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Secția

ŞTIINȚA ȘI INGINERIA MATERIALELOR

SUMAR —	
	Pag.
LENUȚA CIURCĂ, BOGDAN PRICOP, NICANOR CIMPOEȘU, MARICEL AGOP și LEANDRU-GHEORGHE BUJOREANU, Comportamentul la fluaj al unui aliaj FeMn cu memoria formei (engl., rez. rom.) CORNELIA CÎRLAN PALEU, CORNELIU MUNTEANU, ANIȘOARA DASCĂLU și VIOREL PALEU, Deteriorarea componentelor	9
mecanice ale pompelor și soluții pentru realizarea de acoperiri rezistente la uzură (engl., rez. rom.)	19
ELENA IONELA CHERECHEȘ, MARIUS IONUȚ CHERECHEȘ și ALINA ADRIANA MINEA, Analiza comportării în exploatare a unor mixturi:	20
MARIUS IONUȚ CHERECHEȘ, ELENA IONELA CHERECHEȘ și ALINA	29
 RAUL GEORGE CIUBOTARIU, DAN ELIEZER, CORNELIU MUNTEANU şi BOGDAN ISTRATE, Aplicarea structurilor din fibre de sticlă goale ca sisteme de stocare de mare presiune pentru hidrogen (engl. rez.) 	43
rom.)	55
DRAGOŞ-ŞTEFAN GHERGHESCU, Tehnici tradiționale și materiale naturale	
de construcții în România (engl., rez. rom.)	65
ISTRATE, Cercetări recente asupra aliajelor biodegradabile pe bază de Mg – Trecere în revistă (engl., rez. rom.) ANDREI RATOI, DAN ELIEZER și CORNELIU MUNTEANU, O abordare combinată a stiințai materialelor și macanica pentru studiul fragilizării	77
de hidrogen a materialelor structurale (engl., rez. rom.)	95

BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI BULLETIN OF THE POLYTECHNIC INSTITUTE OF IAȘI Volume 67 (71), Number 1-2 2021

Section

MATERIALS SCIENCE AND ENGINEERING

CONTENTS	<u>Pp</u> .
LENUȚA CIURCĂ, BOGDAN PRICOP, NICANOR CIMPOEȘU, MARICEL AGOP, LEANDRU-GHEORGHE BUJOREANU, Creep Behaviour of a FeMn Shape Memory Alloy (English, Romanian summary) CORNELIA CÎRLAN PALEU, CORNELIU MUNTEANU, ANIȘOARA DASCĂLU and VIOREL PALEU, Failure Modes of Pumps' Mechanical Parts and Coating Solutions for Wear Problems (English,	9
Romanian summary) ELENA IONELA CHERECHEŞ, MARIUS IONUŢ CHERECHEŞ and ALINA ADRIANA MINEA, Analysis of the Operating Behavior of Some Mixtures: Water, Ionic Liquid, Nanoparticles (English,	19
Romanian summary)	29
MARIUS IONUȚ CHERECHEȘ, ELENA IONELA CHERECHEȘ and ALINA ADRIANA MINEA, Studies on Phase Change Materials	
Improved with Nanoparticles (English, Romanian summary) RAUL GEORGE CIUBOTARIU, DAN ELIEZER, CORNELIU MUNTEANU and BOGDAN ISTRATE, Application of Hollow Glass Fibers Structures as High Pressure Storage System for Hydrogen (English.	43
Romanian summary)	55
DRAGOŞ-ŞTEFAN GHERGHESCU, Traditional Techniques and Natural	
Construction Materials in Romania (English, Romanian summary) ROXANA OANA NASTASĂ, CORNELIU MUNTEANU and BOGDAN ISTRATE Recent Research on Mg-Based Biodegradable Alloys –	65
ANDREI RATOI, DAN ELIEZER and CORNELIU MUNTEANU, A Combined Materials Science and Mechanical Approach to the Study of Hydrogen Embrittlement of Structural Materials (English,	77
Romanian summary)	95

BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI Publicat de Universitatea Tehnică "Gheorghe Asachi" din Iași Volumul 67 (71), Numărul 1-2, 2021 Secția ȘTIINȚA ȘI INGINERIA MATERIALELOR

CREEP BEHAVIOUR OF A FeMn SHAPE MEMORY ALLOY

ΒY

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Abstract. Slow deformation of metals in time under constant load, known as creep, has been in the center of attention of the specialists in structural applications for more than half a century. Especially in the case of metallic parts, subjected to service temperatures that constantly increased with the advance of technological progress, creep control has become one of the most important engineering issues. In the specific case of shape memory alloys (SMAs) which have a martensitic structure comprising movable plates, at low temperatures, creep occurrence has the potential to develop marked structural changes. The present paper is focused on FeMnSiCrNi SMAs obtained by powder metallurgy (PM). These alloys are corrosion resistant and present fair workability at room temperature (RT). The specimens were prepared from PM 68Fe-18Mn-3Si-7Cr-4Ni (mass %) which were pressed and sintered under controlled atmosphere. Hot rolling was applied in order to increase compactness and to decrease the cross section, such as to avoid intergranular incompatibilities. Hot rolled billets were cut into lamellar specimens (1 x 4 x 50 mm) by wire spark erosion. The critical temperatures for creep tests were determined by temperature scans performed on a dynamic mechanical analyzer (DMA), equipped with dedicated software both for dynamic testing and for creep. Creep tests were done by means of a dual cantilever specimen holder, four different forces being applied at five critical temperatures, respectively. Total creep time was 2000 s. The variations of

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Lenuta Ciurca et a

bending deflections with time emphasized the presence of two stages: (i) initial/ transitory creep and (ii) secondary/ stabilized creep. Creep rates were determined for each stage, force and temperature. The structural evolution of martensite plates, from initial state to the final state resulting after the application of the largest force and temperature, was analyzed by optical and scanning microscopy.

Keywords: creep; creep rate; dynamic mechanical analysis; modelling; shape memory alloy.

1. Introduction

Most of structural materials are subjected to shape distortions developed during great periods of time. This behaviour, characterised by strain increase in time under invariant loading conditions is termed as *creep* being most prominent in metallic parts and especially Superalloys (Reed, 2006).

Though creep is generally approached as a steady-state phenomenon (Nabarro and Villiers, 1995) it actually consists of three stages: (i) primary/ transient creep; (ii) secondary/ stabilized creep and (iii) tertiary/ catastrophic creep associated with failure (Clauer and Wilcox, 1967). But in most cases, it the structures do not collapse, only the first two creep stages are noticed.

In the specific case of powder metallurgy (PM) FeMnSiCrNi shape memory alloys (SMAs), there is an intricate tradeoff between reversible martensitic transformation and porosity degree (Pricop *et al.*, 2020).

The former is strictly necessary for the development of shape memory effect (SME) and consists in the thermally induced reversion to γ -face centered cubic (fcc) austenite of ε -hexagonal close packed (hcp) stress induced martensite (Sato *et al.*, 1982), in spite of the opposition of α '-body centered cubic (bcc) martensite, which is generally present in PM FeMnSiCrNi SMAs with low Mn content (Mocanu *et al.*, 2018).

The latter may vary between 2.51% and 16.85% and contributes to the diversification of martensite plates and to the increase in their intersection complexity since more γ -fcc austenite transformed to α '-bcc martensite during heating (Pricop *et al.*, 2018).

Besides the reverse martensitic transformation of ε -hcp martensite to γ -fcc austenite, occurring during heating at higher temperatures, there is also an antiferromagnetic - paramagnetic transition, appearing at Neel temperature (T_N) which partially overlaps the reversion of α '-bcc martensite to γ -fcc austenite, at lower temperatures (Pricop *et al.*, 2021).

The presence of martensite plates, in the initial structure of the specimens subjected to creep, has the potential to render even more complicated the resulting structural changes thus enhancing the reorientation of the plates and augmenting creep strain, even at low applied loads.

The present study continues the efforts commenced in a previous paper dedicated to creep phenomena occurring in a PM Fe-18Mn-3Si-7Cr-4Ni (mass. %)

SMA subjected to three-point-bending (Ciurcă *et al.*, 2021) and aims to discuss the morphological changes induced within martensite plates.

2. Experimental Procedure

An Fe-18Mn-3Si-7Cr-4Ni (mass. %) SMA was produced by pressing (500 MPa), sintering (1120°C under cracked ammonia), homogenization annealing (1100°C/ 1 hr/ water) and hot rolling (1000°C) to 1 mm thickness (Ciurcă *et al.*, 2019).

A dynamic mechanical analyzer, type NETZSCH DMA 242 Artemis, was used to perform creep tests, using PROTEUS software for creep and relaxation. Four specimens were bent by four different forces, 1 N, 3 N, 6 N and 9 N, respectively, at five different temperatures, during 2000 s. As pointed out in our previous study dedicated to the creep phenomena occurring in PM Fe-18Mn-3Si-7Cr-4Ni (mass. %) SMAs, five representative temperatures were selected by temperature scan - DMA tests, due to their corresponding representative structures: (i) 60°C, 100% antiferromagnetic martensite; (ii) 233°C, 50% antiferromagnetic martensite; (iv) 270°C, 50% paramagnetic martensite; martensite; (iv) 270°C, 50% paramagnetic martensite and (v) 300°C, 100% austenite (Ciurcă *et al.*, 2021).

Structural observations were done by optical and scanning electron microscopy. The former was achieved using an OPTIKA XDS-3 MET microscope equipped with an OPTIKAM 4083.B5 digital USB camera, and OPTIKAM B5 software, while the latter was accomplished by means of a VEGA II LMH TESCAN scanning electron microscope device equipped with silicon SPM cantilevers and easyScope video camera.

3. Experimental Results and Discussion

The variation of bending deflection, at the above five temperatures, while applying the four different forces, are summarized in Fig. 1.

It is noticeable that the variation of creep bending deflection has occurred in the two first stages and has monotonically increased with both applied force and test temperature, reaching 100 μ m for the largest test temperature and applied force. One exception is represented by the results obtained at 270°C, where the structure has been 50% paramagnetic martensite-50% austenite, because these creep strains are generally larger than those recorded at 300°C, in fully austenitic state.



Fig. 1 – Bending deflection in time, at: (a) 60°C; (b) 233°C; (c) 248°C; (d) 270°C; (e) 300°C.

According to the approach reported by Leinenbach *et al.*, for low-temperature creep and stress relaxation behaviour, the strain reached after 1000 s was for each test temperature and applied force, as d_{1000} (Leinenbach *et al.*, 2016). The variations of its absolute values, together with those of total creep deflection Δd are summarized in Fig. 2.



Fig. 2 – Variations with temperature of total creep deflection, Δd and 1000 s deflection, d_{1000} , at different applied forces: (a) 1N; (b) 3 N; (c) 248°C; (d) 6 N; (e) 9 N.

It is noticeable that the two variations are rather similar owing to the high stabilization occurring during secondary creep stage. In Fig. 2, larger total deflections are displayed at 270°C, in the structure comprising paramagnetic martensite and austenite.

This local increase of creep strain could be caused by the higher instability of paramagnetic martensite, associated with larger entropy changes. Such instabilities in FeMn alloys were also reported by La Roca *et al.* during the reversion to austenite of paramagnetic martensite (La Roca *et al.*, 2016).

For a closer look of total creep strain rate variations with force and temperature, Fig. 3 is displayed.



Fig. 3 – Variations of total creep strain with temperature in logarithmic coordinates.

The variations caused by the force of 6 N were irregular so they were disregarded in further discussion. Therefore, creep strain rate variations caused by the applied forces of 1N, 3N and 9N, were precisely fitted with linear functions of the form Dd/Dt = aT + b. The values of the slope *a* and the intercept *b* are listed in Table 1.

 Table 1

 Summary of the Linear Fitting Coefficients, According to the Creep Strain Rate Variations from Fig. 3

j 8					
Force	а	error	b	error	
1 N	0.47593	± 0.08995	-3.51391	± 0.20743	
3 N	0.20232	± 0.06466	-2.29015	± 0.14911	
9 N	0.17969	± 0.14911	-1.78485	± 0.13251	

Considering that the slope a, from the above equations, represents theoretical creep strain rate per unit of time and temperature, one can note that the increase of applied force caused a diminution of creep rate. The values of the intercept b would theoretically corresponds to creep strain rate at 0°C. But, since its values are negative, it has no physical significance, suggesting that creep strain can be negligible at 0°C.

A more comprehensive image concerning the influence of both test temperature and applied force on total creep strain rate is illustrated in Fig. 4.



Fig. 4 – Space diagram illustrating the influence of both test temperature and applied force on total creep strain rate.

This diagram sustains the observation that the largest total creep rates were obtained during the creep tests performed at 270°C, where the transformation rate of paramagnetic martensite to austenite has been maximum, as we have previously reported (Ciurcă *et al.*, 2021)

In order to emphasize the morphological changes induced within martensite plates before and after creep, two representative micrographs are shown in Fig. 5.

The optical micrographs reveal wide disoriented martensite plates in initial state, Fig. 5*a*. After creep occurrence, the specimen deflected more than 100 μ m under the effect of a 9 N force, applied at 270°C. At this temperature 50% of paramagnetic martensite theoretically transformed to austenite, so the specimen experienced the largest instability from the point of view of creep behavior between room temperature and 300°C. From a morphological point of

view, Fig. 5*b* illustrates thinner martensite plates with a more shallow surface relief. In addition, as pointed out by brackets, martensite plates showed an alignment tendency along a common direction.



Fig. 5 – Optical micrographs illustrating representative microstructures: (*a*) before and (*b*) after creep caused by an applied force of 9 N at 270°C.

A better look on surface relief variation can be observed on the image profiles recorded on SEM device by converting color variations into height variations, considering black areas as the deepest and the white ones as the most prominent (Lohan *et al.*, 2011). The representative aspects of surface profile images recorded on SEM are shown in Fig. 6.



Fig. 6 – Surface profile images, recorded on SEM, of the specimen: (*a*) I initial state and (*b*) after creep caused by an applied force of 9 N at 270°C.

Fig. 6*a* illustrates the misalignment of martensite plates, in initial state, which was also demonstrated by the optical micrograph from Fig. 5*a*. After creep occurrence, martensite plates became less prominent and more aligned along a single direction, as suggested by Fig. 5*b*.

4. Conclusions

The following conclusions can be drawn:

- in the case of four among five test temperatures and for all applied forces, creep strain increased with temperature and force;
- the largest creep strains were obtained at the temperature where paramagnetic martensite is still transforming into austenite;
- after creep occurrence, martensite plates became less prominent, thinner and less disoriented.

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COMPORTAMENTUL LA FLUAJ AL UNUI ALIAJ FeMn CU MEMORIA FORMEI

(Rezumat)

Deformarea lentă a metalelor în timp sub sarcină constantă, cunoscută sub numele de fluaj, a fost în centrul atentiei specialistilor în aplicatii structurale de mai bine de jumătate de secol. În special în cazul pieselor metalice, supuse unor temperaturi de serviciu care au crescut constant odată cu progresul tehnologic, controlul fluajului a devenit una dintre cele mai importante probleme de inginerie. În cazul specific al aliajelor cu memorie de formă (AMF) care au o structură martensitică cuprinzând plăci mobile, la temperaturi scăzute, apariția fluajului are potențialul de a dezvolta modificări structurale marcante. Prezenta lucrare se concentrează pe AMF FeMnSiCrNi obținute prin metalurgia pulberilor (PM). Aceste aliaje sunt rezistente la coroziune și prezintă o foarte bună formabilitate la temperatura camerei (RT). Probele au fost preparate din PM 68Fe-18Mn-3Si-7Cr-4Ni (masă%) care au fost presate și sinterizate sub atmosferă controlată. Laminarea la cald a fost aplicată pentru a crește compactitatea și a reduce sectiunea transversală, astfel încât să se evite incompatibilitățile intergranulare. Piesele laminate la cald au fost tăiate în probe lamelare (1 x 4 x 50 mm) prin electroeroziune cu fir. Temperaturile principale pentru testele de fluaj au fost determinate de scanările de temperatură efectuate pe un analizor mecanico-dinamic (DMA), echipat cu soft dedicat atât pentru testarea dinamică, cât și pentru fluaj. Testele de fluaj au fost făcute utilizând un suport de probe cu pârghie dublă, patru forțe diferite fiind aplicate la cinci temperaturi alese. Timpul total de fluaj a fost de 2000 s. Variațiile deformării de fluaj în timp au subliniat prezența a două etape: (i) fluaj inițial / tranzitoriu și (ii) fluaj secundar / stabilizat. Viteza de fluaj a fost determinată pentru fiecare etapă, fortă și temperatură. Evolutia structurală a plăcilor de martensită, de la starea initială la starea finală rezultată după aplicarea celei mai mari forțe și temperaturi, a fost analizată prin microscopie optică și microscopie electronică.

