Securing element with ferromagnetic microwires

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The securing elements presented in the paper are constituted from composite materials, realized by the embedding of the glass-coated ferromagnetic microwires (MW) in a celullosic matrix. These can be used as validating elements in order to identifying the counterfeit products. The advantages of the MW securing were: the possibility of the identifying at distance, stable magnetic properties, even at high temperatures and corrosive media; stability at the mechanical action, small sizes and low consumption. A detector, specially designed, validates the presence of the ferromagnetic MW into the paper. Their metallic core, prepared from soft magnetic alloys, and their sizes, compatible with the sizes of the cellulosic fibers, even they are in the matrix randomly oriented disposed, recommend them as perfect filler for securing elements based on paper.

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1. Introduction

The industrial politic orientation of European Union consists in consolidation of the competitiveness on international level. The result of this orientation is materialized in the entry on the free market of these high-tech products, with high quality level and competitive prices. Counterfeiting and product fraud constitute nowadays a "blooming" business. Losses to Government, Business and Citizens through counterfeiting, tampering and theft around the world now come to over $960 billion Euros annually. They are estimated to account for some 5-7% of world trade, and are growing at around 15% per annum, that is far faster than the total security solutions and security technologies market. Selected European research centers have the mission to perform researches in field of micro technologies what will be placed before some years of the requirement on the market. These research centers have the mission to concentrate above the strategically researches, giving a special attention to support the industry in the security field including methods of safety for valuable papers.

Remarkable is the fact that these centers have a very expansive thematic, consequence of the various problems that will be solved in fundamental domain of the research and in the domain of the technologically procedures that stand at the base of the production, testing these in the process of research and design for achieving new improved products.

To prevent the counterfeit process, the process of laying etiquettes on the products has developed from year to year, reaching in the present to instruments including sophisticated technologies. Thus, all these technologies can be made by those who want to counterfeit, but in the case of the high-tech technologies, the price of the falsification is prohibitive.

As security element, the special fibers are incorporated in the mass of the paper in the fabrication process. There are special properties which make them to be different: the color, UV luminescence feature and the color combinations. Usually are used the following types of fibers: UV colorless luminescence fibers and colored fibers which can be luminescent or not in UV light.

The moment of launching the development technologies of metallic micro-wires has a revolutionary result as on the high-tech technologies market opening the doors for big varieties of technological benefits for the existing applications and in the same time stabling the bases of new applications. The main arguments for this type of technologies are the precision, viability, a high productivity, the possibility of the processing automation and multiple functional possibilities.

Towards this situation, in our days different methods of protection it use at a large scale for the consumer goods protection, bank-documents, and of the commerce. Because of impossibility to obtain the safety's elements without adequate equipment and special conditions based on highest grade of exactly, the advanced technologies permit a high grade of protection against falsification. There are many investment efforts and research to diversify the domain of the realization of the elements with a high grade of security. Thus the manifested tendency in the last time is:

- the realization of research that has at the base the physical principles regarding new methods and the realization middles of security's elements with capacities of falsification reduced;

- process automation of quality attesting in the time of production, in sense of evaluation and conformity's certification;
- the seek of the false through technical middles;
- the introduction of quality's attesting methods and seeking false etiquettes and marks with automate middles;
- introducing safety's elements that make the falsification impossibly of valuable papers and special marks;
- the use of special marks and etiquettes with high quality and high grade of safety.

The securing elements proposed by the authors are constituted from composite materials, realized by the embedding of the glass-coated ferromagnetic microwires in a celullosic matrix. These can be used as anti-shoplifting or validating elements in order to identifying the counterfeit products. The magnetic marker must be realised as glass-coated microwires, flexible, prepared from soft magnetic materials, zero magnetostriction, very low coercivity and high permeabilities. The microwires have good mechanical strength, good flexibility and are corrosion resistant and so can be attached to various flexible and flat articles like clothes, footwear. The advantages of the MW securing were:

- the possibility of the identifying at distance;
- stable magnetic properties even at high temperatures and corrosive media;
- wide range of the functional temperatures;
- stability at shielding – the codes shielded by metallic panels can be read;
- stability at the mechanical action;
- small sizes and low consumption.

and for the microfibers with special properties, from the last generation (which offer the possibility to the magnetic encoding of the information):

- very large amount of the generated codes;
- the information can be read both from a stationary source, and from a source in motion;
- the encoding is impossible to destroy, both in the continuously and also in variable magnetic field, (reliable encoding);
- possibility to read the information from any code randomly oriented in space.

