thermoplastic materials polymers that cannot tolerate high temperature for a long time the polymer matrix composites have the same problem on dimensional stability at high temperatures. According to the literature there are two main methods to evaluate the tolerance of these materials at high temperatures, so-called dimensional and thermal stability (Andrews & Weisenberger 2004; Fiedler *et al.*, 2006; Zhu *et al.*, 2003; Kim *et al.*, 2006; Shen *et al.* 2007). Dimensional stability of a material may be dictated by its coefficient of thermal expansion (CDT).

3. Experimental Results

Dilatometry tests were conducted on samples of natural rubber and natural rubber reinforced with 5, 10, 20 and 30% CNTs and during these tests was examined the differential thermal conductivity of these materials with increasing temperature inside of equipment. In this regard there were two temperatures, the furnace and the sample, registered by 30 to 30 seconds over the entire heating-cooling chamber. Based on the thermal inertia of furnace and sample were further heated first reaching a maximum temperature of 155.3°C and the sample at a maximum temperature of 80.7°C as can be seen from Fig. 3 the differential thermal conductivity was monitored of sample during heating.

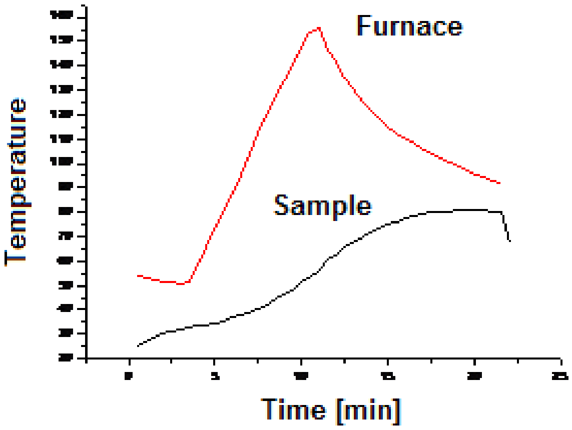


Fig. 3 – Variation of furnace and a natural rubber sample during a dilatometer test.

Analyzing the thermal evolution of material can be observe a maximum difference in temperature variation between the furnace and sample with value of 100.2°C at about 10.5 minutes from the beginning of heating, the difference decreasing gradually with increasing of temperature of the sample composite polymer and stop heating furnace reaching on cooling to a difference of 11.5°C between the furnace and heat transfer test with a very good sample. It will be interesting to follow how will change the thermo-dimensional composite sample along with reinforcement in polymer matrix elements for reinforcement of carbon nanotubes.

At the same time recording data on dimensional change with temperature variation of the material was monitored the differential thermal conduction property of the material once with the heating of furnace.

In Fig. 4 are variations of the two target temperatures, the sample and the furnace, while both during heating and cooling slope of the furnace were registered. There is a change in the thermal conductivity of the material investigated along with changes in furnace temperature reached a maximum temperature of 155.4°C after 10.5 minutes of heating time when the sample was at 52.4°C and thus a difference of 103°C between sample and furnace. In the second part, the further cooling and warming furnace proof there was a difference of 10.4°C after 20.5 minutes of test. It is noted that the differential analysis module reinforced material has a thermal conductivity at low temperatures lower that if we reinforced material but increases with increasing temperature while improving process heating and differential thermal conductivity increases at higher temperatures like 50°C.

Sample temperature decreases with the cooling oven for short periods of time maintaining the same temperature, low levels of constant temperature appearing.

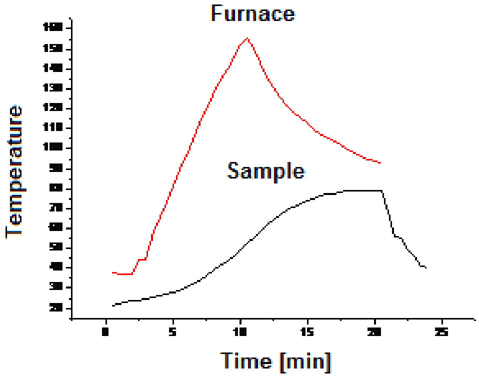


Fig. 4 – Variation of furnace and a natural rubber reinforced with 5% CNTs sample during a dilatometer test.