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FAILURE MODES OF PUMPS' MECHANICAL PARTS AND COATING SOLUTIONS FOR WEAR PROBLEMS

ΒY

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> Abstract. The failure of mechanical parts of pumping stations usually happens in various forms (abrasion, corrosion, cavitation, erosion, pitting, adhesive wear etc.), conducting to the out-of-service state of the entire pumping station and even of the whole water treatment plant. The paper presents the working conditions in designed parameters, the problematics of different pumps, and some solutions found in literature, emphasizing the possibility of refurbishing of worn mechanical parts by applying various anti-wear coatings. Regarding the wear resistance of coatings deposited by Atmospheric Plasma Spray (APS) method, a case study of previous research carried out by the authors is also presented.

Keywords: thin coatings; atmospheric plasma spray; wear; pumps; failure.

1. Introduction

Pumping stations are key points of water supply stations and water treatment and reuse plants. Pumps are the core of pumping stations, but their mechanical parts (impeller, shaft, sleeves, bushes, and bearings) are continuously subjected to various wear mechanisms (corrosion, abrasion,

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erosion, cavitation etc.). The evaluation of the mechanical reliability of a water treatment system consists on precise identification of the key parts, whose failure can affect the normal functioning of the station (within the parameters specified in the design stage). The result of such analysis is a list of mechanical parts, which are the weaknesses of the station (Eisenberg *et al.*, 2001).

Manufacturers are providing to the customers a list of different failure modes of pumps and possible causes that driven to these faults. It is evident that every produced defect is because of either exploiting parameters out of recommended range, or due to inevitably wear manifesting in the system. Multistage vertical pumps are generally used as irrigation and slurry pumps being easy to mount and dismount, but always subjected to abrasive wear. If a pump fails due to abrasive wear, the producer will blame on broken seals, improper lubrication etc.

Often, it is more convenient to recondition the worn components than to replace them with new ones. Budris (2012, 2013) and Bloch and Budris (2014) recommended the reconditioning of different parts of pumps by coating deposition of anti-wear materials, but warned that clearances between functional parts have to be kept as recommended by manufacturer. Recently, Paleu Cîrlan *et al.* (2019) suggested from literature some coatings for each component of the water treatment plant and studied the friction resistance of Al2O3 coating in oil and water lubrication. It seems that water could successfully assure proper lubrication, as the Al2O3 coating behaves like a solid lubricant. Also, Paleu Cîrlan *et al.* (2020) and Paleu *et al.* (2020) reported results of friction tests and microstructural analysis for Al2O3 40TiO2 (AMDRY 6250) coating deposited in different layer thickness on steel substrate. The results of friction tests, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis indicated that, for certain running conditions, there is an optimum thickness of the coating.

This paper emphasizes the connection between performance parameters of pumps, problematics of different pumps, and some solutions found in literature, underlining the possibility of refurbishing of worn mechanical parts by applying different anti-wear coatings. Regarding the wear resistance of coatings deposited by Atmospheric Plasma Spay (APS) method, a case study of previous research carried out by the authors is also presented.

2. Pump Performance Parameters

The main performance parameters of pumps, according to Menon (2010), are: Head (H), Efficiency (Ef, %), Pump Brake Horsepower (BHP), flow rate (Q), and Net Positive Suction Head (NPSH).



Fig. 1 – Efficiency- capacity curve (Bloch and Budris, 2014).

2.1. Head (H)

Pressure or "Head", H [m] or H [feet] - represents the pressure at the outlet, or rather the height at which the pump can lift a column of liquid.

2.2. Efficiency (Ef, in %)

Efficiency % is the ratio of power supplied by the liquid at the output Pw, and power at the motor shaft (at the input), that is Ef (%) = Pw / Ps.

2.3. Pump Brake Horsepower (BHP)

BHP ("Pump Brake Horsepower") - represents the power delivered to the pump shaft, expressed in horsepower, calculated using specific calculation formulas (Bloch and Budris, 2014).

2.4. Capacity, Flow Rate (Q)

Capacity, or flow rate - represents the amount of liquid that can be transported in the unit of time, in liters/hour, m3/hour, or in gal/min.

2.5. Net Positive Suction Head (NPSH)

NPSH - represents the difference between pump pressure and liquid vapor pressure, cavitation occurring in areas with high pressure differences. It

refers to how likely it is that the pump will operate in cavitation mode, cavitation being an unwanted phenomenon, in which the vapor bubbles suffer implosions in the vicinity of impeller surfaces, producing pinching on the pallet surfaces. Considering the previously mentioned parameters, the right pump can be chosen for each application.

3. Wear Modes and Materials for Vertical Pumps

3.1. Wear Modes

The various parts of the pumps are subjected to corrosion, abrasion, adhesive wear, pitting, erosion, and cavitation. These wear modes can be slowed down or prevented by users by appropriate choice of materials, lubricants, and coatings.

Corrosion damage affects pipes but early corrosion may also affect many components of water pumps (Vazdirvanidis *et al.*, 2017). A cost analysis of the corrosion in concrete pipes revealed that the suited choose of coating material is able to extend the service life (MortezaNia and Othman, 2012). Some effective coatings to protect the pump's parts against corrosion are: epoxy (Ep), polyurethane (PU), and combined epoxy - sodium silicate (Ep–SS). For hydrochloric acid environments coatings as Cr-Ni, Ni-Cu and Ni-Mo (*e.g.*, 20Cr 30Ni, 66Ni 32Cu, and 62NI 28Mo) are recommended. 20Cr 30Ni coating proved best resistance to corrosion in mixed acid solutions (Roberge, 2014).

Abrasion wear is produced by hard particles from environment - due to improper sealing, or as result of wear particles trapped between two surfaces in relative motion within the contact - favorited by poor lubrication. Abrasion wear mostly affects the next components of pumps: oil rings, bearings and impeller, but also the sleeves, bushes and cases. Slurry pumps are especially affected by abrasive wear, the wear rate depending by nature (hardness), size and sharpness of slurry abrasive particles. Abrasion can be avoided by proper sealing and lubrication, but in irrigation pumps with the rotor supported by bearing sleeves the lubricant is usually the circulating agent (unfiltered water). It is clear that abrasion affects the counterparts in relative motion with small gaps. Hard coatings of Ti, W, Cr alloys are recommended as anti-wear protection (Wu *et al.*, 2014).

Slurry erosion mainly affects the wastewater plants and sewerage pipes. The erosion takes place due to the impact action of solid particles (erodent) contained in a fluid stream. Some parameters influencing the erosion are: velocity of erodent particles, shape, size, hardness, angle of impact, and number of erodent particles in the fluid stream, but also the strength the material being subjected to the erosion (the target). Even the stainless steel as AISI 316 is subjected to erosion, but its resistance to wear can be improved by deposition of cobalt-based and titanium-based, the titanium alloy coating proving the best

strength to erosion (Singh *et al.*, 2015). For a hydro-turbine made of CA6NM steel, Ni-Al2O3 based coatings proved the best protection against erosion for 40% of Al2O3 in the Ni alloy (Grewal *et al.*, 2013).

Cavitation is produced by rapid change in pressure within a liquid. As a result, small bubbles of vapor (small cavities) are produced in low pressure places. The implosion of bubbles subjected to high pressure generates a shock wave that develops damages if occurs near to solid surfaces. Pump impellers, valves and inlet portions of casing where liquid direction change suddenly happens suffer cavitation wear. Cavitation of pumps can be avoided by designing suction pipes and flattening the pressure within the liquid. Resistance to cavitation can be attained by deposition of hard ceramic coatings to impellers (Budris, 2013). Coatings are recommended usually for the maintenance of larger centrifugal pumps; in this case the thickness of a coating cannot greatly affect their normal functioning (MortezaNia and Othman, 2012; Roberge, 2014).

3.2. Materials for Pump Components and Lubricants

After consulting the online sites of some manufacturers, in this paper only the materials recommended by DP (DP pumps, 2020) for vertical pumps will be presented (Table 1). Notations in Table 1: DPVE = DP Vertical pumps in AISI 304 (1.4301) - Male thread with built-in non-return valve on discharge side; DPV = DP Vertical pumps in AISI 304 (1.4301); DPVS = DP Vertical pumps in superior grade AISI 316 (1.4401); DPLHS = DP Vertical pumps in superior grade AISI 316 (1.4401) 40 Bar.

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Table 1								
Materials for Pump Components (***,2018)								
Pump series	DPVE	DPV	DPVS	DPLHS				
		Ma	terial specification					
Pump shaft and bushes	AISI 303 (1.4305) A		AIS	AISI 316 (1.4401)				
Impeller, diffuser,	AISI 304 (1.4301)		AIS	AISI 316L (1.4404)				
suction/discharge								
casing, sleeve								
Base plate	GG20 (GJL-200) (GG25 (GJL-250)	-				
Top bracket	GG25 (GJL-250)		L-250)	AISI 316 (1.4408)				
(Collar) flange	-	G	GG40 (GJS-400)	AISI 316 (1.4408)				
Elastomers	EPDM			Viton				
Liquid lubricated bearings	- ce		ceramic/tungst	eramic/tungsten-carbide				
Deaerating and drain plug	bı	ass	AIS	SI 316 (1.4401)				
Temperature range [⁰ C]	-15 to 60		-15 to 120					
Max. ambient. temp. [⁰ C]			50					

3.3. Lubricants for Pumps

According to DP pump manufacturer site (DP pumps, 2020), there are three types of lubrication for the bearing line of pumps.

- Oil lubrication (OL) - the line of shaft bearings is lubricated by oil, supplied from an oiler.

– Grease lubrication (GL) – a grease pump supplies the lubricant to line-shaft bearings.

- Clear water lubrication (CWL) – lubrication is realized by circulation agent (pumped clear water), in order to avoid the oil contamination of waters. If the circulating agent is turbid pumped water, lubrication can be done with clean water from an external source.

3.4. Main Failure Modes of Pumps Produced by Excessive Wear

Unfortunately, the wear of various components will certainly manifest after a period of time. The main defects of pumps produced by excessive wear are: excessive vibrations, high temperature of bearings, and leakages along the shaft line.

Excessive vibrations can be caused by an unbalanced rotor, but they can by also the result of the worn components. In the latest case usually, the cause is improper lubrication and worn bearings. High temperature of bearings can be caused by poor lubrication, or by an increase of the thrust load. Leakages along the shaft line are produced by worn seals or worn shaft.

For worn seals and bearings, the solution is to replace them with new ones, but pumps could present improper functioning produced by excessive impeller wear. In the case of worn shafts or worn impellers, coating solutions can be adopted. Published literature (Budris, 2012; Budris, 2013; Bloch and Budris, 2014) recommended the reconditioning of different parts of pumps by coating deposition of anti-wear materials, but warned that clearances between functional parts have to be kept as previewed by manufacturer. This fact is important especially in the case of impeller coating, as cavitation may intensify in change.

4. Case Study

Fig. 2 presents a worn sleeve from a multistage vertical irrigation pump, provided by ANIF Iaşi. One could observe the double wear produced by the action of circulating agent (water): corrosion and abrasion.



Fig. 2 – Worn shaft sleeve from a multistage irrigation pump CWL. General view (left) and section view (right).

Parallelepiped samples cutaway from this sleeve were coated with AMDRY6250 (Al2O3 40TiO2) powder by Atmospheric Plasma Spray (APS) method (Paleu Cîrlan *et al.*, 2020). This powder is recommended by the manufacturer for APS deposition on pump components, due to its resistance to abrasive, fretting, corrosive, and erosive wear. Fig. 3 presents the fine structure of AMDRY6250 microparticles of about 30 µm mean diameter.



Fig. 3 - SEM image of AMDRY6250 powder.

Three different thickness layers of AMDRY 6250 were deposited (5, 7, and 9 layers), the thickness being between 55 μ m (for 5 layers) and 116 μ m (for 9 successive layers). The obtained structure was homogeneous, but with some microcracks and unmelted particles. The microcracks are assumed to different thermal contraction of base material and Al2O3-40TiO2-coated layers during the cooling process. Friction tests were carried out on AMSLER machine (Paleu

et al., 2020) on AMDRY6250 coated samples, and on uncoated samples made of AISI 303 (EN 1.4305) steel.

Preliminary dry friction tests results, Scanning Electron Microscopy (SEM), and Energy-Dispersive Spectroscopy (EDS) analysis proved that there is an optimum coating thickness around 90 μ m (7 layers) from the viewpoint of minimum friction coefficient. More detailed results are given in (Paleu Cîrlan *et al.*, 2020; Paleu *et al.*, 2020).

With the aim to assess the best coating for pump components, the research will continue on various thin coatings (AMDRY 1371: Mo-NiCrFeBSiC, METCO 136F: Cr2O3-xSiO2-yTiO2) with different thickness and also on sandwich coatings deposited by APS on steel substrate of the reconditioned pump sleeve.

5. Conclusions

The papers copes with the problematics of irrigation vertical pumps, presenting the main performance parameters affected by different wear modes simultaneously manifesting in exploited pumps. Wear of machine parts of pumps being in relative motion generates excessive vibrations, increased temperature in bearings and leakages.

Worn components can be reconditioned by coating deposition of antiwear materials, but keeping the exact clearances between functional parts, as recommended by manufacturer. Besides the main wear modes, materials and lubricants used for vertical pumps, a case study was presented. A shaft sleeve from an irrigation pump was coated by APS with AMDRY6250 powder. The obtained microstructure and the results regarding dry wear tests were previously presented by the authors.

Future study will focus on the discovery of best coating for pump components, various thin coatings (AMDRY 1371: Mo-NiCrFeBSiC, METCO 136F: Cr2O3-xSiO2-yTiO2) with different thickness and sandwich configurations being deposited by APS on steel substrate of the reconditioned pump sleeve.

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DETERIORAREA COMPONENTELOR MECANICE ALE POMPELOR ȘI SOLUȚII PENTRU REALIZAREA DE ACOPERIRI REZISTENTE LA UZURĂ

(Rezumat)

Deteriorarea componentelor mecanice ale stațiilor de pompare se produce de obicei sub diferite forme (abraziune, coroziune, cavitație, eroziune, oboseală de contact, uzură adezivă, etc.), conducând la disfuncționalități ale întregii stații de pompare și chiar ale stației de tratare a apei. Lucrarea prezintă condițiile de lucru în parametrii proiectați, problematica diferitelor pompe și câteva soluții recomandate în literatura de specialitate, subliniind posibilitatea recondiționării pieselor mecanice uzate prin aplicarea diferitelor tipuri de acoperiri anti-uzură. În ceea ce privește rezistența la uzură a învelișurilor depuse prin metoda Atmospheric Plasma Spray (APS), este prezentat și un studiu de caz al cercetărilor anterioare efectuate de către autori.

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ANALYSIS OF THE OPERATING BEHAVIOR OF SOME MIXTURES: WATER, IONIC LIQUID, NANOPARTICLES

ΒY

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Abstract. A new class of heat transfer fluids has been developed over the last decade, and these new fluids combine two phases, namely ionic liquids and nanoparticles, known as IoNanofluids. IoNanofluids are of interest to researchers due to improved thermophysical properties compared to the classical heat transfer fluids, e.g. water or ethylene glycol, but also because of their applications in heat exchangers, in the electronics industry or in solar collectors and beyond. The large diversity of nanoparticles that can be added to different ionic liquids transforms them into complex heat transfer fluids. As can be seen from the specialized literature among the thermophysical properties studied for IoNanofluids, there are thermal conductivity, density, specific heat and viscosity. These properties were also determined by these authors for mixtures based on water, ionic liquid and nanoparticles in order to determine some possible theoretical methods for evaluating the heat transfer between the studied IoNanofluids and the fluid used as the base for comparison. In this paper, an analysis of the improvement of the thermal transfer, with reference to the convective heat transfer will be carried out using the IoNanofluids based on alumina, which have as their basic fluid a mixture of ionic liquid and water. The analysis will be performed using several tools that are highlighted in the specialized literature, such as the analysis of the thermal transfer using Prandtl,

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Mouromtseff and with the equations of Gnielinski and Prasher. Further on, for the data interpretation several FOM (figure of merit) will be evaluated and compared. In conclusion, complex studies of these new thermal transfer fluids are needed for a correct description of them and to demonstrate that they have a beneficial behavior in the heat transfer if compared to the basic fluids (*i.e.* water or glycols), obtaining certain advantages in terms of thermal efficiency.

Keywords: Ionanofluids; ionic liquids; nanaparticles.

1. Introduction

At the global level, an increase of the energy performance of the equipment for generating, transferring and storing energy is required. In this sense, new heat transfer fluids have been developed that can reduce energy consumption thus opening up paths to multiple applications.

