FUNCTIONAL MATERIALS PRODUCED ON AN INDUSTRIAL SCALE

The article presents a wide range of applications of functional materials and a scale of their current industrial production. These are the materials which have specific characteristics, thanks to which they became virtually indispensable in certain constructional solutions. Their basic characteristics, properties, methods of production and use as smart materials were described.

Keywords: functional materials, shape memory materials, magnetostrictive materials, rheological fluids, phosphors.

1. Introduction

Functional materials are a specific group of materials, since under the influence of the external field performance (among others, electric, and magnetic) they change their shape and/or physical properties. This change is based on the sensor-actuator principle, according to which the material, taking a certain stimulus, sends a signal to the actuator, causing a specific action. The group of functional materials includes:

- turning colour materials (photochromic, thermochromic, electrochromic),
- light-emitting materials (electroluminescent, fluorescent, photoluminescent, cathodoluminescent, thermoluminescent, radioluminescent),
- materials which change their shape and size (conductive polymers, dielectric elastomers, piezoelectrics, polymer gels, shape memory materials),
- temperature-changing materials (thermoelectric),
- density-changing fluids (magnetorheological, electrorheological),
- self-assembling materials,
- self-repairing materials.
2. Shape memory materials

The shape memory effect occurs in a large group of ceramic materials and metals, and the scope of their applications is systematically growing. The main characteristics of shape memory materials are diffusionlessness and the displacement nature of transformation. The diffusionlessness shows that during the transformation between the parent and martensitic phases, the migration of atoms does not occur. Additionally, the displacement nature of transformation allows only to the coordinated movement of atoms. This type of movement "is done by a homogeneous deformation of the crystal lattice and small movements within a primitive cell. At the same time, the shear with small rigid rotation occurs" [1].

An example of such a material is the alloy of nickel and titanium. It is strengthened in the initial temperature of the martensitic transformation. This material is sensitive to the process of phase transformations and the structure of the alloy [2]. The alloy of nickel and titanium is also resistant to oxidation at high temperatures (however, at 600–1000°C, layers of electrolytic chromium should be used, because the resistance decreases within these limits).

The shape memory effect is divided into three characteristic groups: the one-way shape memory effect, pseudo-flexibility and two-way shape memory effect.

In case of the one-way shape memory effect, in the initial phase, this effect can reach two states: the reverse martensitic transformation and reorientation of the martensitic phase. The first state begins with changing the structure into martensitic one under the influence of deformation of the material in the parent phase. Then it is heated in a characteristic temperature, which results in a return to the parent state. This approach results in a return to the original shape of a sample. In case of the reorientation, it starts with the sample hardening in the initial phase. This results in the creation of martensite, which is deformed (the transition to deformed martensite occurs), and afterwards heated, and then it initially returns to the martensite original phase, and then to the martensite parent phase, resulting in the recovery of the shape. In order to characterise this effect, the graph of stress-deformation-temperature (Fig. 1).

In case of the effect of pseudo-flexibility, we also deal with the reverse martensitic transformation. The transformation occurs only under the influence of the external stress. In order to obtain the deformation at the level of a few to a dozen or so percent, the elastic deformation takes place as a result of the creation of martensite at the temperature higher than the final temperature of austenitic transformation (Fig. 2). After removing the stress, a sample also returns to its original shape.
The last of effects, the two-way shape memory shape effect is characterised not only by the high-temperature transformation of the parent phase, but also the low-temperature transformation of the martensitic phase. These processes occur regularly, which results in a change of shape (the lack of participation of external stresses). In the cooling phase (martensitic phase), there is a macroscopic change in shape and volume of the sample. The reason for this is to create martensitic strips of different orientation. "The preferred orientation of the martensite nuclei affects the martensite variants that cause changes in the orientation of strips resulting in anisotropic, macroscopic and shape changes" [1]. It should be noted that after annealing the sample at the high temperature or during the reverse transformation into the parent phase, the removal of martensite nuclei occurs, which results in stoppage of cyclicity of the shape change.

Other examples of the materials which demonstrate the shape memory characteristics are high-temperature alloys and materials with the magnetic shape memory. The first of those (Ni-Ti, Fe-Ni, Cu-Zn, In-Ti, Au-Cd, Ag-Cd, Cu-Al) allow to increase the operating frequency and the rate of cooling the material, which gives them the possibility of numerous applications, e.g. in the automotive, and refining industry, or as devices to prevent from combustion.