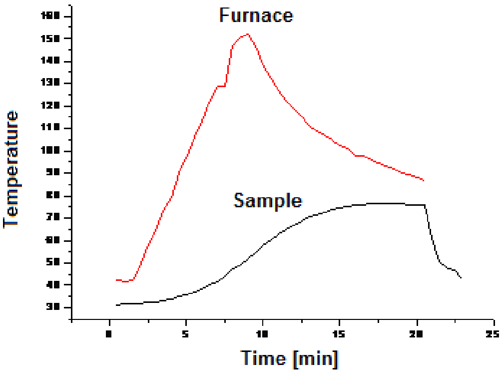


Fig. 5 – Variation of furnace and a natural rubber reinforced with 10% CNTs sample during a dilatometer test.

Fig. 5 presents the composite material and temperature variations during the dilatometry tests. Maintaining a maximum difference of temperature of 99.8°C after 9 minutes of heating, moving to homogenization and near temperatures especially after stopping heating of furnace and in fact after a high temperature composite material over the temperature of 50°C leading to a difference of 9.9°C between the temperature furnace and composite sample temperature.

After the sample received an amount of heat and its temperature went over 75°C the difference between site and sample reached 6.8°C and up to now best results heat transfer between furnace and sample composite matrix polymer. Temperature variations are observed and the stable character of the polymer sample heating with a heat input increase after the sample reaches the temperature of 40-45°C and pass to a different property regime.

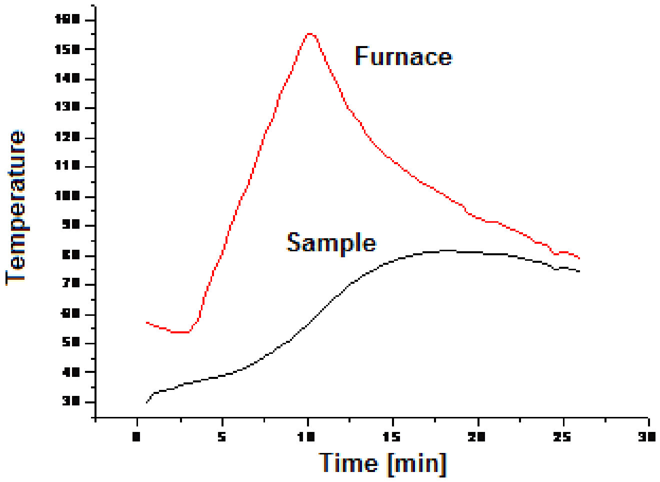


Fig. 6 – Variation of furnace and a natural rubber reinforced with 20% CNTs sample during a dilatometer test.

Fig. 7 shows the change in oven temperature and the sample during the test realized with the differential dilatometer. Is observed the fact that after 10 minutes of heating process that we observe a maximum difference of 104.8°C between sample and furnace and kept a big difference after the sample passed of 55°C temperature resulting in the curve of cooling of the oven a temperature difference of 20°C, values that is much higher than other reinforced materials in heating process while the graph shape of heating process of the material is similar to all other cases.

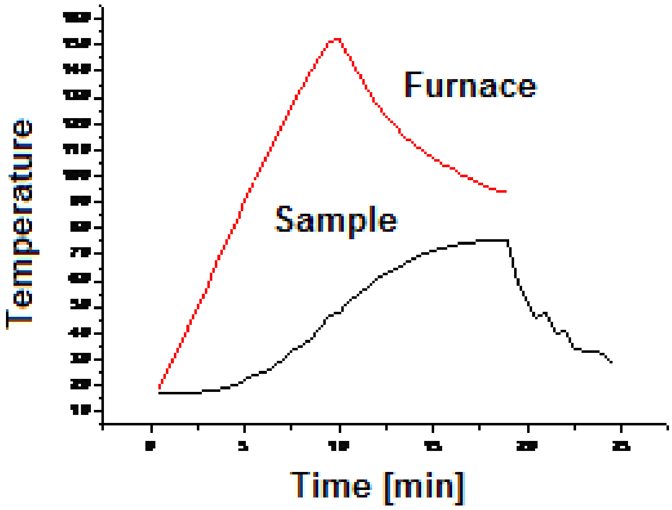


Fig. 7 – Variation of furnace and a natural rubber reinforced with 30% CNTs sample during a dilatometer test.

The analysis highlights the differential conductivity improvement as property during the heating process based on percentage growth of reinforcing elements, in this case carbon nanotubes, which serve to modify the physic-chemical properties of polymeric materials.

4. Conclusions

Differential thermal conductivity of materials represents the property of a experimental material that in many situations suppose to work in different environment temperatures.