Considered in the last years as a new generation of fluids, IoNanofluids have attracted attention due to their unique characteristics and the fact that they can be used in heat exchangers, in the cooling of computer microprocessors but also in different installations. In general, IoNanofluids are defined as two-phase fluids, one liquid based on ionic liquids and one solid based on nanoparticles. In the literature, IoNanofluids are characterized as fluids that increase the heat transfer coefficient and have thermophysical properties that are better compared to another type of heat transfer fluid, namely nanofluids (Cherecheş *et al.*, 2019a; Cherecheş *et al.*, 2019b; Minea and Moldoveanu, 2018; Minea and Murshed , 2018; Minea and El-Maghlany, 2017; Minea *et al.*, 2017; Cherecheş *et al.*, 2019c; Minea, 2020). The convective heat transfer coefficient influences the Prandtl number, Reynolds number and Nusselt number which are functions of thermophysical properties of nanofluids and IoNanofluids respectively (El-Maghlany and Minea, 2019; Cherecheş *et al.*, 2018; Minea and Manca, 2017; Minea and Manca, 2017).

Minea studied the essential aspects of turbulent convective heat transfer of nanofluids that were compared in detail based on few figures of merits relevant to their applications and the results reported are believed to be useful for the thermal optimization of nanofluid flow inside tubes (Minea, 2016).

In an experimental study Cherecheş *et al.*, prepared and studied several ionic liquids enhanced with aluminum nanoparticles and determined their stability, pH, density and thermal conductivity (Cherecheş *et al.*, 2019d). The base fluid was made from different mixtures based on water and 1-ethyl-3-methylimidazolium methanesulfonate ionic liquid, in which different mass concentrations of Al_2O_3 nanoparticles were added. They concluded that these new fluids can be seen as a possible candidate for heat transfer application. Paul has experimentally studied the thermophysical properties of three ionic liquids ([C₄mpyrr][NTf₂], [C₄mim][NTf₂], [N₄₁₁₁][NTf₂]) and their IoNanofluids by

adding spherical and flat Al_2O_3 nanoparticles. The conclusion of the study is that IoNanofluids with Al_2O_3 nanoparticles have high density, thermal conductivity, viscosity and high thermal capacity compared to the basic ionic liquids (Paul, 2014).

In his work, Liu measures the thermal conductivity of IoNanofluids at temperatures above 100°C, the ionic liquid used being 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM]BF₄) based on graphene, the temperature ranging from room temperature to temperatures of about 200°C. Also, as the temperature rises from 25 to 200°C, the thermal conductivity of [HMIM][BF₄] and IoNanofluids increases linearly with the temperature (Liu, 2014). Visser et al. found that $[C_4mim][N(SO_2C_2F_5)_2]$ with MWCNT had the highest increase in viscosity and stated that this occurs due to the interaction of nanoparticles with cations and anions of ionic liquid (Visser *et al.*, 2012). Other research has been found to be contradictory regarding the rheological behavior of IoNanofluids. Compared to the viscosity, the thermal conductivity was studied more intensively and the results were encouraging regarding the increase of the thermal conductivity by adding nanoparticles in the ionic liquid (Atashrouz *et al.*, 2015; He and Alexandridis, 2015).

2. Teoretical Analysis of the Thermal Transfer Behavior

Type the second section of your paper in here. Use as much space as necessary. Theoretical analysis of the heat transfer behavior by convection can be done using dimensional or dimensionless measurements, very often used in specialized literature or based on the established equations (for example, Gnielinski's equation, (Gnielinski, 1976), Dittus-Boelter equation (Dittus and Boelter, 1930), or the Petukhov – Popov correlation (Petukhov and Popov, 1963)). These estimations are made on the basis of the thermophysical properties, taking into account the characteristics of the flow regime, with reference to the laminar and turbulent flow (Yu *et al.*, 2012).

Prandtl's number is a dimensionless number that gives us information on what type of heat transfer predominates and depends on the specific heat, the dynamic viscosity and the thermal conductivity of the fluid. If Prandtl has low values it means that the conduction predominates in the liquid, whereas the higher values mean that the heat transfer by convection is more efficient comparative with the conduction. The Prandtl number is defined in Eq. (1) and the fluids with a small Prandtl number flow easily through the pipes and usually have a high thermal conductivity.

$$Pr = \frac{c_{\rho}\mu}{k} \tag{1}$$

where: c_p – specific heat, μ – viscosity, k – thermal conductivity

The equation of Prasher *et al.* (2006) can be used to determine the efficiency of heat transfer (HTE). The Eq. (2) contains information on the relative viscosity and thermal conductivity of IoNanofluid in ratio to the base fluid and was determined for the case of convection heat transfer in laminar regime.

$$HTE = \frac{(\mu_{nf} - \mu_{f})/\mu_{f}}{(k_{nf} - k_{f})/k_{f}}$$
(2)

where: μ – dynamic viscosity, k – thermal conductivity, indices *nf*, *f* refer to the nanofluid, respectively the base fluid.

The idea of using the HTE parameter is to evaluate the efficiency of the use of nanofluid in laminar flow applications, where the most important thermophysical parameter is the thermal conductivity, but also the viscosity can influence the flow.

Mouromtseff number (Mo) is a dimensional number introduced in 1942 by I.E. Mouromtseff (Mouromtseff, 1942) and represents the effect of the thermophysical properties of a fluid on the convective heat transfer coefficient in forced flow regime. Mouromtseff number is defined as:

$$Mo = \frac{\rho^a k^b c_p^d}{\mu^e} \tag{3}$$

where: ρ – density, k – thermal conductivity, c_p – specific heat, μ – viscosity. The exponents a, b, d and e have values corresponding to each particular situation (Simons, 2006).

Gnielinski's equation is one of the fundamental equations of convection heat transfer in turbulent flow. Gnielinski's equation, considered the most accurate for describing forced convection, is valid for both turbulent and transient flow, for $2300 < \text{Re} < 5 \times 106$ (Yu, 2012).

$$h = \frac{(f/8)(Re-1000)Pr(k/d)}{1+12.7(f/8)^{1/2}(Pr^{2/3}-1)}$$
(4)

where: f is the coefficient of friction of Darcy, which can be determined by the relation proposed by Petukhov (Petukhov and Popov, 1963; Incropera *et al.*, 2007).

$$f = (0.79 \ln Re - 1.64) - 2$$
 (5)

where: Re – Reynolds number, k – thermal conductivity, Pr – Prandtl number, d – pipe diameter.

3. Analysis of the Efficiency of Thermal Transfer of Alumina Nanoparticles Enhanced Ionic Liquids

a) Analysis of the behavior of IoNanofluids on thermal transfer using Prandtl's number

Given that in the industrial practice of heat transfer fluids with the lowest number Pr are preferable, FOM1 will be defined as:

a) For mixture:

$$FOM1_{mix} = \frac{\Pr_{mix}}{\Pr_{INF}}$$
(6)

b) For water:

$$FOM1_{water} = \frac{\Pr_{water}}{\Pr_{INF}}$$
(7)

c) For pure ionic liquid:

$$FOM1_{IL} = \frac{\Pr_{IL}}{\Pr_{INF}}$$
(8)

where: Pr was defined with the Eq. (1) and the *INF* and *IL* indices refer to the IoNanofluid respectively to the ionic liquid. Fig. 1, 2 and 3 presents some data regarding the FOM 1 dependence on the type of base fluid and the nanoparticles concentration.



Fig. 1 – FOM 1 for the studied fluids that have as base fluid (0.25 W + 0.75 IL) and different mass concentrations of Al_2O_3 .

In Fig. 1, FOM 1 > 1 was obtained for all the studied fluids that had the base fluid (0.25 W + 0.75 IL). In addition, the lowest value for FOM 1 was obtained for the fluid with the highest nanoparticles concentration. In this case, the studied fluids can successfully replace classical fluids in any practical application.



different mass concentrations of Al₂O₃.

Also, in Fig. 2, FOM 1 > 1 was obtained for all the studied fluids that had the base fluid water. The highest value for FOM 1 was obtained for the fluid with the lowest nanoparticles concentration. That means that the conduction predominates in the liquid.



Fig. 3 – FOM 1 for the studied fluids that have as basic fluid ionic liquid and different mass concentrations of Al_2O_3 .

In Fig. 3, FOM 1 < 1 was obtained for all the studied fluids that had the base fluid pure ionic liquid. This Prandtl's number values mean that the heat transfer by convection is more efficient comparative with the conduction.

From the analysis of the data presented regarding the variation of FOM 1, it is noted that very high concentrations of nanoparticles in the host fluid can ensure an improvement of the thermal transfer, if it is evaluated based on the number of Pr.

b) Analysis of the behavior of IoNanofluids on thermal transfer, Mouromtseff number

For the laminar flow regime, FOM 2 is defined, based on the Mo number (Mouromtseff, 1942).

$$FOM 2 = \frac{Mo_{nf}}{Mo_f} = \frac{h_{nf}}{h_f} = \frac{k_{nf}}{k_f}$$
(9)

where: Mo - Mouromtseff's number, h - convection heat transfer coefficient, k - thermal conductivity.



Fig. 4 – FOM 2 for IoNanofluids with IL and (0.25 W + 0.75 IL) as the base fluid.

The studied IoNanofluids can successfully replace classical fluids in heat transfer operations under laminar regime if FOM 2 > 1. From the data analysis, it is observed that all IoNanofluids can replace the classical fluids as a thermal agent in laminar regime, the improvement being between 2 and 5%, depending on the type of base fluid and the concentration of the nanoparticles.

Moreover, IoNanofluids with (0.25 W + 0.75 IL) as the base fluid presents lower values for FOM 2 than the fluid with which the comparison was made. Alternatively, the relationship provided by Vajiha and Das (2012), based on the ratio of Mo number for IoNanofluid to the reference fluid, can be used alternatively for forced internal flow.

$$FOM3 = \frac{Mo_{nf}}{Mo_{f}} = \frac{h_{nf}}{h_{f}} = \frac{\rho_{nf}^{0.8} c_{pnf}^{0.5} k_{nf}^{0.5}}{\mu_{nf}^{0.3}} \frac{\mu_{f}^{0.4}}{\rho_{f}^{0.8} c_{pf}^{0.4} k_{f}^{0.6}}$$
(10)

In addition, Yu *et al.* (2012), proposed for the internal turbulent flow (through pipes) the following equation, valid for heating:

$$FOM 4 = \frac{Mo_{nf}}{Mo_f} = \left(\frac{\rho_{nf}}{\rho_f}\right)^{0.8} \left(\frac{c_{pnf}}{c_{pf}}\right)^{0.3} \left(\frac{\mu_{nf}}{\mu_f}\right)^{-0.5} \left(\frac{k_{nf}}{k_f}\right)^{0.7}$$
(11)

In the previous Eqs. (10) and (11), where: Mo – Mouromtseff's number, h – convection heat transfer coefficient, ρ – density, μ – dynamic viscosity, c_p – specific heat, k – thermal conductivity. Fig. 5 show the data on FOM 3 and FOM 4.



Fig. 5 – FOM 3 and FOM 4 for the IoNanofluids with (0.25 W + 0.75 IL) as the base fluid and different mass concentration of Al_2O_3 .

From the analysis of Fig. 5 we can see the differences between the two approaches (FOM 3 and FOM 4), the values being obviously higher if the equation proposed by Vajiha and Das (2012) is used. It can be stated that the IoNanofluids with different concentrations of alumina perform better than the conventional fluids in internal forced convection, leading to the improvement of
the thermal transfer with minimum 0.5% and maximum 6.4%, depending on the concentration.

c) Analysis of IoNanfluid behavior at thermal transfer on the basis of Gnielinski equation

Keeping the same flow conditions can be evaluated comparatively the coefficient of heat transfer by convection for a number Re = 1000 and the same pipe. Gnielinski's equation (Gnielinski, 1976) studied for IoNanofluids with (0.25 W + 0.75 IL) as the base fluid and different mass concentrations of Al_2O_3 (1%, 5%, 10%, 15% wt) derives the expression:

$$FOM5 = \frac{h_{nf}}{h_f} = \frac{Pr_{nf} k_{nf}}{1 + 12.7(f/8)^{1/2} (Pr_{nf}^{2/3} - 1)} \frac{1 + 12.7(f/8)^{1/2} (Pr_f^{2/3} - 1)}{Pr_f k_f}$$
(12)

where: the index nf and f refer to the nanofluid respectively to the base fluid; h – convection heat transfer coefficient, Pr – Prandtl's number, k – thermal conductivity, f – friction coefficient.



Fig. 6 – FOM 5 for the studied fluids.

In Fig. 6, an increase in flow efficiency is observed once with the increase of the percentage of nanoparticles in suspension. Specifically, an increase in the convection heat transfer coefficient is obtained with a percentage between 13.2% and 66.5% depending on the nanoparticles concentration. The highest value was obtained for the nanofluid with 15% alumina.

d) Analysis of the IoNanofluid behavior of thermal transfer based on the equation of Prasher et al.

The equation of Prasher *et al.* represents another form of determination of the laminar regime convection compared to the Mo number, using the HTE parameter defined by Eq. (2) (Prasher *et al*, 2006). To determine HTE, the viscosity of IoNanofluids is also taken into account. Prasher et al. state that a nanofluid performs better than the base fluid when the value is HTE < 4.



Fig. 7 – HTE for the IoNanofluids with (0.25 W + 0.75 IL) as the base fluid and different mass concentration of Al_2O_3 .

The results presented in Fig. 7 show that the two studied IoNanofluids cannot successfully replace the classical fluids because they have HTE > 4. The lowest value is for IoNanofluid with the highest concentration of Al_2O_3 nanoparticles.

4. Conclusions

This paper deals with some theoretical aspects and a comparison on different approaches and several mixtures and suspensions was accomplished based on state of the art.

The main conclusions may be summarized as follows:

- If the results are reported in FOM 1, it is observed that the IoNanofluids presented in this study have a beneficial behavior compared to the basic fluids (0.25 W + 0.75 IL) and water.
- In contrast, IoNanofluids that have as their basic fluid the pure ionic liquid do not have a beneficial behavior.
- The results regarding FOM 2 lead to an increase of the heat transfer coefficient with percentages between 2-6%.
- In turbulent regime, the best performances are obtained for IoNananofluid with 1% wt Al₂O₃, from calculations resulting in an

increase of the thermal transfer coefficient up to 54% by adding nanoparticles in the base fluid (0.25 W \pm 0.75 IL).

In conclusion, it is considered that all the IoNanofluids presented in this study have a beneficial behavior in heat transfer compared to the reference fluid (in this study: water, pure ionic liquid or mixture). Nevertheless, more experimental studies are needed in order to draw a solid conclusion about the overall benefits of ionic liquids as the base for future heat transfer fluids development.

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ANALIZA COMPORTĂRII ÎN EXPLOATARE A UNOR MIXTURI: APĂ, LICHID IONIC, NANOPARTICULE

(Rezumat)

O nouă clasă de fluide de transfer termic a fost dezvoltată în ultimul deceniu, iar aceste noi fluide combină două faze și anume lichide ionice și nanoparticule, fiind cunoscute sub denumirea de IoNanofluide. IoNanofluidele prezintă un interes în rândul cercetătorilor datorită proprietăților termofizice îmbunătățite comparativ cu fluidele clasice de transfer termic, de ex. apa sau etilenglicolul, dar și datorită aplicațiilor lor în schimbatoarele de căldură, în industria electronicelor sau în colectoarele solare și nu numai. Diversitatea mare de nanoparticule ce pot fi adăugate în diferite lichide ionice le transformă în fluide complexe de transfer termic. După cum se poate observa din literatura de specialitate printre proprietățile termofizice studiate pentru IoNanofluide se numără conductivitatea termică, densitatea, căldura specifică și vâscozitatea. Aceste proprietăți au fost determinate și de către acești autori pentru mixturi pe bază de apă, lichid ionic si nanoparticule pentru a putea determina câteva metode teoretice posibile de evaluare a transferului termic comparativ dintre IoNanofluidele studiate si fluidul utilizat ca bază. În această lucrare se va realiza o analiză a îmbunătățirii transferului termic, cu referire la transferul termic convectiv, prin utilizarea IoNanofluidelor pe bază de alumină ce au ca fluid de bază o mixtură formată din lichid ionic și apă. Analiza se va realiza folosind unele abordări din literatura de specialitate, cum ar fi analiza transferului termic cu ajutorul numărului lui Prandtl, Mouromtseff sau cu ecuațiile lui Gnielinski și Prasher. În continuare pentru interpretarea datelor se va determina FOM (figure of merit) pentru fiecare parametru de evaluare a transferului termic. În concluzie, sunt necesare studii complexe ale acestor noi fluide de transfer termic denumite IoNanofluide pentru o descriere corectă a acestora și a demonstra că au un comportament benefic în transferul de căldură comparativ cu fluidele de bază, obținându-se certe avantaje din punct de vedere al eficienței termice.