The main applications were related to the securing of the value papers, fiscal documents and special stamps, through the magnetic encoding. A magnetic field sensor, especially designed for the securing elements, can be used for electronic detection.

2. Experimental

The microwires (MW) are formed by a metallic core and a continuous insulated coating from glass. The MW are obtained by Ulitovsky–Taylor method [1,2]. In order to improve the MW quality, during the process of drawing, the MW is quenched by a liquid stream (water or oil). The MW length reach up to 1 km (laboratory conditions) and, by continuous drawing process, can be obtained length up to 10 km (industrial conditions). The diameter of metal core can be between 1- 50 μm, with thickness of glass coating between 1 - 20 μm, depending of the metallic materials which are used. Fig. 1 presents the structure and the thickness of a MW, analysed by optical microscopy.

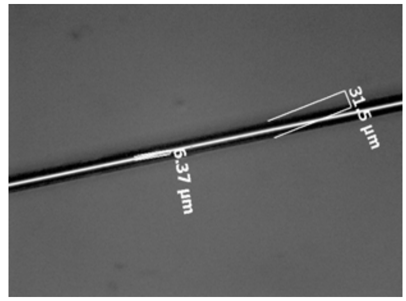


Fig. 1. Optical micrograph of the $Fe_{77}B_{13}Si_{10}$ MW. Can be observed the metallic core and the glass coating.

For the experimental work are used various types of MW, based on the ternary system Fe-B-Si, from which, taking into account the criterion of drawing behavior, was selected the $Fe_{77}B_{13}Si_{10}$ alloy. The MW ferromagnetic core are structural and magnetic characterized, by XRD, respectively by plotting of the hysteresis loops. The ferromagnetic glass-coated MW are embedded, under specific conditions, in a cellulosic fiber matrix. So, was achieved a new securing element for paper, which will be electronically detected and validated using a field sensor, specially designed for this aim.

3. Results and discussion

The ultrafast solidification process which takes place during the drawing of MW from melting leads to the appearance of a quasiamorphous structure, revealed XRD investigation. Fig. 2 presents the XRD spectra of the metallic core for a ferromagnetic $Fe_{77}B_{13}Si_{10}$ MW. The sample revealed a crystalline structure, structure which is very similar to those of α-Fe, but with a smaller elementary cell, with cell parameter a = 2.837 Å, in comparison with a = 2.866 Å, specific for α–Fe.

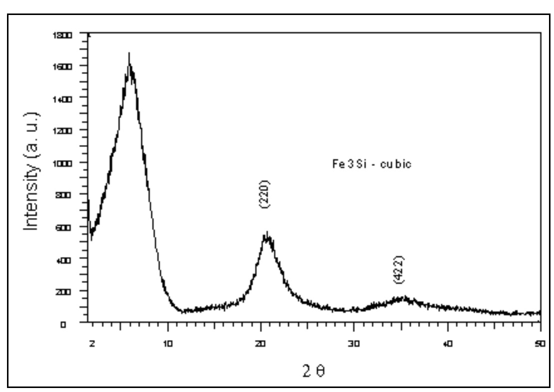


Fig. 2. XRD spectra of $Fe_{77}B_{13}Si_{10}$ MW.

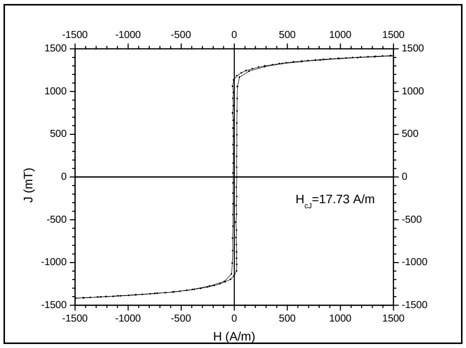


Fig. 3. Hysteresis loops of $Fe_{77}B_{13}Si_{10}$ MW.

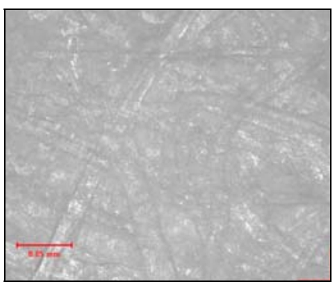
Together with this phase occurs also an amorphous phase, $Fe_{82}Si_5B_{13}$, which crystallize in the tetragonal system. The medium size of Fe_3Si crystallite, calculated by Debye-Scherrer formula, based on the XRD spectra form Fig. 2, is 5.4 nm.