Taking the applications of natural rubber materials in automotive domain and them implications with temperature modification can be considered the differential conductivity more important as results then the static conductivity at room temperature.

The results present a better behavior of the reinforced samples comparing to the natural rubber one with the decreasing of maximum temperature difference and the final difference temperature between the sample and the environment represented by furnace.

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CALORIMETRIE DIFERENŢIALĂ A COMPOZITELOR CU MATRICE POLIMERICĂ RANFORSATĂ CU NANOTUBURI DE CARBON

(Rezumat)

In orice circumstanţe, comportarea materialelor suferă modificări când se schimbă mediul şi sunt influenţate proprietăţile acestora. Din acest punct de vedere proprietăţile termice ale unui material se modifică cu temperatura respectiv şi conductivitarea termică diferenţială. Utilizând doi senzori de temperatură, unul pentru probă şi unul pentru cuptor, două variaţii ale temperaturii crescătoare au fost analizate pentru diferiţi polimeri şi materiale compozite polimerice. Influenţa procentajului elemetului ranforsat a fost urmărită în scopul determinării conductivităţii termice diferenţiale a unor materiale compozite ranforsate cu nanotuburi de carbon.

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DIMENSIONAL BEHAVIOR OF POLYMER COMPOSITE UNDER THERMAL SOLICITATION

BY

RĂZVAN IULIAN LIŢOIU * **and DAN-GELU GĂLUŞCĂ**

“Gheorghe Asachi” Technical University of Iaşi,
Faculty of Materials Science and Engineering

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Abstract. Dimensional stability of polymeric materials represents an important fact for all materials applications that involves polymers or composite based polymers materials. Preparing samples and using a thermal heating regime with a dilatometric equipments the dimensional stability of some polymer matrix composites with CNT reinforcement elements was determined and compared. The results present an improve of dimensional behavior of the reinforced materials with temperature and different dilatation values function of the material temperature.

Key words: polymer matrix, carbon nanotubes, dilatometry.

1. Introduction

Coming from laboratory- scale exercises, part of the activities have over the years reached the levels of industrial scale up to initial commercial and industrial applications (www.ChemicalVision2020.org; www.royalsoc.ac.uk/ policy. or www.raeng.org.uk; Anon 2004).Over the last decade a large increase in carbon nano-tubes (CNT) and CNT related research activities has been

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*Corresponding author; *e-mail*: razvan_cel_cam_bun@yahoo.com

observed. CNT composites is a major area of research and development in recent years, where CNT's are used as reinforcing particles embedded in a matrix (polymeric, ceramic, or metallic), to confer the CNT's inherent properties to the composites that gains enhanced functionalities. The main aim of producing CNT composites is to exploit the CNT's inherent properties of stiffness, tensile strength, damping properties, flame resistance, thermal and electrical properties, barrier properties, etc. (Breuer & Sundararaj, 2004; Thostenson *et al*., 2005; Moisala *et al*., 2006; Gou *et al*., 2006 ; Gojny *et al*., 2006 ; Shadler *et al*., 1998). Bulk polymer carbon nano-tubes composites, are the most developed and studied so far, targeted at applications, such as: conductive polymers for electrostatic paint applications; multi-layer fuel pipes for no electrostatic charging and improved leak proof; sports equipment with better impact stability; conductive films and applications for antistatic packaging; and lithium–ion batteries to improve storage capacity and other.

Much of the development efforts concerns with retaining the CNT's large aspect ratio, achieving good interfacial stress transfer (surface modification), improving dispersion and alignment in the polymer matrix during processing. As a result of the technical progress in this area, and the perceived market potential, a growing number of companies are now offering CNT-based concentrates, master-batches, for use in polymer composite production.

However, the technical and economical issues (the high cost and relatively short lengths of CNT's, the limited ability to effectively disperse and align them within a host matrix) currently still prevent CNT composites from being applied to large-scale composite structures, supplementing or replacing conventional composites.

2. Experimental Details

Dimensional stability sensibility of a composite material with polymeric matrix was established for a certain heating rate and a temperature domain. The samples has different reinforcement elements, carbon nano-tubes, percentages like 5, 10, 20 or 30% and the experiments were realized on a laboratory equipment type Linseis L75 from Materials Science and Engineering Faculty from Iasi. The dilatometry tests represent well known method for dimensional stability determination of materials with them temperature variation.