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STUDIES ON PHASE CHANGE MATERIALS IMPROVED WITH NANOPARTICLES

ΒY

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Abstract. In the last years, thermal energy storage is among the highly efficient approaches to overcome the energy crisis. Recent research has been carried out on improving heat transfer using a phase change material (PCM) which has a high fusion temperature and, by melting and solidifying at a certain temperature, is capable of storing and to release large amounts of energy. PCMs can be divided into solid–solid, solid–liquid, solid–gas and liquid–gas types, while the solid–liquid ones are the most widely applied in various applications. For the development of these new materials it is necessary to understand the effect of adding different types of nanoparticles on the thermophysical properties of PCM. Concluding, this paper aims to build on previous research on PCMs as potential materials for heat storage. Particular attention will be paid to experimental studies on PEG 400 materials as well as improving their properties by adding nanoparticles.

Keywords: nanoparticles; PCM; PEG 400; thermophysical properties; thermal conductivity.

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1. Introduction

Heating and cooling processes use half of the EU's energy consumption. Currently, cooling operations are a part of energy consumption, but demand is constantly increasing, due to climate change and global temperature rise. In this context of environment and policies, thermal energy storage systems (TES) are considered a very effective alternative for meeting EU energy efficiency objectives. Cooling thermal storage systems allow the decoupling of energy production and consumption and save energy by reducing the peak load of electricity, is storing cold air during peak hours and using during high demand hours. Phase change materials (PCM) thermal storage systems can store a greater amount of thermal energy per unit of volume than sensitive heat storage systems. A phase change material (PCM) is a substance with a high fusion temperature which, by melting and solidifying at a certain temperature, is capable of storing and releasing large amounts of energy.

2. Classification of PCMs

The two main premises of a PCM are a suitable phase change temperature and a high melting enthalpy. However, for most applications, more requirements are required, and these can be grouped into physical, technical and economic.

From the point of view of the physical properties we can talk about the repeated modification of the phase and of good thermal conductivity. From a technical point of view, PCMs must have low vapor pressure, chemical stability and compatibility with other materials. Finally, economically speaking, we can talk about the cost of PCM raw materials and the ability to easily recycle or dispose of material at the end of its life (Lohse and Schmitz, 2012). The four types of phase change are solid - liquid, liquid - gas, solid - gas and solid - solid. PCMs that convert from solid to liquid and back to solid state are the most commonly used latent heat storage materials (Cheng et al., 2012). Phase change from solid - liquid and vice versa through melting and solidification, respectively, can store large quantities of cold or hot air. The best example is ice with water where the solidification and melting takes place at a phase change temperature of 0°C. The stored energy can be calculated by the enthalpy difference (Lohse and Schmitz, 2012; Joworschi, 2012). PCMs can be classified into two categories: organic and inorganic PCMs. Organic PCMs are still classified as paraffinic and non-paraffinic materials; these materials melt and freeze repeatedly without isolating the phases and degrading the latent heat of fusion. Organic phase change materials include Bio, Paraffin (C_nH_{2n+2}) , or carbohydrate and lipid derivatives (Muratore et al., 2012; Weng et al., 2011; Rentas et al., 2004).

Inorganic PCMs are further classified into salt and metal hydrates. These advanced PCMs do not significantly recover heat and do not break down with each cycle. The most common and well-known inorganic PCMs are salt hydrates (M_nH_2O) (Sarier and Onder, 2012).

a) Advantages and disadvantages of organic and inorganic PCMs

In general, PCMs can be classified as inorganic and organic compounds. Most organic PCMs, such as paraffin wax, are chemically stable and non-corrosive. They also have low or no coverage properties, high latent heat and are recyclable, making them adaptable to most building materials. However, they have disadvantages such as low thermal conductivity, large volumetric changes during the phase change process and flammability (Mondal, 2008). As a result, most organic PCMs need to be encapsulated in a capsule before being used in a thermal energy storage system. This additional requirement not only increases the cost, but also reduces the performance of the system due to the increased thermal resistance caused by encapsulation (Farid et al., 2004). Compared to organic compounds, inorganic compounds, such as salt hydrates, have much higher latent heat per unit volume, higher thermal conductivity, lower costs, are recyclable and non-flammable (Mondal, 2008). However, a major disadvantage is corrosion for most metals, which leads to their short life, as well as the high costs of packing and maintenance (Farid et al., 2004). Unlike organic compounds, inorganic compounds can also undergo phase separation and overlap, which will greatly affect their phase modification properties (Mondal, 2008; Khodadadi et al., 2013). However, metallic materials do not have the disadvantages of inorganic salts, which makes them a potential solution for PCMs at high temperatures.

b) Areas of applicability of PCMs

There are several areas where PCM materials can be exploited. PCMs have been commonly used in buildings and air conditioning systems. The examples presented are intended to highlight the variety of uses of PCMs. The applications presented are: temperature regulation in electronic devices, food, medical purposes and textile materials.

Electronic devices. The importance of temperature is well known in electronics both for the proper functioning of the devices and for their lifetime, as it is the main factor that influences their performance. For optimum performance a constant temperature must be maintained. For example, Lohse *et al.* (2012) presents an approach to designing latent composite heat deposits (CLHS) that combines PCM with an aluminum frame structure for heat energy transport. Cheng *et al.* (2012) focused on packing the phase change thermal control unit, so that a new PCM was proposed, which would overcome the typical problems regarding low thermal conductivity. Jaworski *et al.* (2012) developed a heat distributor which is a kind of pin radiator, but instead of pins, the small diameter thin pipes form a heat transfer surface and the pipes are filled

with PCM, resulting in a large heat transfer surface and a high thermal capacity. Muratore *et al.* (2012) have evaluated the usefulness of PCMs encapsulated in micro-tanks for attenuating transient temperature rise. Weng *et al.* (2011) have studied the thermal performance of a PCM pipe for cooling electronics that covers the adiabatic section of the pipe that releases heat with a PCM storage container.

Food and drug protection. Food and medical supplies are different sectors in which PCM can be applied and used for different purposes. Maintaining the temperature of the food in a suitable range is crucial for proper preservation and quality, to prevent their deterioration. Rentas *et al.* (2004) have proposed different types of PCM containers to keep the red blood cells between 1 and 10°C, while they are exposed to outdoor temperatures of -24° C and 40° C.

Textiles. Clothing and many other textile products play an important role in our lives. We need people to feel comfortable and textiles to provide favorable conditions around our body to allow us to survive. The main role of clothing is to protect the body against the outside environment with a layer (or layers) of barriers. Thermal comfort is defined as that condition of the mind that expresses satisfaction with the thermal environment. The thermal properties of the textile materials involve thermal conductivity, thermal insulation and heat transfer between the body and the environment. In addition, air permeability and humidity permeability influence the thermal balance of the body and consequently affect comfort (Sarier and Onder, 2012). Some of the convenient methods for incorporating PCM into the textile matrix are coating, laminating, finishing, melting, extrusion with synthetic bi-components, injection molding or foam (Mondal, 2008), taking into account that the microcapsules must be resistant to mechanical action, to heat and in most types of chemicals used to wash clothes.

c) Future trends

PCMs are chemicals in which thermal energy is stored during a nongaseous phase change. The development of PCMs has usually been achieved by studying the phase modification properties. In the last decade, this trend has changed with the development of PCMs. For a PCM thermal storage system to work successfully, the stability of the heating-cooling cycle, the effects of undercooling, corrosivity, thermal conductivity and thermal stability must be considered. During the heating-cooling cycle, the multi-component PCMs can be separated due to the density differences of each component (Farid *et al.*, 2004). Depending on the volume of the PCM, the undercooling may be severe, preventing the PCM from successfully cooling in the storage system. The thermal conductivity of the PCM can affect the thermal transfer between the PCM and the heat exchange fluid and, therefore, must be large enough to allow efficient heat transfer. Finally, the PCM must not corrode the material or decompose within the operating temperature limit of the storage system. In general, the development of PCMs must be connected to the application considered. This future direction of research will likely strengthen as applications using PCMs will be successful.

3. Thermophysical Properties in Particularly Thermal Conductivity

The process of selecting a suitable PCM is very complicated, but crucial for thermal energy storage. A potential PCM should have an appropriate melting temperature, desired fusion heat and a specific thermal conductivity depending on the practical application. Thus, the thermal and thermophysical properties of PCMs are very important. The thermal conductivity of PCMs will be discussed below as it is the most studied property in the literature.

Numerous researches have been carried out to solve the problems regarding the low thermal conductivity of the phase change materials. Various methods have been adopted to improve the thermal conductivity of PCMs. Carbon, ceramic and foam/metal-based nanomaterials have been used to improve the thermal conductivity of PCMs.

Some authors (Khodadadi et al., 2013; Fan and Khodadadi, 2011) have discussed this problem in detail and have studied different methods for increasing the thermal conductivity of PCMs. However, a large volume of work is needed to improve the thermal properties, in particular the thermal conductivity of PCMs. Due to the low thermal conductivity, the heat storage and release of PCMs is quite low (Jegadheeswaran et al., 2012), which limits their practical applications. Thus, the thermal conductivity of PCMs should be improved to increase the heat transfer and the coefficient of use of stored energy. Different authors have used different types of nanoparticles to increase the thermal conductivity of the phase-shifting material. Nanomaterials (metallic and non-metallic) have a high thermal conductivity, therefore added in PCMs improve their thermal conductivity. Liu et al. (2018) have improved the thermal conductivity of polyethylene glycol (PEG). In the first step, they prepared a PEG/SiO₂ phase change composite material followed by the addition of different carbon fiber (CF) concentrations in PEG/SiO_2 in the second stage. The thermal conductivity results of PEG, PEG/SiO₂, CF (1%)/PEG/SiO₂, CF (2%)/PEG/SiO₂ and CF (3%)/PEG/SiO₂ were 0.17, 0.26, 0.39, 0.44 and 0.45 W/mK respectively. The improvement of the thermal conductivity of the PCM was 73.1% for CF (3%)/PEG/SiO₂.

Tang *et al.* (2014a) used carbon nanotubes to improve the thermal conductivity for polyethylene glycol (PEG)/PCM inorganic composite with SiO₂. They added multilayer carbon nanotubes with a mass concentration of 0.5, 1.2 and 3 wt % in composite PCM. Thermal conductivity was measured using a DRL-III tester (range: 0.05-45 W/mK). The results regarding the thermal conductivity of pure PEG, PEG/SiO₂ and PEG/SiO₂/MWCNT (0.5-3% wt) were

0.290, 0.359, 0.389, 0.421, 0.444 and 0.463 W/mK. The thermal conductivity of PCM with 3% wt MWCNT increased by 53.1% compared to PEG. Tang *et al.* (2014b) prepared a stable PCM PEG/SiO₂-Al₂O₃ by the sol-gel method. Thermal conductivity was measured using a DRL-III tester (measurement range: 0.05-45 W/mK). The recorded thermal conductivity of PEG, PEG/SiO₂ and PEG/SiO₂-Al₂O₃ (3 wt %) was 0.297, 0.36 and 0.435 W/mK respectively. The thermal conductivity of PEG increased by 46.5% with the addition of Al₂O₃ (3 wt %).

Yang *et al.* (2018) used graphene oxide (GO) and boron nitride (BN) to increase the thermal conductivity of polyethylene glycol (PEG). They made a PEG/BN/GO composite PCM with 4 and 30 wt % graphene oxide and boron nitride. The thermal conductivity of the phase change composite material (CPCM) increased by 900% compared to pure PEG. Zeng *et al.* (2010) proposed a technique to improve the thermal conductivity of the phase change material (1 tetradecanol) by adding silver nanowires. They used (Zeng *et al.*, 2010) the Hot Disk thermal analyzer with a sensor with a diameter of 2.001 mm to determine the thermal conductivity. The results showed a thermal conductivity of Ag nanowires with Tetradecanol increased from 0.32 W/mK to 1.46 W/mK by adding 62.37% wt silver nanowires.

Sahan *et al.* (2015) added 20% wt Fe_3O_4 in paraffin and obtained a growth of only 1.6-fold compared to pure paraffin. In Fig. 1 are presented the values regarding the increase of the thermal conductivity, a study that was carried out by different researchers. Fig. 2 shows that (Liu *et al.*, 2018; Tang *et al.*, 2014a; Tang *et al.*, 2014b) dispersed 3% wt CF, CNT and Al₂O₃ respectively to improve the thermal conductivity of PEG-based paraffin. The carbon fiber had a much better performance (thermal conductivity and stability) compared to the other two additives due to the high dispersion capacity in PCM.

Karaman *et al.* (2011) used expanded graphite (EG) to increase the thermal conductivity of diatomite composite (PEG)/PCM. First, composite PCM based on PEG/diatomite was prepared by integrating PEG into diatomite pores. The measured thermal conductivity for diatomite, PEG, EG, CPCM (PEG: diatomite: EG: 45: 45: 10 % wt) was 0.07, 0.29, 4.26 and 0.67 W/mK, respectively. The thermal conductivity of PEG/CPCM diatomite increased by 103 % by adding 10 % wt EG.

Ahmet Sari (2004) prepared a high-density paraffin/polyethylene (HDPE) composite phase change material (CPCM). It used two types of paraffin with melting temperatures of 42-44°C (Sample 1) and 56-58°C (Sample 2) and 3% wt expanded graphite and exfoliated graphite were used as amplifier of the thermal conductivity. The S1/HDPE and S2/HDPE samples showed an increase of 14% and 24%, respectively.



Fig. 1 – Improvement of the thermal conductivity obtained by different researchers by adding nanoparticles.



Fig. 2 – Improvement of thermal conductivity obtained by different researchers by adding nanoparticles with a concentration of up to 3%.

Cui *et al.* (2011) measured the thermal conductivity of the soybean wax as a phase change material, which has a thermal conductivity of 0.324 W/mK. The melting temperature is in the range 52-54°C. The thermal conductivity was improved by adding carbon nanofibers (outer diameter 200 nm) and carbon nanotubes (average diameter 30 nm, average length 50 mm) with a mass concentration of 1-10% wt. The experimental results regarding the thermal conductivity of the soybean wax increased to 0.469 and 0.403 W/mK by adding

10% wt of carbon nanofibers and carbon nanotubes respectively. The thermal conductivity of CNF/soy wax was higher than CNT/soy wax due to better distribution of carbon nanofibers in soy wax. Tian et al. (2017) prepared a composite phase change material (CPCM) by mixing ternary carbonate (thermal conductivity 1.33 W/mK) with magnesium particles (100-200 mesh, thermal conductivity 156 W/mK). The results showed that the thermal conductivity of the composite phase change material increased by about 19.55% by adding 0.1% wt magnesium particles. The measured thermal conductivities of CPCM with 0.1-2% wt Mg were in the range of 1.59-1.93 W/mK corresponding to 19.55-45.11 % higher than pure ternary salt carbonate. Wang et al. (2009) have prepared a phase change material with high and stable thermal conductivity by mixing polyethylene glycol, silica gel and aluminum b-nitride. The results showed that by adding 5-30% wt b-aluminum nitride in PCM, the thermal conductivity increased from 0.3847 to 0.7661 W/mK. Wang et al. (2010) studied the effect of carbon nanotubes (CNTs) on the thermal conductivity of the palmitic acid matrix. The carbon nanotubes were treated by mechanicalchemical reaction with a mixture of KOH (potassium hydroxide) and pure carbon nanotubes for the production of stable and homogeneous CNT composites. The treated carbon nanotubes (TCNT) with a mass fraction of 0.002, 0.005 and 0.010 were added to palmitic acid (PA). The average thermal conductivity of palmitic acid was 0.22 W/mK in solid state and 0.16 W/mK in liquid state. The results showed that the thermal conductivity of the treated palmitic acid composite/carbon nanotubes increased to 0.33 W/mK (46% higher) in solid state and 0.21 W/mK (38% higher) in solid state liquidate. An improvement of the thermal conductivity near the melting point was found. The thermal conductivities were lower at temperatures below 55°C and higher than 65°C.

Harish et al. (2015) studied the effect of graphene nanoplates (GnP) on the thermal conductivity of the phase change material based on lauric acid. The results showed that the addition of 1% by volume of graphene nanoparticles in lauric acid increased the thermal conductivity by 230%. Graphene nanoplates have increased the thermal conductivity of lauric acid largely without affecting its melting temperature and phase change enthalpy. Karaipekli et al. (2017) have proposed a method to improve the thermal conductivity of the expanded perlite/paraffin composite (EXP/C20) phase change material by adding carbon nanotubes. They prepared EXP/C20/CNT composites in two stages. The EXP/C20 composites were prepared by the vacuum impregnation method in the first step. In the second step, carbon nanotubes were added to EXP2/C20. The thermal conductivity of EXP/C20/CNT increased to 0.19, 0.24 and 0.28 W/mK by adding carbon nanotubes with a mass fraction of 0.3%, 0.5% and 1% respectively the material with composite phase change. Xiao et al. (2015) used carbon nanotubes (average length 10-30 mm, average diameter 10-20 nm, specific area 60 m^2/g) to improve the thermal conductivity of palmitic acid (thermal conductivity, 0.214 W/mK). Carbon nanotubes were first oxidized by

mixing with sulfuric acid and nitric acid. These oxidized carbon nanotubes were then grafted with γ -(2,3-epoxypropoxy) propyltrimethoxysilane. CNT, O-CNT and G-CNT were added in palmitic acid with a mass percentage of 1%. The results showed that the thermal conductivity of the PA/CNT, PA/O-CNT and PA/G-CNT composites increased to 0.292, 0.288 and 0.287 W/mK respectively. The PA/G-CNT composite had a high thermal stability compared to O-CNT and CNT due to better dispersion of G-CNT.