In case of materials with the magnetic shape memory (Fe-Pd, Fe-Ni, Fe-Pr) the deformation reaches up to 8%. This effect occurs when the martensitic transformation has a thermoelastic nature, and the ferromagnetic martensite is characterised by the large magnetocrystalline anisotropy.
The shape memory materials are most commonly used in the medical, car and aviation industry (Fig. 3). These are mainly pipe fittings on spaceships, systems regulating the supply of fuel and air in carburettors, mechanical vibration damping pads, pressure valves, flight stabilisers to change the geometry of the aircraft wings (piezoelectric materials), shaft couplings as well as conditioning and cooling devices.

Fig. 3. The prototype of the helicopter flight stabiliser [http://science24.com/paper/23220]

The shape memory materials also used in the construction of machines and devices (simplifying and miniaturisation of products). This allows to significantly reduce the costs of production of individual machine elements. Actuators, temperature sensors and fire detectors, regulatory systems in water heaters, temperature safety valves, protection against the electrical equipment overheating, or fan screens are most commonly used. The permanent mechanical and electrical con-
functional materials produced on an industrial scale

connections as well as the noise and vibration damping units, or power elements in switches are created.

In the medical industry, the use of shape memory materials include medical equipment, predominantly made of titanium and its alloys. Currently, among the used elements, it is possible to distinguish: bone rods, arch wires in orthodontics, tissue spacers, staples for osteosynthesis, Harrington rods, surgical instruments and spacing sleeves. After the introduction of shape memory materials, the already existing solutions changed their capabilities, e.g. dialysis pumps (miniaturisation), artificial hearts or endoscopes (fitting to the anatomical features of patients).

In the remaining scope of industry, among others, mobile phone housing, spectacle frames, the equipment for compression of transformer cores, recorder nibs, vibration-damping devices in the construction industry, activation systems of solar panel covers or self-opening aerials are used.

3. Magnetostrictive materials

The magnetostrictive materials operating principle is based on the change of their linear dimensions under the influence of remagnetisation. The magnetic coupling of the spin and orbital momentum of electrons. In the materials with high magnetocrystalline anisotropy, this process results from the additional coupling of the orbital momentum of electrons with the crystal lattice of the material. The result is that deformation of the crystal lattice of the material constitutes the essence of magnetostriction. The deformation is caused by the shift of the torque vector (the shift of the spin momentum of electrons in accordance with the direction of the applied magnetic field). In the magnetostrictive materials, this process occurs with different intensity, e.g. in materials of the magnetostriction of approx. 50·10⁻⁶, it is applied in the construction of the deformation sensors (nickel, iron, cobalt, and their alloys). In case of the hybrid materials with the shape memory (Ni₂MnGa, Fe₇₀Pd₃₀), the deformation is even 50 times greater. However, such a combination can reduce the dynamic properties of the material.

Currently, the area of the researchers' interest involves the use of the rare-earth metals Tb and Dy (magnetostriction approx. 3600·10⁻⁶), which demonstrate surprising properties, such as the linear magnetostriction of approx. 0.2%, operating stress of 500÷600 MPa and the response time during the magnetisation of only 1·10⁻⁶s. However, it should be noted that they are not resistant to corrosion, they are very expensive in terms of the extraction and they generate heat (with frequent magnetic changes). In order to produce magnetostrictive materials,
a method of directional crystallisation (pouring the fluid alloy through a hole in the bottom of the previously heated mold, which was removed from the heating zone of the furnace), a typical method for the creation of nanocrystalline and amorphous strips and a method of powder metallurgy (sintering the mouldings that were obtained from powder oriented within the magnetic field of 30-50 nm under high pressure at the temperature of 1800 °C).

Magnetostrictive materials are used in different types of sensors, among others, vibration sensors, static force and pressure sensors, sensors intended for use under water (Fig. 5), or torque sensors. They are also used in aircraft constructions, surgical or acoustic instruments, and ultrasound generators. Their ability to dampen and generate vibrations.