Bodies dilatation is a phenomena of increasing of a heated body dimension named thermal dilatation. Dilatation phenomenon can be explained based on the fact that body dimensions are determined by an average distance, *r* between the atoms that compound the material so on dilatation can be talk about the result of increasing of these distances during heating (Ishikawa 2006).

Samples of natural rubber and natural rubber reinforced with 5, 10, 20 and 30% CNT were prepared by cutting in square shape with 10x10 mm base and lengths between 20 in 25 mm. Plan rectangular faces of the samples were polished with metallographic papers of 100, 250, 400, 800 and 1200 types to improve the dilatometry results. For each type of sample were prepared 3 pieces for repetitive tests. In Fig. 1 a plain natural rubber sample dimensional (linear) behavior is presented for a sample with 23.88 mm length for a heating range between 25 and 55°C.

The equipment is continuously chilled with water system creating a especially temperature control from the apparatus working room. The materials were heated with a 5 K/min rate in the experiments the authors pay respect for thermal inertia also and general thermal conductivity of polymer composite materials.

3. Experimental Results

Nonmetallic materials and especially those polymeric, with soft structure, behave different on dilatometry tests based on equipment working principles. Analyzing the first image can be observed an unstable behavior of this sample with temperature variation registering contractions and dilatations of the material on the heating range. The first contraction is also observe further on all other experiments based on material relaxation and more on the contact between samples and the apparatus movement sensor.

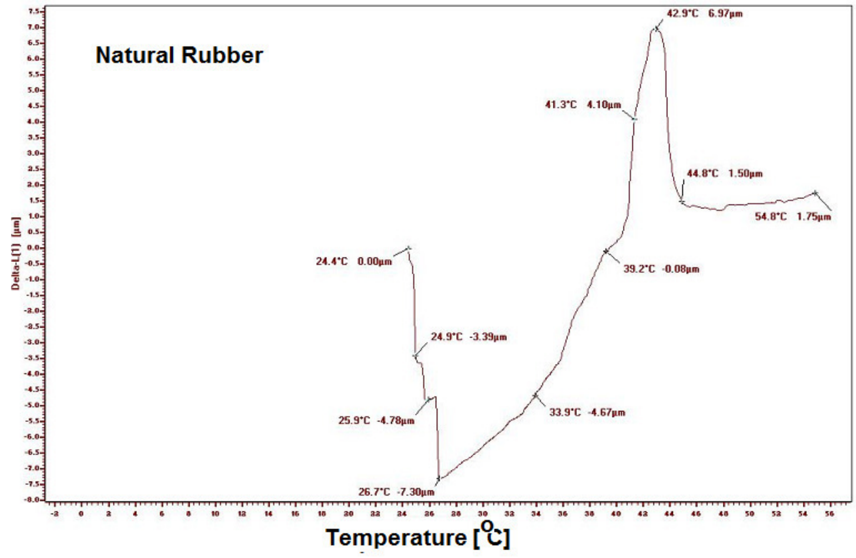

Fig. 1 – Dimensional behavior of a natural rubber sample.

Continuing the material heating, the natural rubber increase in dimension until 43°C gaining 7 µm in length over the initial contraction and after that the material suffer a new contraction decreasing the material dilatation to 1.5 µm at 45°C and 1.75 µm at 55°C temperatures.

Closest to structural applications are the efforts aimed at using CNT loaded matrices in reinforcing conventional, continuous fiber-based composites. In this way, matrix-dominated composite properties, such as inter-laminar shear strength, fracture toughness, through-thickness conductivity, glass transition temperature (Tg) could be improved (Rice *et* al., 2004; Ishikawa, 2006).

In Fig. 2 is represented the dimensional variation of a sample prepared from a composite material having a natural rubber matrix and 5% reinforcement elements with a 24.3 mm length from room temperature to 55°C. The material behave first a "contraction" based on polymeric manifestation at a contact resistance and after that the material suffer a dilatation of 16.53 µm at 52.8°C with a smoother dilatation until 46°C and a bigger rate on the next temperature range. Analyzing the second result a better dimensional stability can be observed based on the reinforcement elements at least for a heating until 55°C comparing with the behavior of the plain matrix material experimented in similar conditions.