A brief review of the work on improving the thermal conductivity of PCMs was carried out. In most cases, the improvement of thermal conductivity was achieved by adding additives with high thermal conductivity, for example carbon nanotubes, metallic and non-metallic materials. As a result of these improvements to the PCMs, the thermal conductivity has also increased by almost 50%.

4. Conclusions

Future directions of research can be mentioned. Energy storage is an essential issue in order to overcome the intermittency of different renewable sources and promote the development of environmentally friendly thermal installations, such as those based on solar technologies.

Among the different ways of storing heat energy, phase change materials (PCMs) are particularly interesting, as these materials allow high densities of energy storage at low temperature intervals.

The temperature range offered by PCM offers a new horizon for the field of construction and refrigeration engineering in terms of energy storage applications at medium and high temperatures. The fields of application of these materials are: solar energy collection, water heating and thermal energy storage applications.

The growth potential of the thermal storage properties of PCMs can be effectively achieved by incorporating nanomaterials into pure PCMs. Nanomaterials based on metals or combinations of metals and carbon have been applied due to their high thermal conductivity. Incorporating nanomaterials into pure PCMs can lead to better thermal storage of PCMs compared to their initial state.

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STUDII PRIVIND MATERIALELE CU SCHIMBARE DE FAZĂ ÎMBUNĂTĂȚITE CU NANOPARTICULE

(Rezumat)

În ultimii ani, stocarea energiei termice se numără printre abordările extrem de eficiente pentru a depăși criza energetică. S-au efectuat cercetări recente privind îmbunătățirea transferului de căldură utilizând un material de schimbare de fază (PCM) care are o temperatură de fuziune ridicată și, prin topire și solidificare la o anumită temperatură, este capabil să stocheze și să elibereze cantități mari de energie. PCM-urile pot fi împărțite în tipuri solid-solid, solid-lichid, solid-gaz și lichid-gaz, în timp ce cele solid-lichid sunt cele mai utilizate în diverse aplicații. Pentru dezvoltarea acestor noi materiale este necesar să se înțeleagă efectul adăugării diferitelor tipuri de nanoparticule asupra proprietăților termofizice ale PCM-urilor. În concluzie, această lucrare se bazează pe cercetările anterioare privind PCM-urile ca materiale potențiale pentru stocarea căldurii. O atenție deosebită va fi acordată studiilor experimentale pe materiale PEG 400, precum și îmbunătățirii proprietăților acestora prin adăugarea de nanoparticule.

54

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APPLICATION OF HOLLOW GLASS FIBERS STRUCTURES AS HIGH PRESSURE STORAGE SYSTEM FOR HYDROGEN

ΒY

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> Abstract. Glass has different outstanding material-specific properties which offer theoretically the application of thin-walled hollow fibers in the field of high pressure gas storage. Especially the storage of hydrogen as renewable and environmental friendly energy carrier is possible. Glass is an amorphous and brittle material which is characterized by a theoretical strength much higher than this of other materials. However, in practice the strength is decreased significantly by defects on the glass surface or in the material and its network structure. A calculation of the failure-causing defect size from measured burst pressure is possible. Dependent on the dimension and determined burst pressure value of each single fiber defect sizes of less than one micron were calculated. The influence of the dimension of hollow glass fibers on their resistance against inner pressure load is the ratio between wall thickness and inner diameter which was investigated. It was also inverstigated the combination of different glasses and the utilization of their disparate coefficient of thermal expansion which lead to pretension of the hollow glass fiber. Using the hollow glass fibers for hydrogen storage system for automotive industry was described in our research.

> **Keywords:** Hydrogen storage system; Automotive industry; Glass fibers; Environmentally friendly; Hydrogen cars.

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1. Introduction

About keeping global warning below 2°C we need to made a sever reduction for emissions according declarations from Paris Agreement in 2015. The European Union (EU) and all members from states are focused to reduce gas emissions in next targets: All compared cases are made to 1990 years and for 2020 they want to reduce GHG (greenhouse gas) emissions with 20%, for 2030 by 40% and for 2050 to be reduced like 80 to 95% (EU 2020 Climate and Energy Package, 2009). All members from European Union made from that target a emergency and national goals. Some studies made in European Union show us that air pollution is responsible for 487,000 premature deaths every year and costs from health domain it's at least 215 billion of euros/year which mean health impact it's very high because the fossil fuel generates a big quantity of emissions like nitrogen oxides, fine particulate matter and sulphur dioxide. To improve local air quality, we need to reduce local emissions urgently (Health and Environment Alliance, 2017).

To be able to make this goal realisable, all the countries around the globe need to do a mainly from renewable sources and change people's mind about green energy systems (Hydrogen Joint Undertaking, 2020).

2. Glass Properties for Hydrogen Applications

Glass is defined as non-crystalline and often transparent amorphous solid (Begriffe für Glasarten und Glasgruppen, 2001).

Glass have special properties how is shown in Fig. 1 with specific volume against temperature when manufacturing process is in work (Eliezer *et al.*, 2015).



Fig. 1 – Dependency of specific volume of glass to temperature during melting and cooling process (www.benbest.com).

From special properties of glass we have high strength and also high chemical resistance most importantly. The strength of glass is named the resistance against break or any deformation. Even if glass is considered a fragile material, the production of the risk of failure has two phenomena: degradation: fast broke or fatigue degradation. Time is the only factor that can make the difference between these two phenomena (Eliezer *et al.*, 2015).

From all special properties of hollow glass fiber we can see tensile strength three times higher more than steel and the density three times lower than have materials from steel. Glass and hollow glass fibers can storage hydrogen for months or years in systems without lose pressure that mean it's a great barrier (www.cenh2.com).

Table 1 schows Estimated theoretical tensile strength of tested glass types.

Estimated Theoretical Tensile Strength of Tested Glass Types(www.cenh2.com)			
Glass material	Young's modulus E	Estimated theoretical tensile	
	[MPa]	strength oth [MPa]	
Fused silica	75,000	7,500	
Borosilicate 3.3	63,000	6,300	
Soda-lime	73,000	7,300	
Aluminosilicate	81,000	8,100	

 Table 1

 timated Theoretical Tensile Strength of Tested Glass Types(www.cenh2.com)

The theoretical tensile strength result from Eq. (1) (Scholze, 1994):

$$\sigma th = \sqrt{\frac{4 E\gamma}{\pi l_0}} \tag{1}$$

where $\gamma =$ surface energy, E = Young's Modulus, $l_0 =$ atomic distance.

Because that, it is expected that a split form on new surface with a surface energy and the chemical bonds between the atoms has to be break. Consequently, the necessary energy, attached by acting stress, need to be higher than the energy of the chemical bonds (Scholze, 1994).

Anyway, the tensile strength depends on shape and composition from tested glass and we can obtain different measured values. All of that procedures and standardized tests are characterized and described in DIN EN ISO 1288-1, also all of the test specimen are standardized likewise (Eliezer *et al.*, 2015).

Because that hydrogen storage it's made from a bundle of thin hollow glass fibers offer different many advantages like a remarkably higher volumetric storage capacities it's realisable up to vsc = 48.3 g l^{-1} (Zhevago *et al.*, 2007) (Zhevago *et al.*, 2010). Packing ratio influence and it's a main advantage too for less unused space (Zhevago *et al.*, 2010).

Hydrogen storage systems based on hollow glass fibers with brevet number US9882229, are made from many glass capillaries. Glass capillaries are made with a diameter of only a few microns (approximately 40 μ m) (Fig. 2) and are high pressure resistant, each tube having a sealed extremity from a side and at the end open extremity.



Fig. 2 – Microscope pictures of hollow glass fibers structures as high-pressure storage system for hydrogen.

These glass capillaries are embedded in a bundle of capillaries which is called "multi-capillaries" (MC) then that MC are stacked in a higher bundle which is named "multi multi-capillaries" (MMC).

All of the MC are being stacked in a fused block which is a large structure with thousands of multi-capillaries and can be manufactured in different shapes and dimensions (Eliezer *et al.*, 2009).

The open end of capillaries from the fused block is docked in an adaptor to allow hydrogen to be filled in system and in another hand have important role for sealing hydrogen inside the capillaries without losing pressure (Eliezer *et al.*, 2010).

A supplementary valve can be fitted in adaptor for more security in terms of the loss of hydrogen from the storage. Assembly of a multi-capillaries or an multi multi-capillaries to an adaptor can be realisable with a glue like epoxy resin and there are many other opportunities. Likewise, to increase security of the system, after the adaptor is installed on the system to that multi-capillaries or multi multi-capillaries can be sealed with additional operation. For example a feasible adaptor is made from stainless steel 1.4301 with wall thickness of material of 0.75 mm and is capable to make the connection between glass and steel at pressures up to 40 MPa glued with Loctite 9483 A&B. In the final resin is left to strengthen at 30°C for 24 hours (Eliezer *et al.*, 2010).

In the world, safety of hydrogen supply and storage is most important. If a rift take place in a classic storage system (one-vessel), the quantity of hydrogen released would be very dangerous, being able to generate an aggressive explosion in atmosphere. The advantage of C.En's technology is in the bundling of many single capillaries. Each single capillary it's acting like own high pressure resistant vessel. In that way each capillary it's capable to support and it increase the resistance of the other capillaries around it. If that single capillary is damaged, the pressure of hydrogen released in the atmosphere will be too small to be able to create explosive atmosphere (Eliezer *et al.*, 2010).

The major problems in automotive industry and many industries for pick hydrogen like an alternative method for fossil fuels was the size, weight of the tanks where was hydrogen stocked and as well as safety issues about the transfer and release of the hydrogen (Eliezer *et al.*, 2010).

3. Applications

In highly populated areas around the world, many peoples depend on two-wheeled vehicles like scooters and motorized bicycles as their main way of transportation. Scooters are very common especially in India (European Commission, 2019). From specialized research we see the ratio was about 6 to 1. Despite the compact dimensions, they are not at all efficient. In the worst case, they can emit 30 times more emissions than a decent passenger car. If we look at these figures, we can easily realize that under such conditions there is a large market for hydrogen-powered vehicles on two wheels in this area that could benefit from that hydrogen storage system in hollow glass fibers (www.cenh2.com, 2020).

For hydrogen storage systems made by C. En. Corporation, maximum operating pressure is 700 bar. The open area glass in hollow fibers it's around 90% which present a big advantage. Required burst pressure to operate at 700 bar with safety factor 2 need to be 1400 bar. The strength required for glass tensile is 3000 MPa. Lifecycles of the system are around 8000 and lifetime up to 20 years (Eliezer *et al.*, 2015).

For H2 scooter and H2 bike, the storage systems have 60l hydrogen capacity, are equipped with electric engines with 250 W powered by a fuel cells with 300 W power. A fuel cell is a electrochemical cell that generate electricity. Every fuel cell can produce electricity with two electrodes, the anode and respectively cathode. That fuel cell requires continuous source of oxygen and hydrogen to produce electricity and the reaction is produced at the electrodes (Smithsonian Institution, 2017). The cooling of system it's made directly by the coolers mounted on the fuel cell so they have double roles, pushing the air in the system to produce electricity and cooling the system. The speed of prototypes it's around 25 km/h with a pressure in system around 60 bar. Refuelling time for prototypes it's around 1 minute so that it's another big advantage of hydrogen storage in hollow glass fibers. The range of distance remain to be defined because there are a lot of factors which can influence that range. Temperatures to operate the system can be between -20°C and +80°C (assusming 60% fuell cell efficiency) (Eliezer *et al.*, 2015).

Another storage module is capable to store 1 kg hydrogen at 70 MPa storage pressure, used glass free space is 80%, overall weight storage up to 25 kg, storage volume is 24 l and storage hydrogen is 11132 litres (Eliezer *et al.*, 2015).

In the figure below is presented a hydrogen storage system in glass capillaries which have 2 elements (Operating part and storage part with 15 arrays) (Eliezer *et al.*, 2015).



Fig. 3 - Hydrogen storage system in glass capillaries (Eliezer et al., 2015).

The optimal solution for the powertrain implies the use of fuel cells. However, these are very expensive, especially in the power range required by even a small size car.

An alternative solution is to develop or to adapt a hydrogen fuel system for classic internal combustion engines. Main advantage will be the price of this solution and the main disadvantages will be the efficiency of the system which is half that of a fuel cell system.

There are three methods of hydrogen injection with C. En. Corporation hydrogen system storage:

First is the central (or throttle-body) injection where the main advantages are the price, injection of the hydrogen during the intake stroke from inlet of the air intakes and the main disadvantages are likely to cause pre-ignition/backfire and power is about 20% lower than the original IC engine (MacCarley *et al.*, 2010).

Second is direct injection where we can involve mixing the air and fuel in the combustion chamber after the air intake valves has closed, prevents preignition in the intake manifold and produces about 40% more power than the central injection method and about 20% more power than original gasoline engine. The main disadvantages of this method are the price because it's more expensive than first one for example and production of higher nitrogen oxide (NOx) emissions due to short mixing time and the highest supply pressure between these three methods (MacCarley *et al.*, 2010).

Third method, which of them it seems to be the most reliable is port injection (Fig. 4). Some of the main advantages could be: air is supplied separately at the beginning of the intake stroke to cool down any hot spots in the cylinder, hydrogen is then injected at the inlet port just after the beginning of the intake stroke, prevents pre-ignition in the intake manifold, the supply pressure needed is higher than for the central injection, but lower than direct injection, low chances of knock and backfire, power loss is smaller than in the case of central injection (Mohammed *et al.*, 2010). Some disadvantages of port injection method are the price, because it's more expensive than the central injection and requires some research to adapt to existing engine.



Fig. 4 – Hydrogen injection system (Mohammed et al., 2010).

Because the hydrogen storage systems in hollow glass fibers are customizable in dimensions and shape, there are a lot of domains of application for hydrogen systems in hollow glass fibers and we can structure the most important like:

a) Transportation: Automotive (Cars, Motorbikes), Aircraft/Aerospace, Marine vessels (Ships, Submarines, Etc.), Railroad trains;

b) Electronics: Communications, Electric and power (Mobiles, PCs, Laptops), Defence industry;

c)Infrastructure: Manufacturing (fiber materials, containers, etc.), Large & bulk storage hydrogen stations (Eliezer *et al.*, 2010).

4. Conclusions

Resistance of tensile strength it's influenced by the dimension of the hollow glass fiber. From the research and calculations made so far it turns out that the strength of the glass should be a constant value (Griffith, 1921). With all these investigations, it has been shown that if the thickness of inner wall of the glass is thinned it will decrease the resistance according to Barlow's formula (DIN Deutsches Institut für Normung, 2011) decreased pressure resistance. In case of decreasing the thickness of the wall and the outside diameter directly proportionally we can observe an increase of the resistance of hollow glass fiber. As a result the strength of the glass is not constant and it matters to a large extent the size of the material (Eliezer *et al.*, 2015).

The both mobile prototype are tested with success for now at 70 bar pressure, the pressure will gradually increase in tests until tested results will be more closely with calculated results.

The safety of the hydrogen storage system is very important. At this point has been shown that the pressure resistance of each capillary is a high one and placing them next to each other this increase the resistance of the entire hydrogen storage system and if a capillary suffer a rupture, the hydrogen pressure released into the atmosphere is too small to create an explosion in the atmosphere (Eliezer *et al.*, 2015).

Among the three possible approaches to this injection system, we consider hydrogen port injection to be most feasible solution because the price and current technology used in automotive.

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APLICAREA STRUCTURILOR DIN FIBRE DE STICLĂ GOALE CA SISTEME DE STOCARE DE MARE PRESIUNE PENTRU HIDROGEN

(Rezumat)

Sticla are proprietăți extraordinare, care oferă în mod teoretic posibilitatea aplicării tuburilor cu pereți subțiri din fibră de sticlă în domeniul stocării gazelor de mare presiune. În mod special este posibilă stocarea hidrogenului ca purtător de energie regenerabilă și prietenoasă cu mediul. Sticla este un material amorf și fragil care este caracterizat de o rezistență teoretică mult mai mare decât a altor materile. Totuși, în practică rezistența este diminuată semnificativ de defectele din suprafața sticlei, din interiorul materialului și din rețeaua sa structurală. Se poate face un calcul al dimensiunii defectului care produce ruperea prin măsurarea presiunii care produce spargerea. S-au calculat dimensiunile defectelor mai mici de un micron pentru fiecare fibră ținând cont de dimensiune și de presiunea de spargere determinată. Influența dimensiunii fibrei de sticlă goale asupra rezistenței sale în funcție de presiunea internă aplicată este raportul între grosimea peretelui și diametrului interior. A fost investigată și combinarea diferitelor tipuri de sticlă și utilizarea coeficienților de dilatare termică diferită a lor, fapt ce produce pretensionarea fibrelor de sticlă goale într-un sens controlat. Utilizarea fibrelor de sticlă goale pentru sisteme de stocare a hidrogenului pentru industria automoto este descrisă în această cercetare. BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI Publicat de Universitatea Tehnică "Gheorghe Asachi" din Iași Volumul 67 (71), Numărul 1-2, 2021 Secția ȘTIINȚA ȘI INGINERIA MATERIALELOR

TRADITIONAL TECHNIQUES AND NATURAL CONSTRUCTION MATERIALS IN ROMANIA

ΒY

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Abstract. In the context of environmental protection, by reducing pollution and energy consumption, the field of constructions stands out as having negative effects on the high degree of energy consumption and the production of a large amount of waste.