Fig. 5. Magnetostrictive sensor intended for use under water at the pressure of less than 15 bar (Posichron PCST27) [http://automatykab2b.pl/katalog-produktow/produkt/3500-czujniki-magnetostrykcyjne-do-zastosowan-pod-woda-przy-cisnieniu-15-barow]

4. Rheological fluids

A characteristic feature of the rheological fluid is the ability to change their properties in a way that is reversible and constant under the influence of the applied magnetic or electrical field. Fluids are subject to the laws of fluid dynamics (prior to applying the field), and then during the interaction, fields behave like solids (Fig. 6). Their consistency includes the range from sticky oil to gel (almost solid form). The change of viscosity depends on the shear rate, temperature and the interfering field strength. Electrorheological fluids can be single-and two-phase, and the magnetorheological ones only two-phase. Single- and two-phase fluids significantly differ from each other in composition.
Fig. 6. Ferromagnetic material under the action of a magnetic field
[http://pl.wikipedia.org/wiki/Ferrofluid]

| Properties of electrorheological fluids [3] |
|------------------------------------------|
| **Properties** | **Parameter values** |
| Single-phase fluids | |
| Operation temperature | 10÷120 ºC |
| The response time for the presence of an electric field | 10÷80 ms |
| Dynamic viscosity in the absence of an electric field | 1÷100 Pa·s |
| Max. shear stress | 1,5÷5 kPa |
| Max. strength of the magnetic field | 4 kV/mm |
| Two-phase fluids | |
| Operation temperature | -30÷120 ºC |
| Dimensions of the molecules | 0,1÷100 μm |
| The content of the solid phase | φ₀ = 0,05÷0,5; φₔ = 0,2÷0,8 |
| The response time for the presence of an electric field | 2÷5 ms |
| Dynamic viscosity in the absence of an electric field | 0,1÷10 Pa·s |
| Density | 1000÷2000 kg/m³ |
| Max. shear stress | <2 kPa |
| Max. strength of the magnetic field | 6 kV/mm |

Single-phase or homogeneous fluids and the increase in their viscosity are explained by the change in the orientation of the polymer molecules (the disc shape) under the influence of the applied electric field. In case of two-phase flu-
ids, each phase (solid and liquid) is characterised by different characteristics (Tab. 1). In order to classify them, the coefficients determining the volume and mass share of solid molecules in the basic liquid are used. Both coefficients determine the viscosity, density, specific heat, thermal expansion, thermal volumetric expansion coefficients. In case of modifications of the viscosity, the field affecting solid molecules of the fluid, which are combined in chains resulting in the increase of resistance to the flow of the liquid phase.

Single-phase electrorheological fluids usually constitute polymeric liquid crystals and polymer blends, and two-phase ones – natural organic materials and produced (starch, cellulose, polyaniline, polypyrrole), and inorganic (metal oxides, glass, silica, zeolites). In order to increase the effectiveness of the impact of the electric field in the production process, the additions, which can provide up to 3% of their volume, are applied. It also limits the possibility of agglomeration and sedimentation.

However, the magnetorheological fluids constitute suspended solids (magnetic fluids) or colloids (ferrofluids) (Tab. 2). In the production of such materials in the liquid phase, in both cases, the engine oil or water is applied. In the solid phase, the molecules of cobalt, iron or their alloys (magnetics) or iron oxides (ferromagnetic materials). In this case, the additions, which prevent the agglomeration, sedimentation and corrosion, are also applied.

### Table 2

| Characteristics of magnetorheological fluids [2] |
|------------------------------------------------|
| **The type of the magnetorheological fluid** | **Ferromagnetic** | **Magnetic** |
| Solid phase | Fe₃O₄ | iron, cobalt |
| Liquid phase | water, glycerin, oil | water, oil |
| The diameter of the molecules | 3±15 nm | 0,5÷10 μm |
| Saturation magnetisation | to 0,15 T | to 1,3 T |
| Density | 850±1600 kg/m³ | 1500±3500 kg/m³ |
| Shear stress | 1÷5 kPa | 10÷100 kPa |
| Operation temperature | -20÷150 ºC | -20÷150 ºC |
| The content of the solid molecules | φ₀ = 0,1±0,3; φₚ = 0,3±0,5 | φ₀ = 0,2±0,4; φₚ = 0,6±0,85 |
| Magnetic field strength | 100÷250 kA/m | 100÷250 kA/m |
| Response time | 5 ms | 10 ms |
| Resistance to contamination | small | large |
In order to characterise rheological fluids, the identification of their viscosity, viscoelasticity and viscoplasticity is used. Viscous and viscoplastic fluids are used in clutches, brakes, shock absorbers and rotary dampers. In case of viscoelastic fluids, the application includes dampers for damping vibrations of the low amplitude and high frequency. Other applications include, among others, systems of the suspension bridges protection against a gust of wind, energy absorbers and dissipators, aircraft landing systems, automatic press machines, throttle valves, systems of the high building protection against earthquakes or medical and sport equipment.