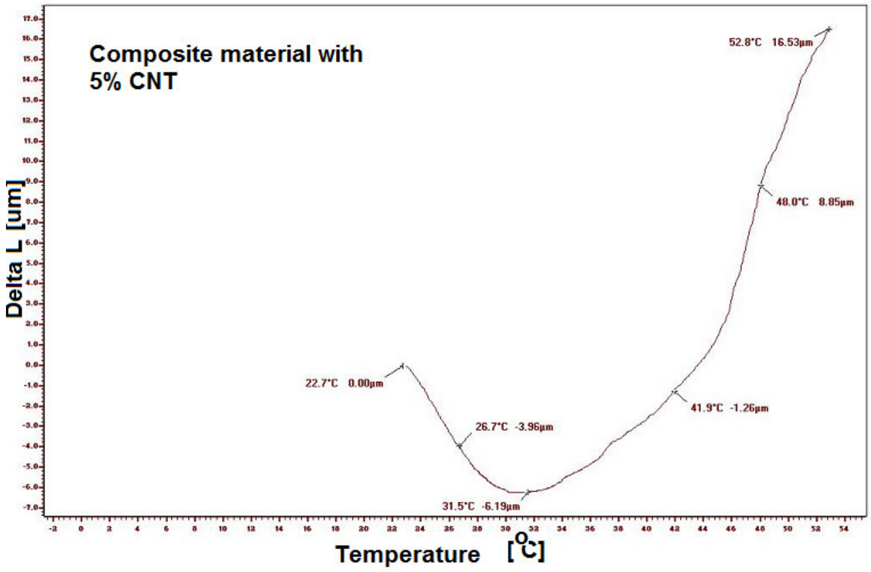

Fig. 2 – Dimensional behavior of a composite material with natural rubber as matrix and 5% CNT reinforcement elements.

In Fig. 3 the result of a more reinforcement composite material, 10% CNTs respectively, is analyzed for a sample length of 27.49 µm. A stable dimensional evolution of the material is observed and a dilatation of material with 16.5 µm at 55°C.

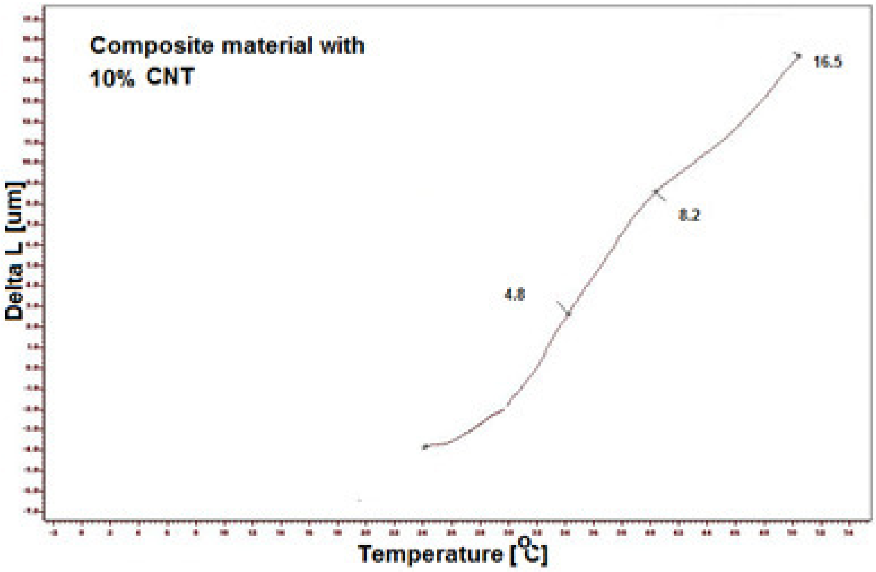

Fig. 3 – Dimensional behavior of a composite material reinforced with 10% CNTs.

Forward, in similar conditions a sample with 20% reinforcement CNTs was experimented having a 28.04 mm length and the dilatometry test result being presented in Fig. The material present a stable behavior at the heating beginning with a reduce dimensional increase until 45°C temperature of 9.31 µm and after that on a 10°C temperature domain the material dimension increase two times faster until 55°C the composite material suffering a 18.47 µm increase.