As a result of the globalization process, there is a small number of building materials at a global level, in countries of different levels of development, which leads to a standardized process of construction and the neglect of the local resources. The contemporary tendency of building and materials techniques brings architectural influences specific to the contemporary architectural styles. By analyzing the small height constructions, a gradual disappearance of the local values and traditions can be observed as these contemporary tendencies grow. Local building materials are replaced with other materials from far away countries with a totally different climate or other materials fabricated with a high level of energy consumption.

By changing the optics on the required materials for low height constructions we can help the growth of environmental protection and the revival of the local natural and cultural values (Correia *et al.*, 2014).

Romania benefits from natural riches especially natural resources and a long and beautiful history with cultural witnesses that can be found not only at national museums but also in the rural parts of the country. History shows that

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Romanian vernacular architecture has cultural value starting from small rich wooden decorations to complex wooden joints of a wall, or complex wattle dry from wool, hempseed and twigs.

From all this Romania's richness, the paper focuses only on the natural architectonic aspect, namely the natural resources exploration, fabrication process and the methods of using them in construction in an ecological way responsible for the wellbeing of the environment highlighting the Romanian tradition.

Keywords: wood; straw-bale; thatched straws; clay; adobe; lath and plaster.

1. Introduction

The world is at a place in time where it searches simultaneously into the future by constant high-tech studies and discoveries, and into the past by studying the history for new ways of using what nature can offers us and how to cohabitate with and in it, in an environmentally friendly way.

In the last three centuries the technology evolved more than it evolved in the last 3000 years. In this rapid rhythm, from time to time, it is necessary to provide a throwback, to observe from where it all started, how the technology evolved in time and to mark the deviations from the trajectory of a safe developing in relation to the nature. Basically, every physical resource used in any artistic or fabrication process it is offered by nature. So, altering the source, the origin of all things, the final product is altered.

In the rapid process of the globalization, the number of industrialized products is increasing, and with it, the level of cultural identity decreases. By looking back in history and rethinking the ways of living and of building the houses, at first, the future vision of habiting might present itself in better condition in relation to nature and cultural preservation.

In architecture, the whole needed knowledge is found in vernacular architecture. At first, our ancestors learned how to build due to the need of a shelter. After they gained experience in basic housing building, it followed cultural and other public buildings, where attention to details became the most important matter of interest.

Romania has a long history of vernacular architecture. Due it's richness of resources, it's geographical variety and its climate, Romania had a lot of villages spread all across the country. These many factors influenced a large number of differences in vernacular housing architecture. Using only natural building materials found near their site, the Romanian villagers managed to obtain beautiful works of earth, wood, stone and straws. The use of these raw materials led to beautiful decorations of each material, or to creative ways of successfully combining them for a better resistance to extreme factors of rain, snow or of direct sunlight. Studying the ways these raw natural building materials were used, it can be determined precisely each material's qualities and weaknesses. Besides the technical specifications, the study should mark the limit where the functionality stops, and where the architecture begins.

2. Romanian Vernacular Architecture

The diversity of the Romanian traditional houses can be found in the entire architecture of the house. Each region has its unique characteristics, and so, the architecture differs completely, firstly by responding to different needs in the day to day activity and secondly, by having different natural resources. The differences are not only in size, colour or façade's image, they are highly related to the house's constructive system, leading to a sincere and faithful representation to their building materials (Oar.archi, 2020).

The main building materials used in the constructive elements of a house were earth, stone and wood. By getting through a series of different fabrication processes realised in the working site, these raw materials were the primary building materials, from which were made different end products. Depending to the local resources, the use of each material can be found in different parts of the building elements, in a higher or smaller percent. But it can be stated as a fact that all materials stood as building materials along the country.

Earth was used for walls, slabs and ceiling in form of adobe bricks with straws, lath or twigs with plaster, and lastly, as smooth plaster for the façade's finishing.

Wood had the widest use due its high mechanical resistance quality. In forested areas wood was used for all the building elements. In the rest of the regions it was used for columns and beams, foundation as beams, slab, roof structure, and as finishing in all the parts of the house: façade, window joinery, interior wall, floor, ceiling and roof cover. It also had the largest use for decorations in joinery at any element of the house: doors, entrance gates, wall corners, end of the beams, fascia and many other parts. Its great workability offered many possibilities which Romanian villagers took advantage of, as much as possible.

Stone represented an expensive material which had a small area of applicability. River stones were used in foundations, walls of the semibasement and fences. In the mountain areas cut stone was used as it was plentiful and was a mandatory requirement to provide resistant walls as the terrain was rough.

Straws had multiple uses, especially as straw-bale for reinforcing the plaster or the clay bricks, thus preventing cracks. Another application was for the roof-covers using thatching techniques, with high efficiency in roof insulation.

It is notable that using only these raw materials, the Romanians managed to obtain sustainable and durable constructions in given Romanian conditions, with high level of recyclability, and most important, that they were able to achieve a high level of architectural details and decorations perfectly integrated in the house's simple architecture.

3. Natural Building Materials

One of the greatest qualities of vernacular architecture is represented by the high number of experimentations in time accomplished by the Romanians with no education on this matter. These experimentations led to a high number of great technological solutions of raw material applications in the perfect place in the perfect form in a building. Knowing how and where each material is best suited for use according to its specifications, it leads to a good behaviour of the building in the face of seasons, year after year.

The building techniques and the architectural solutions used in Romania had as raw materials earth, wood, stone and straws. Because Romania has different climate conditions on the same geography (*e.g.* two plains regions, one in Moldova, one in Dobrogea, have different quantities of precipitations, different low temperatures during the winter, and different high temperatures in the summer.) there are different architectural solutions.

EARTH

Earth renders one of the most natural feelings that a building material can have. Even processed as plaster, as bricks or even as rammed earth wall, it still gives a natural touch. Having the property to be modelled both in organic forms and straight lines, the earth has the capacity to express and to reproduce the nature's forms.

Earth represented the infinite resource for building. From a childish activity of gathering mud and forming bumps, by practice locals managed to use in a more creative form, the oldest and most efficient type of house in Romanian territory is the hut. As a part of it is dug in the ground, and a part above the ground, the hut represents an ancient type of house which behaves very well in the extreme temperatures in the summer or in the winter. The wall represented by the natural soil has a great thermal inertia. Hence the earth started to represent a building material above ground.

Dug up from a delimited area, only few types of earth, hence called clay, responded to the required criteria: to contain very small particles and to have plasticity when mixed with water. Called "yellow earth" in popular language, was mixed with sand for structural strength and for reinforcement were used fibres like dry straws or horsehair. When needed to add more volume to the composition, adding manure was a good solution which would replace fibre adding, and would offer great insulation due it's aerated mass. All applications of clay had this basic composition, except the final finishing, the plaster, which, for a smooth and earth like texture, didn't contain fibres.

Water infiltration and permanent humidity might affect the clay-based products. For this reason, the foundation was from a different material like wood beams or stone masonry. For rain protection the plaster on the façade was shielded by long eaves. Usually, on the exterior, the first meter from the ground was repaired once every few years, due the exfoliation of the plaster. But having enough clay around, that wasn't a problem.

The traditional techniques that use clay can be categorised by the way of implementation, rather than destination as a building element. Same technique can be used on vertical and horizontal surface, the adobe being the exception in Romania, even if in hot climates it was used for roofs.

Adobe technique has as basic element unfired clay bricks, dried in direct sunlight, Fig. 1. The composition which contains clay, sand, short straws, water and, if necessary or at hand, manure, is put in a wooden formwork, and after short time the formwork is removed, and let the brick to dry. The main ingredient is straw; without it, the bricks would crack in the drying process. The bricks obtained, usually had the dimensions of 30x20x10 cm (L x l x h) and are installed using clay-based mortar with no vertical structural elements. The roof would unload the weight on wooden beams. The adobe wall would be finished with plaster with the same composition as the mortar or bricks (Stănculescu *et al.*, 1957a; Stănculescu *et al.*, 1957b; Stănculescu *et al.*, 1958).



Fig. 1 – Adobe wall. On the left vertical section, and on the right front view of the adobe masonry, with no plaster.

Laths or twigs with clay was a technique used at large scale in Romania. On a wooden structure formed with columns and beams, repetitive elements were installed at small distance from one-another, for allowing the clay-based plaster reinforced with straws, to be able to enter between the small gaps and form a stronger layer. It is almost like rammed earth wall, but the formwork remains in the wall, and the stuffing is not rammed but slightly pressed between the formwork. Laths were used for rectangular shaped columns, being easier to be assembled and twigs were used with small logs because it is easier this way to weave the twigs along the wall and around the

Reinforced plaster	1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1	1 1 m 2 1 mm
(clay with straws)	121111221	N. 2. V. S. W. V. S. V.
Wooden column 150x150mm	NU 10 - 18-4	N. 8. 7 10 1 10 1
Lath 20x40mm	NINERI	NEINERE
Wall stuffing clay-based composition	VAL. VAL	25 NY 9 K.
reinforced with straws 150mm	1.1.4.1.4.2.1.1.1	- 9 1 K B 11 1 F 1
	Reinforced plaster (clay with straws) <u>Wooden column 150x150mm</u> Lath 20x40mm Wall stuffing clay-based composition reinforced with straws 150mm	Reinforced plaster (clay with straws) Wooden column 150x150mm Main Participant Participant Lath 20x40mm • Wall stuffing clay-based composition • reinforced with straws 150mm •

logs, Fig. 2. Same technique is applied on the ceiling (without the stuffing), only by applying plaster between the repetitive wooden elements.

Fig. 2 – Lath and clay wall. On the left vertical section, and on the right front view of the lath, with no plaster.

Plaster or mortar was used for every application where was a finishing needed: floors, ceilings, walls or even on wooden planks or logs, to protect them against extreme temperature changes, or insects. All the clay-based techniques had the same recipe. The final finishing layer had a smoother surface and so smaller straws were used (or even no straws at all), in case of first reinforced layer.

WOOD

Wood is a very beautiful resource offered by nature; it may represent an image of sensibility, of how a beautiful small fragile plant is able to grow into a very strong stem that also has in turn small fragile sprigs and leaves. It is a resource of nature that expresses tenderness and also toughness Fig. 3.

In Romania forests exist all over the country and every household used to have trees and also on the boundary of the yard, this being a way to mark the limit of the yard, as a more permanent solution than a fence. One of the most common trees were walnut trees and acacia trees, which are very strong wood essences. At higher altitude the fir tree is the one that is the best adapted.

Besides the forested mountains regions where the wood was used at every element of the building, wooden planks for floors and walls, shingle for the roofs and logs for beams and columns, whereas in the other regions as hills and plains, locals used the wood mainly for the house's structure and window and door framing.

Having a great workability, wood represented the element that offered the best support for decorations. The Romanians carved the wooden elements with floral symbols, knots and Christian cross motives. The carvings were present on the beams under the eaves, on the columns and the railing of the porches, windows and door framings. In the north of the country beautiful pieces of art, can still be found, unique in the world: the front gates of the household, full of carvings and every inch of the gate was decorated with beautiful motives and bas-relief. Besides the beautiful image, the front gates also have a great symbolism; it purifies the one that passes of the disturbing and bad thoughts, and it also keeps the bad spirits away in the same manner the bas-reliefs were used in cathedrals in Medieval times (Stănculescu *et al.*, 1957a; Stănculescu *et al.*, 1957b; Stănculescu *et al.*, 1958).

Another way of expressing the love and skills of the wood building techniques, the Romanians modelled the joints of the structural wood elements in a high variety of screwless joints Fig. 4.



Fig. 3 – Load bearing wall. Vertical section though vertical wall and foundation.

When structural wood elements had to be fastened wooden big nails were used, with holes performed before the installation. In a more recent period, metal big staples were used for fastening two big wooden elements. It's important to be mentioned that for small section wooden elements screwless joints were used, for avoiding the cracks generated by the nails. The planks were the elements that always needed nails.



Fig. 4 – Wooden screwless joinery. On the left hinge tail joinery front view and axonometry, and on the right "în căței" joinery horizontal section and axonometry.

The techniques used for woodworking, compared with the other materials, are special in a more architectural way; they are special due to their technical applicability. For this paper is important to point out were and how the wood was used in constructions and leave open direction for research that highlights the beauty of the Romanian traditional architectural wood decoration, the content being vast and analysed in detail.

STONE

Stone is a very noble and beautiful material, and since the beginning of ancient civilisations it was used for the building of the castles, palaces and temples. The people on the Romania territory, since the Dacians, were simple men, with mainly agricultural occupations. In the antiquity there was no high contrast between the social classes. Stones were seldom used for residential buildings, but it was used for temples, for administrative buildings like citadels from the antiquity throughout the Middle Ages until the Modern times. Along the country there are examples of ancient ruins from Orşova and Histria, and citadels like Suceava or Rasnov which remain as witnesses of the use of stone throughout the Romania territory.

Due to the abundance of earth and wood, the stone wasn't used at a large scale. The regions situated near rivers used river stones especially for the foundations, for the fences, or some types of elevation for the annexes in the households to protect the corn and the cereals from snow and rain.

In the mountains and in the hill regions the river stones and the cut stones where both used for the buildings the first floor or the semi-basement of the houses. The stones were installed with limestone-based mortar or with marble dust-based mortar.

STRAW

One of the oldest types of harvest is wheat, and its derivates from it, barley, oat and rye. From very old times straws were used for many applications in the household of the villagers around the globe. They were used for stables's cleaning, for mattresses and finally in construction, for the reinforcement the clay products and for the roof covers. It was - and it still is - a great way to reuse the waste from harvesting.

One resource is associated with the picturesque image of a recently harvested yellow field; landscapes of rivers in autumn with beautiful dancing reeds can be associated with the regions where thatching roof techniques were practiced.

Straws are tubular vegetal materials, represented by the stem of the plant. In mid-summer, the dried straws were harvested for cereals, by hand, and stored on site or in household in form of haystack. The straws needed for building should not be affected by humidity or fungus and had to be used shortly after harvesting.

72
The reeds straw on the other hand were harvested from the late autumn until the beginning of the spring, stored in sheaf and kept in a safe and dry place until they were needed to be used. In Romania, the thatching technique was the symbol of the Dobrogea region with the Danube Delta, one of the richest resources of reeds in Europe. The characteristics of the Romanian thatched roofs are the curved eaves and the beautiful textures of straws arrays on the roof, with a natural earthy colour, usually contrasting with whitewashing of the façade and the blue of the windows framings, specific to the Dobrogea region, Fig. 5.



Fig. 5 – Reed's sheaf installation. Horizontal section through the roof.

The thatched roof technique, proudly practised by the dobrogeans, was used by applying the sheaf of reed in the direction of the slope, on a wooden structure and horizontal laths, starting from the eave to the ridge, Fig. 6. A long metal needle was used to wave the sheaf to the wooden structure. The final touch of the artisan consists in the way he trimmed the straws, which gave the specific image of the roof. The trimming was accomplished on the edges of the eaves, ridges and fascia.



Fig. 6 – Thatched roof and adobe wall. Vertical section through the eave level.

4. Conclusions

Romania has a beautiful cultural inheritance from our ancestors. As the country has settlements consisting of inhabitants that worked the land for agriculture, apiculture and pomiculture, the people were permanently in touch with nature and with its resources and managed to use in a useful way everything nature offered. In time, after years of practicing, they achieved an advanced level of building skills which has materialized in the houses that still remain even in our days as witness of history.

Hundreds of years of experience of building with natural materials is and it must be taken as - a very important milestone, that we should keep in mind, and check if the current practice is going in a good or in a bad direction that affects the environment. Most importantly, often neglected, our wellbeing, which is not always at a good level in some high-tech solution. should be our priority Sometimes, the good way, can be the simple way, the nature's way.

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TEHNICI TRADIȚIONALE ȘI MATERIALE NATURALE DE CONSTRUCȚII ÎN ROMÂNIA

(Rezumat)

În contextul actual al protejării mediului înconjurător, prin reducerea poluării și a consumului de energie, domeniul construcțiilor se evidențiază negative prin gradul ridicat de consum de energie și producerea unei cantități mari de deșeuri.