The presence of a quasiamorphous structure of the metallic core of MW, visible in the XRD spectra (see Fig. 2) favors the existence of magnetic characteristics convenient to the applications, specific for soft magnetic materials: high magnetisation, small coercivity. For these samples, the coercivity is around 0.1 kA/m and the remanent magnetisation is 1.25 T (see Fig. 3).

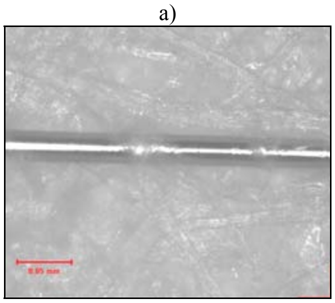
In order to obtain compatibility between the filler and cellulosic matrix, the both materials are characterised from the point of view of sizes, density, viscosity and resistance at corrosion. The cut MW, with 5-8 mm length, are mixed with different cellulosic fibers, sizes comparable with those of MW (see Table 1). The MW diameters are smaller than of cellulosic fibers (see the Fig. 4).

Table 1. Comparative sizes: wood fibers / ferromagnetic microwires.

Wood type / Medium sizes	Pine	Abies	Spruce	Poplar	Birch	Beech	$Fe_{77}B_{13}Si_{10}$ MW
Length, mm	3.5	3.2	3.05	1.15	1.15	1.13	5 - 8
Diameter, mm	0.05	0.047	0.035	0.030	0.025	0.022	0.007 – 0.023



a)



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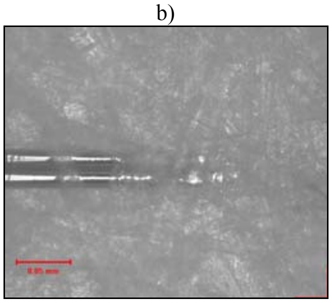

c)

Fig. 4. Optical micrograph of the cellulosic matrix a), and of the same matrix, with $Fe_{77}B_{13}Si_{10}$ MW filler, randomly b) and oriented aligned.

For establish the MW behaviour as suspension, was measured the densities of cellulosic fibers and ferromagnetic MW. The results show a great density difference: 3200 kg/m^3 for MW against 1300 kg/m^3 for cellulose.

Table 2. Viscosity measurements for sheet paper samples (mass:2.4 g material, a.u.) with increasing ferromagnetic MW additions.

Sample code	Specification	Brookfield viscosity LVT, cP, (23^{o}C)
1	Paper samples, without ferromagnetic MW addition	15 – 16
2	Paper samples, with 0.002 g ferromagnetic MW	15 - 16
3	Paper samples, with 0.003 g ferromagnetic MW	16 – 16.5
4	Paper samples, with 0.005 g ferromagnetic MW	17 - 18

For viscosity measurements were prepared paper samples with increasing MW quantities: 0.002 g, 0.003 g and 0.005 g. By increasing of the ferromagnetic MW addition, from 0.083% la 0.208%, the Brookfield viscosity of the paper pulp change only with 1 ... 2 cP (see Table 2)

For study the compatibility of the ferromagnetic MW with the component materials of the paper, was tested the corrosion resistance of the alloy at the contact with different usually auxiliary materials for the paper pulp. Were prepared a lot of solutions and suspensions, starting from the main components used in the papermaking process: cellulosic fibers, fillers, and retention, glue and bleach agents, with increasing ferromagnetic MW amounts. The durations of contact between the ferromagnetic MW and the technological blends were: 15, 30, 60 and 180 min. The obtained results of tests show that the ferromagnetic MW present a slight oxidation tendency, only in the case of the matrix with alkaline pH, at contact durations more than 30 min. In order to avoid this oxidation process, the paper pulp preparation take place immediately after the MW dosage and homogenization in the cellulose matrix.

After the experimental work performing, was concluded that can be obtained paper with ferromagnetic embedded MW, as filler. In the paper structure, these materials cannot realize forces type ion – dipole or dipole-dipole, specific to the van der Waals bonds. Also, due their chemical composition, the filler cannot form hydrogen bonds specific to the cellulosic matrix. In this case, the ferromagnetic MW don't participate to the structural reinforcing pf the cellulosic matrix, and their retention in the paper sheet is produced by filtration, adsorption and co-flocculation with different materials introduced in the paper composition.