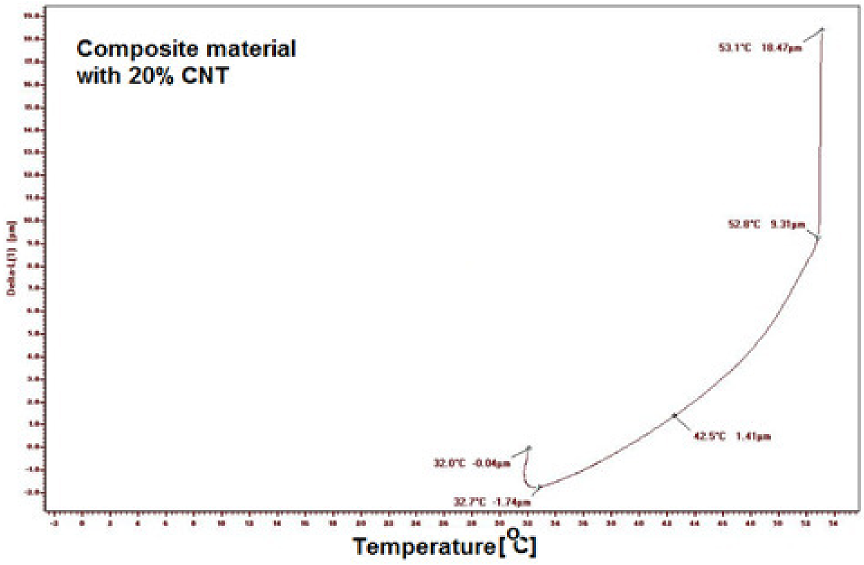

Fig. 4 – Dimensional behavior of a composite material reinforced with 20% CNTs.

In Fig. 5 is comment the result of the dilatometry test realized on a sample composite and reinforced with 30% CNTs with 27.34 mm in length. Can be observe a stabilized behavior of dimensional variation also with two different increasing rates, first until temperature of 35-40°C with a linear increase of 4.3 µm and then a more accentuated increase with a dilatation of 43.3 µm, ten times bigger in less than ten Celsius degree until 46.1°C. This modification can be put on the heating modification regime process that occur around 40°C and which modify the composite material properties.

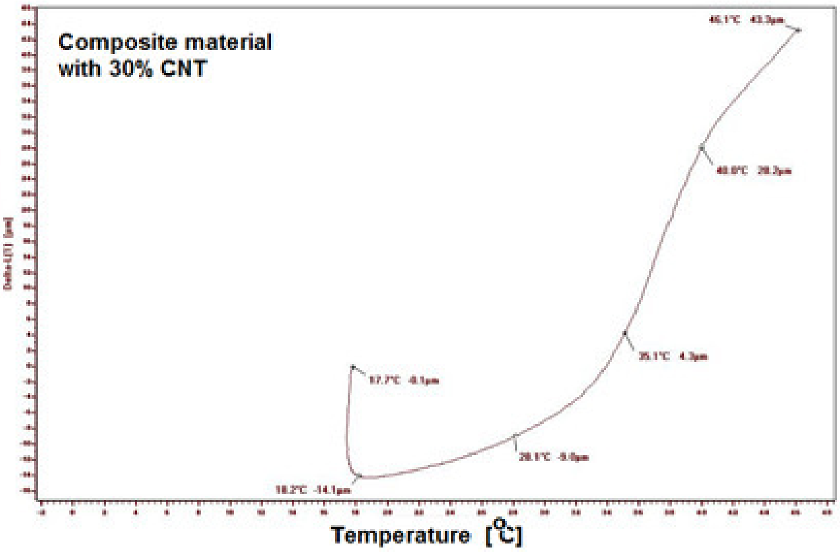

Fig. 5 – Dimensional behavior of a composite material reinforced with 30% CNTs.

The material modifies his behavior after a certain temperature splitting the dimensional behavior in two different areas with different rates. Analyzing the materials behaviors can be observe some improvements in dimensional stability of the materials with the increase of the reinforcement elements.

Conclusions

Analyzing the materials behaviors can be observe some improvements in dimensional stability of the materials with the increase of the reinforcement elements. The material dimensional behavior modifies with temperature in this case around 40°C. This modification can be put on the heating modification regime process that occur around 40°C and which modify the composite material properties.

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COMPORTAMENTUL DIMENSIONAL SUB SOLICITARE TERMICĂ A UNOR COMPOSITE POLIMERICE

(Rezumat)

Stabilitatea dimensională a materialelor polimerice reprezintă un factor important pentru toate aplicaţiile materialelor ce conţin polimeri sau composite bazate pe materiale polimerice. Preparând probele şi utilizând un regim de încălzire cu un echipament de analiză a dilatometrie a fost determinată şi comparată stabilitatea dimensională a unor composite cu matrice polimerică ranforsate cu nanotuburi de carbon. Rezultatele prezintă o îmbunătăţire a comportamentului dimensional a materialelor ranforsate cu variaţia temperaturii şi diferite valori a dilatării în funcţie de temperatura materialului.