Ca urmare a procesului de globalizare are loc reducerea numărului de tipuri de materiale de construcții folosite la nivel mondial, atât în țările dezvoltate cât și în cele mai puțin dezvoltate, având ca rezultat standardizarea procesului de construcție și neglijarea resurselor locale. Tendința contemporană de a utiliza tehnici și materiale de construcție noi aduc odată cu ele și influențe arhitecturale corespunzătoare acestora în opoziție cu stilurile locale. Analizând construcțiile cu înălțime mică, se poate observa, odată cu dezvoltarea acestor tendințe, o dispariție treptată a valorilor și a tradițiilor locale, materialele de construcții fabricate cu resurse locale fiind înlocuite cu materiale naturale din alte regiuni climatice sau produse prin multiple procese de fabricație cu consum mare de energie, ori transportate de la mare distanță.

Prin schimbarea opticii asupra materialelor necesare unei construcții cu înalțime mică putem ajuta la protejarea naturii și la reîntoarcerea către valorilor locale naturale și culturale.

România beneficiază de numeroase resurse naturale și de o istorie bogată cu martori culturali ce se regăsesc nu numai la muzee naționale, ci și în zona rurală a României. Istoria arată că arhitectura vernaculară românească cuprinde valori începând de la decorații bogate ale elementelor din lemn, la îmbinări eficiente la nodurile construcției, până la împletituri complexe din nuiele, lână sau cânepă.

Din toată această bogație a României, lucrarea se axează doar pe caracterul arhitectonic: exploatarea resurselor naturale, modul de fabricare și punere în execuție a acestora, totul într-o maniera ecologică și responsabilă față de mediul înconjurator, cu evidențierea tradiției românești.

Această direcție vernaculară nu urmărește reinventarea tehnicilor sau principiilor de construcție, ci întelegerea simplității lor și a sincerității construcției față de mediul înconjurător, putem astfel duce mai departe aceste principii autentice și a le perfecționa fără a le altera caracterul natural.

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RECENT RESEARCH ON Mg-BASED BIODEGRADABLE ALLOYS - REVIEW

ΒY

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> Abstract. Metallic biodegradable materials represent a topical approach in the medical field, especially in orthopedics. Magnesium based alloys such as Mg-Ca, Mg-Si, Mg-Y, etc. have been the subject of previous research, in order to establish optimum concentrations, from the microstructural, mechanical and wear resistance point of view. Among the major advantages offered by Mgbased alloys are: low modulus of elasticity (similar to biological bone) and high biocompatibility, and as disadvantages, it is identified: high degradation rate and subcutaneous hydrogen release. Also, Mg-based biodegradable alloys have superior advantages over other types of biodegradable alloys, such as Zn or Febased biodegradable alloys. The purpose of this review is to identify and compare microstructural analysis, mechanical characteristics and electrochemical results of the various systems of biodegradable magnesium-based alloys.

> **Keywords:** Biodegradation; Magnesium alloys; Microstructural analysis; Mechanical properties; Corrosion.

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1. Introduction

The significant advancement in medical science and technology has considerably improved the quality and longevity of human life, and the development of a variety of biomaterials is among the most notable innovations. Biomaterial is a wide-ranging field, covering medical science, chemistry, biology and materials science (Ratner *et al.*, 1996). Biomaterials are inorganic or organic materials that are designed to mimic physiological components and/or processes.

The role of biodegradable implants is to support tissue regeneration, heal the specific trauma and finally disappear through degradation in biological environment. Among biodegradable metal implants Iron, Zinc and Magnesium have been widely investigated for medical application.

Iron (Fe) prostheses and fixation screws were used by Lambotte in 1906 in a surgical attempt to treat a fracture, the treatment being a failure due to the alloys' detachment from the bone tissue (Lambotte, 1932).

To minimize trauma to the patients, and decrease medical costs, magnesium based biodegradable alloys implants started being analyzed in order to replace traditional metal implants and remove the need for secondary surgeries.

Mg was first reported for medical application in 1878 as ligatures when the physician Edward C. Huse used Mg wires to stop the bleeding vessels of three pacients (Huse, 1878). While the corrosion of the Mg in vivo was slower, the pure Mg wires were too brittle to knot easily; therefore, some elements were alloyed into Mg to increase its ductility.

In 1900, Mg sheets were implanted in the knee joint of dogs and rabbits by the physician Erwin Payr, but the materials completely corroded after few weeks (Rostock *el al.*, 1937).

In recent years, magnesium (Mg) alloys have gained significant attention in the area of biomaterials due to their good biocompatibility, biodegradability, and acceptable mechanical properties (Shadanbaz and Dias, 2012). Mg is an element essential in many metabolic processes and is primarily stored in bone tissue. It is taken into the body daily in substantial amounts, stimulates the growth of bone cells, and accelerates the healing of bone tissue. Magnesium (Mg) can dissolve in body fluid that means the implanted Mg can degrade during healing process, and if the degradation is controlled it would leave no debris after the completion of healing. Hence, the need for secondary surgical operation(s) for the implant removal could be eliminated. Besides its biocompatibility, the most attractive physical characteristics of Mg are its high specific strength and an elastic modulus that closely resembles human bone (DeGarmo, 1979). Therefore, the stress shielding from the notable mechanical mismatch between natural bone and metal implants should be reduced (Brar *et al.*, 2012).

While researches have led to significant progress over the past 20 years, the currently available Mg alloys degrade too quickly to hold well during implantation, resulting in the formation of hydrogen gas cavities, rapid loss of mechanical integrity of the implants, and adverse host tissue reactions. Nowadays, a lot of researchers are working in this pioneering field to develop new magnesium alloys for medical applications and to investigate their mechanical properties and corrosion performance (Witte *et al.*, 2005).

2. Magnesium (Mg) Alloying Elements

Magnesium is an essential mineral for human metabolism and its deficiency has been linked to various pathological conditions. It is the second most common intracellular ion and serves as a cofactor for more than 300 enzymatic reactions ranging from muscle contraction to neuronal control. Most of the Mg in the body (53%) is stored in bones.

Pure Mg implants have low corrosion resistance, and Mg fast degradation and distribution over the body may cause clinical complications.

To improve magnesium's mechanical properties, corrosion resistance as well as the production cost, alloys development is necessary (Witte *et al.*, 2008).

The basic elements used for Mg alloying are Aluminium, Calcium, Copper, Iron, Lithium, Manganese, Nickel, Strontium, Yttrium, Zink, Zirconium, and Rare Earth Elements (Witte *et al.*, 2005).

Metals	Young's modulus (GPa)	Density (g/cm ³)	YS (MPa)	UTS (MPa)	Elongation (%)
Stainless steel (SS316L, annealed plate, ASTM F138)	193	8	190	490	40
Co–Cr alloys (ASTM F90)	210	9.2	310	860	20
Tantalum (annealed)	185	16.6	138	207	-
Pure iron (99.8 wt%)	200	7.87	150	210	40
Mg-based alloy (WE43, ASTM B107/B107M)	44	1.84	170	220	2
DL-PLA	1.9	-	-	27-41	3-10

 Table 1

 Mechanical Properties of Medical Metals (Chen et al., 2014;

 Middleton and Tinton 2000)

2.1. Mg-Ca Based Alloys

Calcium (Ca) is the most abundant mineral in the human body and it plays a significant role in bone function, vascular and heart physiology (Renkema *et al.*, 2008).

Mechanical properties and corrosion behaviour of Mg–Ca alloys can be adjusted by controlling the Ca content. The solubility of Ca in Mg is about 1.34 wt.% and under the equilibrium conditions Ca contributes to solid strengthening solution and precipitation. It also acts to some extent as a grain refining agent and additionally contributes to grain boundary strengthening. However, excessive addition of Ca (>1 wt.%) in magnesium will deteriorate the corrosion resistance (Witte *et al.*, 2008).

Rad *et al.* (2012) studied the effect of calcium content on microstructure of Mg-Ca alloys containing 0.5, 1.25, 2.5, 5.0, and 10.0 wt.% Ca (Fig. 1). Their results revealed that the grain size and dendritic cell size decrease significantly with higher amount of Ca while more Mg₂Ca intermetallic phase appears in grain boundaries for higher Ca content. A fine grain structure possesses the lowest ductility and with increasing grain size ductility increases.



Fig. 1 – Optical micrographs of (a) pure Mg, (b) Mg-Ca0.5, (c) Mg-Ca1.25, (d) Mg-Ca2.5, (e) Mg-Ca5.0, and (f) Mg-Ca10.0 (Rad *et al.*, 2012).

Cytocompatibility evaluation results indicated that Mg-1Ca alloy induces no toxicity to cells.

Mg-Ca alloys have good potential to be used as bone screws for internal fracture fixation.

2.2. Mg-Zn Based Alloys

Zinc (Zn) is one of the most abundant essential nutrients in the human body that plays significant role in human metabolism as a co-factor for optional enzymes in bones and cartilage (Brandão-Neto *et al.*, 1995; Nagata and Lönnerdal, 2011), and it is essential for immune system.

Zn content which is up to 4 wt.% significantly increases the ultimate tensile strength and elongation of as-cast Mg–Zn alloys, but any higher percentage of Zn would lead to the reduction of both properties and decrease the corrosion resistance of the alloy. But it was shown that amorphous Mg–Zn-based alloys containing about 5.0 wt.% of Zn had excellent strength, high corrosion resistance, low hydrogen evolution rate and good biocompatibility in animals, therefore, they became promising candidates for biodegradable bone implants. Besides, Mg-Zn alloys have good potential to be used as suture materials and intestinal tract and bile repairing materials (Chen *et al.*, 2014).

From the perspective of medical applications, Mg-Zn-Ca alloys are attractive because all the alloying elements are naturally present in the human body, can be naturally metabolized, and released.

Ca improved mechanical properties and resistance mainly due to the formation of Mg₂Ca precipitates (Ortega *et al.*, 2008), improved the oxidation resistance (You *et al.*, 2001), and reduced the grain size of alloys when adding approximately 0.5-1.0 wt.% Ca (Zhang *et al.*, 2008; Hirai *et al.*, 2005). The addition of 1-4 wt. % Zn (when Ca < 1.0 wt.%) resulted in Mg-Zn-Ca alloys with corrosion rates promising for biomedical applications (Zhang *et al.*, 2011; Bakhsheshi-Rad *et al.*, 2012).

Mg-Zn-Ca-based alloys have recently attracted much attention to be used for orthopedic applications due to their biocompatibility and the possibility to tailoring their properties by post-fabrication processes (*e.g.* heat treatment) (Ibrahim *et al.*, 2016). At the same time, these alloys have a fast degradation rate and do not present sufficient strength that is required for holding fractured bones during the bone healing period. To enhance mechanical and corrosion properties of these alloys the addition of more alloying elements such as Mn and Zr (Kirkland *et al.*, 2011), mechanical treatments, and heat treatments such as annealing and age hardening (Oh-Ishi *et al.*, 2009; Ibrahim *et al.*, 2017).

Fig. 2 shows the SEM observation of the as-cast Mg-1.2Zn-0.5Ca alloy (Fig. 2a and Fig. 2c) and the as-cast Mg-1.2Zn-0.5Ca-0.5Mn alloy (Fig. 2b and Fig. 2d).



Fig. 2 – SEM micrographs and the corresponding EDS analysis of the as-cast (a), (c) Mg-1.2Zn-0.5Ca alloy, and (b), (d) Mg-1.2Zn-0.5Ca-0.5Mn alloy (Ibrahim *et al.*, 2017).

2.3. Mg-Mn Based Alloys

Manganese (Mn) is an essential element that plays important role in metabolic cycle of lipids, amino acid and carbohydrates. Also, it influences the function of immune system, bone growth and blood clotting (Aschner *et al.*, 2007). In Mg alloy Manganese is mainly used to enhance ductility.

A lot of researches show non-toxic influence of Mn during cell culturing but its poisonous effect from magnesium alloys on the cell viability and the proliferation has also been observed (Witte *et al.*, 2008).

The corrosion resistance and tensile strength of Mg-Mn alloys are significantly improved by adding Zn (Yin *et al.*, 2008; Xu *et al.*, 2008). Mg-Mn-Zn alloys could bio-degrade in a biological environment without leaving residues at the implantation site and in the surrounding bone tissue (Xu *et al.*, 2007a; Xu *et al.*, 2007b).

As can be seen in Fig. 3, the microstructure of Mg-Mn alloy is much coarser than those of Mg-Mn-Zn alloys. The grain size of the Mg-Mn-Zn alloys decreases with increasing of Zn content.

82

The addition of Mn to different Mg alloys was found to be a useful technique to improve the mechanical and corrosion properties by incorporating essentially insoluble metallic impurities such as Fe and Ni into harmless inter metallic phases (Hamdy *et al.*, 2017).



Fig. 3 – Microstructures of the alloys (a) Mg-Mn alloy; (b) Mg-Mn-1Zn alloy;
(c) Mg-Mn-2Zn alloy; (d) Mg-Mn-3Zn alloy; (e) Mg-Mn-4Zn alloy; (f) Mg-Mn-5Zn alloy (Ibrahim *et al.*, 2017).

In general, heat treatment processes are more feasible than mechanical treatment when the part is fabricated into its final shape.

As shown in Fig. 4 the heat treatment process resulted in a more uniform size and shape of grains for both alloys.



Fig. 4 – SEM micrographs of the heat-treated (a) Mg-1.2Zn-0.5Ca alloy; (b) Mg-1.2Zn-0.5Ca-0.5Mn alloy (Ibrahim *et al.*, 2017).

The as-cast Mg-1.2Zn-0.5Ca-0.5Mn alloy has better mechanical properties compared to the as-cast Mg-1.2Zn-0.5Ca alloy. This enhancement is represented in the higher strength and ductility of the Mg-1.2Zn-0.5Ca-0.5Mn

alloy, which can be attributed the significant grain refinement after the addition of Mn. Moreover, the heat treatment response of the Mg-1.2Zn-0.5Ca-0.5Mn alloy was higher than that for the Mg-1.2Zn-0.5Ca alloy. As seen in Table 2, the tensile strength and hardness increased significantly for both alloys after the heat treatment process.

 Table 2

 Mechanical Properties of the Mg-1.2Zn-0.5Ca and Mg-1.2Zn-0.5Ca-0.5Mn

 Alloys, As-Cast and Heat-Treated (Ibrahim et al., 2017)

Drawsing		Micro-	Compression properties		Tensile properties			
Alloy	history	hardness (HV)	Yield strength	Ultimate	Max. strain	Yield strength	Ultimate strength	Max. strain
			(MPa)	strength (MPa)	(%)	(MPa)	(MPa)	(%)
Mg-1.2Zn- 0.5Ca	As-cast	50.6 ± 6.1	60.9 ± 10.5	260.2 ± 5.9	18.1 ± 0.7	59.7 ± 4.2	120.6 ± 4.7	3.2 ± 0.2
0.504	treated	61.4 ± 2.8	118.8 ± 12.7	306.5 ± 7.3	19.8 ± 1.3	83.1 ± 6.4	150.8 ± 7.3	4.7 ± 0.3
Mg-1.2Zn- 0.5Ca-	As-cast	51.6 ± 3.6	71.7 ± 5.3	304.1 ± 8.2	28.9 ± 0.8	63.4 ± 3.5	125.1 ± 6.1	4.4 ± 0.1
0.5Mn	Heat- treated	62.9 ± 4.7	122.8 ± 9.4	352.8 ± 24.1	25.63 ± 2.2	88.9 ± 5.2	158.0 ± 8.4	4.8 ± 0.2

If the Mg-1.2Zn-0.5Ca-0.5Mn alloy is to be compared with the Mg-1.2Zn-0.5Ca alloy, it can be easily seen that both the as-cast and heat-treated samples of the Mg-1.2Zn-0.5Ca-0.5Mn alloy showed lower corrosion rates than the Mn-free alloy. This is mainly attributed to the role of Mn in grain refinement and eliminating the harmful effect of impurities in the alloy (Hamdy *et al.*, 2017).

2.4. Mg-Zr Based Alloys

Zirconium (Zr) is a powerful grain refiner for Mg alloys; it is usually used in alloys containing Zn, RE, Y, and thorium (Th) and it cannot be used together with Al and Mn since they form stable compounds with Zr. Recently, the Mg–Zr alloys had attracted considerable attention due to their high specific damping capacity (around 80%), which may help to suppress the vibrations generated during movement and stress at the implant/ bone interface (Tsai *et al.*, 2011).

It was indicated that 1 wt.% of Zr addition in Mg resulted in significant improvement of the strength and ductility of the metal and reduced the degradation rate by 50%, and co-addition of Sr and Sn could effectively reduce the degradation of as-cast Mg–Zr–Ca alloy (Zhang *et al.*, 2009).