5. Luminophores

Luminescent materials emit light, which is defined as the excess of radiation over the thermal radiation (longer than $10^{-10}$s). This process takes place only when the substances are appropriately prepared and chosen. In order to create luminescent materials, three components are used: a basic substance, flux and actuator. The basic substance most often consists of crystalline salts, which are mixed in the appropriate weight ratio, and then sintered at the temperature of 1000÷1500 K. The flux and actuator, after entering to the luminescent centre, affect the colour of the emitted light (during the absorption of energy quanta).

Luminescent materials can be divided according to the type of luminescence [4, 5]:
1) photoluminescence – induced by visible or ultraiolet radiation,
2) electroluminescence – induced by the potential difference,
3) luminescence induced by fast molecules – depending on the type of molecules, it is possible to distinguish cathodoluminescence, radioluminescence and X-ray luminescence,
4) luminescence thermally or optically induced,
5) chemiluminescence and bioluminescence – induced by a chemical reaction in the inorganic matter and living organisms,
6) triboluminescence – mechanically induced,
7) sonoluminescence – induced by ultrasounds.

On the industrial scale, the photo- and electroluminescent materials are most commonly produced. In case of photoluminescent materials, the fluoro- and phosphorescence occur. The fluorescence is when the emission occurs at one or more spontaneous passes and after cessation of the absorption of energy quanta. In this form, the illumination takes place only for fractions of a second. However, this phenomenon was used, among others, in fluorescence microscopes, oscillo-
scope and X-ray screens, scintillation counters, electronic calculating machines and fluorescent lamps.

The phosphorescence occurs when the system passes through a transient state, then it returns to an excited state, drawing energy from the surrounding medium. The length of light emission is much longer here – from several minutes to weeks. It depends on the temperature and type of the substance and the technology of its generating and sintering. These substances are used, among others, in measuring instruments, clock faces or on the surface of road signs.

The electroluminescence is a process that occurs "as a result of relaxation of a physical system from the state with greater energy to the state with less energy" [6]. The radiation is present in the form of a characteristic line spectrum using the difference in energy that is specifically determined. In order to induce the system, the direct flow of the electric current is used. The most commonly used objects using the effect of electroluminescence are diodes, which are mounted in traffic lights, street lamps, highlighting bridges and buildings, domestic lights, LED screens and in many devices used in the medical and automotive industries. Belonging to energy classes of different light sources is presented in Fig. 7.

Fig. 7. Belonging to energy classes of different light sources
[http://www.elektroonline.pl/a/4603,Efektywnosc-energetyczna-w-elektronice-uzytkowej]
6. Other applications

In addition to the previously listed materials, ceramic materials are used in the industry. This option involves the elimination of the need of using the control and executive systems. Due to the influence of external stimulation, a spontaneous reaction of a complex size in the desired narrow range takes place. The use of smart ceramic materials includes the lighting industry (diodes, photovoltaic cells), cooling (thermoelectric cooler) or non-conventional energy sources (thermoelectric power generator, high-temperature fuel cell). These materials are also used in the MEMS microelectromechanical systems, in which the mechanical and electronic components are integrated on a common ground (Fig. 8).

![MEMS measuring sensor](http://sbanalyzer.pl/dobor-czujnikow-pomiarowych/)

Polymers constitute another group of functional materials. In this case, the functional characteristics are based on the confirmation to the characteristics of LED diodes (polymer diodes and displays). The scope of this material application includes sensors and actuators, and it consists of, among others, underwater acoustic relays, seismic monitors, artificial muscles and organs, microphones, pumps, high pressure injectors, smart skin as well as devices for monitoring blood flow and medical imaging.

In case of composite materials, carbon nanotubes predominantly constitute an additional component. Thanks to their use, materials are strengthened, and their properties are repeatedly increased. The special properties of smart composite materials strengthened with carbon nanotubes include:
1) increased electrical conductivity,
2) fire resistance and reduction of the risk of explosion in flammable environment,
3) prevention of the load deflection,
4) prevention of the magnetic radiation interference,
5) high ductility,
6) high thermal conductivity,
7) high thermal stability.

7. Conclusion

Each of the mentioned groups of functional materials has a wide range of applications. Thanks to them, progress in the development of technology took place. We encounter them at every step, and it should be noted that the research on them is still conducted.

Along with the developing technology and computational capabilities, numerous applications of these specific materials will be most probably discovered. There are grounds for hoping that scientists and producers will not approach these research in a sceptical way, as it was made in the past, sometimes restraining the development and questioning the importance of functional materials.

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