The diameters of the prepared MW are comparable or smaller than the cellulosic fibers, provided from different wood sorts, hard- or softwoods. Their presence in the paper structure doesn't affect in a significant way the vicinity between the cellulosic fibers which constitute the reinforcing source for the paper structure. In the same way, the microfibers, with a small diameter, will not suffer significant damage of the glass-coating in the area of the paper machines, where involve pressing processes.

Taking into account that the paper is obtained from an aqueous suspension, the ferromagnetic MW will present the sedimentation tendency. From these reasons, to achieve a uniform distribution of the ferromagnetic MW in the paper sheet, the pulp should be under continuous stirring up to paper sheet forming.

By introducing of the MW in the pulp composition, their rheological properties don't significant changed. Therefore, the drying process of paper pulp during forming will not be affected. The amounts of additives in the paper pulp being so small, the pH of the paper pulp will be practically pH of the technological water. In this environment, the potential for oxidation of metallic microwires comes only from the water. Therefore, it is noted that the duration of contact between metallic microwires with paper pulp should be limited.

Table 3. Physical and mechanical characteristics of the paper sheets (mass: 2.4 g material) with various amounts of ferromagnetic MW.

Characteristics	Sample without MW	Samples with various amount of MW		
		0.002 g	0.003 g	0.005 g
Basis weight , g/sq.m	80.4	80.4	79.8	79.8
Thickness, mm	0.126	0.129	0.128	0.127
Apparent density, g/cm^3	0.64	0.62	0.62	0.63
Breaking load, N	68.5	68.9	68.3	68.6
Breaking length, m	5770	5794	5757	5758
Number of double foldings	101	97	93	104
Burst strength, kPa	242	252	261	236
Tear strength, mN	590	630	600	610
Gurley porosity, F/S, s	28/25	24/24	25/24	26/25
Ash content, %	9.26	9.06	9.32	9.18

The data obtained after the physical and mechanical characterisation of the paper sheets with embedded ferromagnetic (see Table 3) show that:

(i) with increasing ferromagnetic MW amount in paper sheets composition laboratory (from 0.002 to 0.005 g / sheet 2.4 g), does not change their thickness and density. Therefore, the microwires have not a substantial contribution to increasing the sheets density of paper with "extra" weight which is brought. Also the MW, having a thickness even smaller than cellulose fibers, does not contribute to the deformation of the cellulose matrix construction. This finding is supported by results obtained from determinations of porosity which oscillates very close to values determined for the paper sample without MW;

(ii) from the same reasons, (unaffecting of the cellulosic fibrous structure) have not found substantial differences in the case of resistance characteristics - breaking length, number of double curvature, tear or burst;

(iii) the data concerning the ash content cannot be correlated with the increase of the ferromagnetic MW amount, because in this case was involved the quality of the water used on the paper sheets forming (the water contributes by its own loading with mineral suspensions).

Therefore, the results show that additions of the ferromagnetic MW, used to the experiments, from 0.083 to 0.208%, have no significant influence on key physical and mechanical characteristics of laboratory paper sheets.

Fig. 5. Securing elements with ferromagnetic MW embedded in the cellulosic matrix.

Fig. 6. Detector of the ferromagnetic MW in the cellulosic matrix.

Due to the ferromagnetic character of the metallic core of the MW, these fillers can be detected in the cellulosic matrix of the new composite materials (see Fig. 5), which act as a securing element. Equipped with a specially designed coil, this device can detect the presence of the microwires in the paper (see Fig. 6), so this assembly can be used as field sensor in the processes of the electronic validation of the value papers, labels and tags, leading to the elimination of the counterfeits.

4. Conclusions

The development of the processing techniques of the metallic microwires offered the possibility to prepare new class of materials, namely glass-coated metallic microwires, with special applications in sensoristics, electromagnetic shielding, securing systems, resistive elements, etc.

Using the Ulitovsky-Taylor method for the preparation of $Fe_{77}B_{13}Si_{10}$ ferromagnetic glass-coated microwires can be achieved quasiamorphous structures, with characteristics specific for a soft magnetic material. The coercivity and the remanent magnetisation of the ferromagnetic microwires are 17 A/m, respectively 1.25 T.

The magnetic detection systems are devoted to identify the counterfeits in the field of value papers. The system accuracy depends on the use of small, sensitive composite magnetic devices. So, by the development of the composite materials, constituted by the embedding of ferromagnetic microwires in a cellulosic matrix, can be created new and performant securing elements, which make possible the validation with detection devices, special designed for this goal.

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