It can be seen that the Mg–1Zr–1Ca alloy exhibits the finest microstructure (Fig. 5) among these alloys, which supports the previous conclusion that Zr can refine the grains of Mg alloys (Xu *et al.*, 2007).



Fig. 5 - Microstructures of as cast Mg-Zr-Ca alloys (Xu et al., 2007a; Xu et al., 2007b).

2.5. Mg-Al Based Alloys

Aluminum (Al), as a widely used element for Mg alloying is improving the mechanical properties and corrosion resistance (Witte *et al.*, 2008). The Al addition of Mg alloys leads to strength improvement and the small increase of density (the density of Al is close to that of Mg), but it causes the decrease of elongation (Wu *et al.*, 2010). Insoluble aluminium oxide (Al₂O₃) will be formed in the corrosion products layer in alloys containing Al and Magnesium during corrosion (Wang *et al.*, 2011). Aluminum should be used carefully due to possible biological complications such as risk factor in Alzheimer's disease, muscle damage and decrease of activities of osteoclasts (Ferreira *et al.*, 2008). The potential toxicity of Al-containing Mg alloys needs further studies.

2.6. Mg-REEs Based Alloys

Rare Earth Elements (REEs) are improving the mechanical properties of Mg alloys due to solid solution and precipitation strengthening. Rare earth elements are not essential for humans and are not found in the human body. For Mg alloy processing a lot of Rare Elements have been used, such as Cerium (Ce), Lanthanum (La), Neodymium (Nd) and Praseodymium (Pr), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb), and Lutetium (Lu) (Witte *et al.*, 2008). Usually they are

used in combination with other alloying elements but currently there are some Mg alloys containing only Rare Earth Elements. Addition of REEs into Mg–Al–Zn alloys is reported to further improve the corrosion resistance.

Table 3
Mechanical Properties of Some Representative Biodegradable Magnesium Alloys

Alloys	Condition	Ultimate tensile strength (MPa)	Yield strength (MPa)	Elongation %	References
Mg-(2, 3)Ca	Rolled	-	136–162	1.9–2.4	(Seong and
					Kim, 2015)
Mg-(4, 6) Zn	Extruded	240-315	100-235	8–17	(Hradilová et
					al., 2013; Huan
					et al., 2010)
Mg-(1, 2, 3, 4)Sr	Rolled	110-213	80-148	2.8-3.2	(Gu et al., 2011)
Mg-0.6Si	Cast	166	60	6.62	(Zhang et al.,
					2010a, 2010b)
Mg-Y	Extruded	> 275	> 250	> 10	(Windhagen et
(MgYREZr)					al., 2013)
Mg-Nd (JDBM)	Extruded	194–240	90–189	12–25	(Zhang et al.,
					2012)
Mg-Gd	Extruded	~260	~210	~30	(Zhang et al.,
					2016)

Most of the research studies reported promising results for the application of Mg alloys as implant material due to their desirable mechanical properties, biocompatibility, and biodegradability. It is believed that Mg and Mg alloys are a new generation of biomaterials and they will play an important role in revolutionizing orthopedic, cardiovascular and dental applications. Magnesium (Mg) or its alloys are widely tested as potential orthopedic implants, particularly as biodegradable alloys for fracture fixation due to their mechanical properties are close to those of bone.

Overall, the rapid corrosion rate of Mg and Mg alloys could be useful to avoid a second surgery for remove the implants, in fast wound-healing processes, but premature degradation may provoke loss of implant mechanical integrity, limiting its application for longer periods.

3. Magnesium Alloy Degradation

Despite their highly advantageous properties, magnesium and its alloys are not commonly used as degradable implants. The major drawback of magnesium alloys as implants is their high corrosion rate in the physiological environment, which promotes fast degradation of the mechanical properties, leading to the premature failure of implants before the completion of the tissue-healing process.

Generally, the microstructure involves the grain size, the phase constituents and their distribution. The corrosion performance of magnesium alloys is closely related to the microstructure (Lunder *et al.*, 1989), and the second phase has a profound impact on the corrosion performance of magnesium alloys. Magnesium is highly susceptible to corrosion in most aqueous environments, including human body fluid. Corrosion of magnesium produces an oxide/hydroxide layer on the surface, which is not protective in most aqueous environments (Godard *et al.*, 1967). The following reactions represent the corrosion of magnesium alloys in most aqueous environments, including the physiological environment (Zheng *et al.*, 2014):

Anodic reaction:
$$Mg(s) \rightarrow Mg_2 + (aq)^{+2e}$$
 (1)

Cathodic reaction:
$$2H_2O(aq)^{+2e^-} \rightarrow 2OH^-(aq) + H_2(g)$$
 (2)

Overall reaction: $Mg(s)+2H_2O(aq) \rightarrow Mg(OH)_2(s)+H_2(g)$ (3)

In general, immediately after contact with moisture/ body fluids, Mg is oxidized to form cations following an anodic reaction (Eq. (1)).

The generated electrons are consumed for reduction of water corresponding to cathodic reactions. The hydroxide anions generated through the cathodic reaction cause an increase of the pH of the solution (Wang *et al.*, 2009) (Eq. (2)).

Even though the formed hydroxide layer covers the surface of magnesium, this hydroxide layer is not stable in the presence of chloride ions in human body fluid. The presence of chloride ions quickly converts the hydroxide layer into highly soluble magnesium chloride (Song, 2004).

$$Mg(OH)_{2}(s)+2Cl-(aq) \rightarrow MgCl_{2}+2OH^{-}(aq)$$
(4)

The disappearance of the hydroxide layer due to chloride ions hastens the corrosion of magnesium alloys. Additionally, hydrogen gas (H2) evolution during magnesium corrosion can create subcutaneous gas bubbles (Poinern *et al.*, 2012) and gas bubbles adjacent to the implants, which can cause the separation of tissues and/or tissue layers (Song, 2007).

In order to identify ways to improve the corrosion resistance of magnesium implants, it is important to investigate their corrosion rates and mechanisms in the presence of a physiological environment. The basic conditions which determine the corrosion rate are alloy compound and environment around implant. Due to high electrochemical activity of Mg, and numerous environmental factors (*e.g.* temperature and surrounding ion composition) influence its corrosion behaviour making it unpredictable. Therefore, the need of reliable in vitro model(s) to predict in vivo implant degradation is increasing.



Fig. 6 – Mg and Mg alloys: in-vitro and in-vivo corrosion factors (Martinez Sanchez *et al.*, 2015).

In vitro and in vivo Mg alloys degrade through a series of corrosion reactions that depend on numerous circumstances. In vitro degradation techniques include electrochemical experiments, hydrogen development and mass/volume loss after immersion test (Sanchez *et al.*, 2015).

The electrochemical test approaches to boosting the corrosion that does not correlate with in-vivo degradation (Zhen *et al.*, 2013).

The mass or volume loss approaches are similar to in vivo conditions but impediments were observed (*i.e.* mass-loss without removing the corrosion products can lead to negative degradation rate (Seitz *et al.*, 2011)).

The temperature is also a factor that can notably influence degradation of Mg alloy in vitro. It was demonstrated that if temperature is increased to 40 Celsius the corrosion rate is accelerating by 50% resulting in a substantial Mg alloy corrosion after implantation (Kirkland *et al.*, 2011).

Recent research showed slower degradation in vivo but all factors that determine Mg alloy corrosion in animal and human body are still not found.

The amount of water and blood flow affects the removing of degradation product and prevents the formation of protective layer on alloy surface (Witte *et al.*, 2008). Chloride-contained environment can transform Mg(OH)₂ into soluble Magnesium Chloride that is accelerating the corrosion. The level of Chlorine Ion depends not only on the species but even on the tissue and body condition. This represent the main factor that determines the difference between in vitro and in vivo experiments (Badawy *et al.*, 2010).

pH is one of the factors that determine degradation rate in vitro, therefore inflammation and foreign body response were observed after the metal implantation which can lead to formation of stable corrosion layer in first term after the surgical procedure (Witte *et al.*, 2005). Body fluid ion concentration as well as temperature can also change the rate of Mg corrosion (Erdmann *et al.*, 2010).

Based on the data for in vitro and in vivo degradation it was observed that the different corrosion rate that depends on the numerous factors. In vitro test gives us only general information about alloy degradation. Only the systematic analysis of clinical trial and in vivo animal studies with different condition can give complete information about the relations between the degradable Mg alloy and hosting organ.

4. Conclusions

Metals have more desirable mechanical properties due to their relatively high strength and fracture toughness. However, the conventional surgical alloys, like stainless steel, cobalt, chromium and nickel-based alloys have limitation due to possible release of toxic ions during corrosion or wear processes and non-compliance with elastic module of natural bone. Secondary surgical operation(s) usually become inevitable to prevent long term exposure of body with the toxic implant contents leading to possible complication the rise of treatment cost.

In contrast to other metals, Magnesium has density and elastic module close to natural bone. Mg and its alloys differ from other biomaterials by presenting compatible mechanical and physical properties to human bone. Their densities and elastic modulus are fairly close to each other which remove elastic mismatches between implants and the bone.

Moreover, Mg is naturally present in bone composition, and it is one of the required metals for the metabolism. During the degradation, Mg alloy releases non-toxic Mg oxide that is most completely excreted in the urine. Hence, the need for secondary surgical operation(s) for the implant removal could be eliminated.

It is believed that Mg and Mg alloys are a new generation of biomaterials and they will play an important role in revolutionizing orthopedic, cardiovascular and dental applications. However, the very high corrosion rate limits their use as an implant as it may potentially degrade even before the healing has been completed.

Magnesium's low corrosion resistance also leads to the rapid production of hydrogen gas that leads to the formation of gas bubbles. These bubbles can accumulate around the implant and delay the healing of the tissue. The localized formation of hydrogen gas can also result in a pH increase around the implant. This can cause local alkalization and severely affect the pH dependent physiological processes in the vicinity of the implant. In-vitro and in-vivo studies have been used for evaluation of degradation rate and host response. There is no correlation between these methods and they should be used together for better alloy assessment.

Electrochemical method and emersion in saline solution do not give reliable results. The results of in-vivo research depend on animal species, implant anatomical location and some physiological parameters such as pH, blood flow speed and chloride ion concentration.

Alloying elements can significantly improve mechanical properties, control corrosion rate and influence biological response on Mg alloy. But it is difficult to choose the best alloy and in order to do this we need some more invitro and in-vivo experiments and clinical investigation. Hence for extensive use of Mg and its alloys in biomedical implant applications, a better understanding and control over the degradation rate is required.

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CERCETĂRI RECENTE ASUPRA ALIAJELOR BIODEGRADABILE PE BAZĂ DE Mg – TRECERE ÎN REVISTĂ

(Rezumat)

Materialele metalice biodegradabile reprezintă o abordarea locală în domeniul medical, în special în ortopedie. Aliaje pe bază de Mg cum sunt Mg-Ca, Mg-Si, Mg-Y etc. au constituit deja subiecte de cercetare, în scopul determinării concentrațiilor optime din punctul de vedere al microstructurii, proprietăților mecanice și a rezistenței la uzare. Printre avantajele majore oferite de aliajele pe bază de Mg sunt: modulul de elasticitate redus (similar cu cel al osului biologic) și biocompatibilității ridicate, și ca dezavantaje, au fost identificate: rata mare de degradare și eliberarea de hidrogen subcutanat. De asemeni, aliajele pe bază de Mg biodegradabile au avantaje certe în comparație cu alte tipuri de aliaje biodegradabile cum sunt cele pe bază de Zn sau Fe. Scopul acestei treceri în revistă este de a identifica și compara analizele microstructurale, caracteristicile mecanice și rezultatele electrochimice ale diferitelor tipuri de aliaje biodegradabile pe bază de magneziu.

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A COMBINED MATERIALS SCIENCE AND MECHANICAL APPROACH TO THE STUDY OF HYDROGEN EMBRITTLEMENT OF STRUCTURAL MATERIALS

ΒY

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Abstract. The hydrogen embrittlement in structural materials is more often investigated from material science point of view. In this paper, the study is focused on better understanding of actual state of the art of hydrogen mechanics in the structural materials.

The object of this study is to develop fracture criteria with predictive capabilities against the degradation of materials in the presence of hydrogen. Design criterias referring to the hydrogen effect on material safety and reliability are also studied.

In order to investigate the material microstructure, optical analysis and Scanning Electron Microscopy (SEM) were used. The interaction between hydrogen and defects of material is studied using the Scanning Electron Microscopy (SEM).

The approach is to integrate the mechanical property and microstructural analysis of deformation processes of materials at micro and nano scales.

Keywords: Hydrogen embrittlement; premature failure; microstructure; fracture; scanning electron microscopy (SEM).

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1. Introduction

The negative effects of the internal or external interaction between hydrogen and structural materials, known as hydrogen embrittlement, is well documented since 1875 (Johnson, 1875). The studies shows that even the contact with a small amount of hydrogen can lead to a serious degradation of the mechanical properties resulting in failures of components at loads below the designed ones. This phenomenon appears due to the hydrogen's chemical interaction with the material, hydrogen absorption and hydrogen trapping levels (Eliezer and Silverstein, 2018). The problems are getting worse when in the material exist multiple cracks. The contact with hydrogen leads to an accelerated process of crack growth that means at the end high risk of fracture.

In order to describe the hydrogen embrittlement phenomenon in nonforming hydride systems, different models were developed, but the most applicable ones are the following:

- The decohesion model, which is based on hydrogen causing a reduction in the strength of atomic bonds (Martin *et al.*, 2011)
- The hydrogen-enhanced dislocation emission (HEDE) model in which hydrogen lowers the surface energy (Martin *et al.*, 2011)
- The hydrogen-enhanced localized plasticity (HELP) mechanism in which the hydrogen atmosphere attached to the dislocation effectively lowers the interaction with elastic obstacles, which means that the shear stress for dislocation motion is reduced (Martin *et al.*, 2011)

In this paper, the current status regarding the microstructure changes in the presence of hydrogen is shown based on the investigations done using different techniques like optical analysis and Scanning Electron Microscopy (SEM).

2. Results and Discussions

To perform this investigation, different materials were used: duplex stainless steels (DSS), austenitic stainless steel (AUSS), super martensitic stainless steels (SMSS) as annealed sheets and probes of pipeline steels API grade X80 and X60 HIC.

The probes from annealed sheets were charged with hydrogen for 72 hours and after that the cracks were analyzed on electron microscope like can be seen in Fig. 1.



Fig. 1 – SEM observations of surface cracking of 72 hours exposure (Eliezer and Silverstein, 2018).

In Fig. 1 can be observed the cracks on probes after 72 hours exposure to hydrogen as follows: (a) and (d) austenitic stainless steel, (b) and (e) duplex stainless steel and (c) and (f) super martensitic stainless steel.

One important aspect is related to the appearance of the ε -martensite phase after one month at Room Temperature (RT) as result of the interaction with hydrogen Fig. 1 (d), (e). According to the work of others (Eliezer and Silverstein, 2018), during the hydrogen absorption, an internal stress is created which leads to a transition from γ phase to ε -martensite.

In order to observe deeper the behaviour of cracks a comparison was made between an exposed probe to hydrogen and a non exposed probe.



Fig.2 - SEM microstructural observation of cracks (Eliezer and Silverstein, 2018).

As can be observed in Fig. 2, there is a comparison between the aspect of cracks of a non exposed probe (b) and an exposed to hydrogen probe (c). The exposed probe (c) shows a multiplication and a growth of cracks compared to the other probe which for sure leads to a premature failure of part after applying the mechanical load.

Using the Scanning Electron Microscopy (SEM), different morphologies on fracture surfaces of exposed to hydrogen probes were observed. Based on other studies (Martin *et al.*, 2011), different morphologies can be found: secondary cracks, cracks at inclusions, "quasi-cleavage" and flat "featureless" regions.



Fig.3 – SEM images showing typical features of fracture surface (Martin *et al.*, 2011)

Fig. 3 shows secondary cracks (a), inclusions (b), flat features (c) and quasi-cleavage features (d).

3. Conclusions

Based on the results observed on the Scanning Electron Microscopy (SEM), the exposure of the structural materials to hydrogen leads to a reduction of the strength of material by increasing the number of cracks and also facilitating the growth of them. Beside this, changes in the material phases were also observed after some time from the exposure to hydrogen.

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O ABORDARE COMBINATĂ A ȘTIINȚEI MATERIALELOR ȘI MECANICA PENTRU STUDIUL FRAGILIZĂRII DE HIDROGEN A MATERIALELOR STRUCTURALE

(Rezumat)

Lucrarea descrie comportamentul materialelor structurale la contactul cu un mediu bogat în hidrogen. În urma studiilor se constată o scădere a proprietăților mecanice ale materialelor în comparație cu cele ce nu sunt expuse hidrogenului. Pe de altă parte, interacțiunea hidrogenului cu materialul respectiv are un efect negativ asupra defectelor acestuia provocând o creștere a numărului de fisuri precum și a mărimii acestora.