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PRODUCTION AND PROPERTIES OF COMPOSITE MATERIAL COMPRISING Gd MULTISCALE PARTICLES

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Abstract
The article presents a novel method of producing Gd particles and preserving them from oxidation. The particles were produced in liquid paraffin by means of AC electric discharge and stored in the solidified paraffin. After seven months, the surface of the Gd was found to be exempt of oxidation. Moreover a composite material formed from mixing paraffin with Gd particles was conductive and magnetic and also presented photovoltaic effect. This method is a promising means of producing, at an industrial scale, particles from materials extremely sensitive to environment such as rare earth materials. Also the new material consisted of Gd particles in a paraffin matrix can find applications in many branches of industry.

Keywords
gadolinium, producing Gd particles, multiscale particles, paraffin, AC electric discharge.

Introduction

Gadolinium is a silvery-white ductile rare-earth ferromagnetic metal with a Curie temperature at 292.5 [K] [1, 2]. This metal also demonstrates a magneto-caloric effect [3]. Like other lanthanides, Gd is a strong reducing agent and oxidizes very easy and even removes hydrogen from water to create gadolinium hydroxide. Two isotopes of gadolinium have the highest neutron cross-section among any stable nuclides: 61,000 barns for ^{155}Gd and 259,000 barns for ^{157}Gd [4]. Because of the properties, gadolinium is used in many technical applications ranging from catalysts, phosphors ceramics, contrast agents in magnetic resonance imaging [5], room temperature refrigeration, radioactive shielding and control rods in the nuclear industry as well as target tumors in neutron therapy by taking advantage of its high thermal neutron absorption cross section So far studies on particles rich in rare earth metals are relatively scarce because the reactivity of these elements with oxygen has so far prevented the fabrication of small sized particles.

This paper presents a novel method of preparing metallic Gd particles and preserving them from oxidation. The main idea was to find a medium, which could be for the production of Gd particles and which could protect these produced particles against reaction with oxygen for a long period of time. This article presents the production of Gd particles by applying an AC electric arc between two electrodes: one made of high purity Gd and second one – high purity carbon, which are immerged in paraffin heated at 90 [°C], i.e., in the liquid state. After solidification, the paraffin insulates the Gd particles from air and hinders the oxidation. The efficiency of the insulation has been verified by analyzing the composition of the Gd particles after seven months.

The new composite material of Gd particles immersed in a paraffin matrix was tested for electrical conductivity and photosensitivity with different ratio of Gd particles to paraffin.

Characterization of materials

Gd and C high purity 99.99 [%] were used as electrodes and paraffin called normal paraffin [6] defined as saturated hydrocarbons with molecules containing carbon atoms linked in a straight chains in the range C18 to C40 with melting point 60 [°C].

Microscopic examination was carried by scanning electron microscope Inspect F50. The electrical resistance and photovoltaic effect of the composite material of Gd particles in the paraffin matrix were measured by means of a multi-meter with an accuracy of a resistance of 0.1 [Ω] and a voltage – 10^{-4} [V].

Experimental, results and discussion

Gd particles were produced by means of an electric arc using as medium solution liquid paraffin heated at 90 [°C] in a glass vessel. The method used an AC electric arc of low power created between vibrating rod-type electrodes immerged in liquid solution. Electrodes touched each other periodically and, in a receding phase, created electric arc which melted the electrodes' materials and sputtered them into the liquid. This method requires an applied power of about 5 to 50 [W] [7], which is much less power applied than in standard DC arc-discharge methods using a power ranging from 0.8 to 3 [kW] [8, 9]. This method enabled the production of particles from conductive materials in wide range of temperatures of liquids. Also in contrast to methods like laser ablation method [10], it did not require liquid medium with optical transparency. Moreover the solvent can be either an electrolyte or insulating liquid.

In these experiments the device for the production of these multiscale (mixture of nano- and micro-) particles consisted of two electrodes: Gd and C, immersed in a glass vessel with 100 [cm^3] liquid paraffin supplied by AC current of 5 [A] and a voltage of 1 [V]. The carbon electrode was fixed and the gadolinium electrode was movable in the vertical plane. A contact between these electrodes was established periodically by vibration of the Gd electrode with a frequency of 2 [Hz] creating an electric. The advantages of this method consist in applying a low electric power, the possibility of using a variety of liquid media and electrodes, of operating in a wide range of temperatures, and the fact that the liquid medium do not need to be transparent. Next particles from surface of the suspension were collected by a permanent magnet with a magnetization near 345 [mT]. Though the Curie temperature of bulk gadolinium is 16 [°C], the Gd particles were found to be magnetic even at 90 [°C] and they could thus be collected by the magnet. The mixture of paraffin and Gd particles became solid after cooling to room temperature. The so-produced composite material with dimensions of 15×15×5 [mm] was also magnetic at room temperature and displayed electrical conductivity, which value of the resistivity varying with the concentration of Gd particles in the paraffin. For a high volume fraction of Gd, the resistivity was similar to that of semi-conductor, but below a certain ratio of Gd particles volume to paraffin volume the composite material behaved as an insulator. Furthermore, the composite with resistivity in a range of semiconductor resistivity presented photo-galvanic (Fig. 1) effect under visible light radiation and generated voltage of millivolts was observed to be dependent upon the material resistivity.

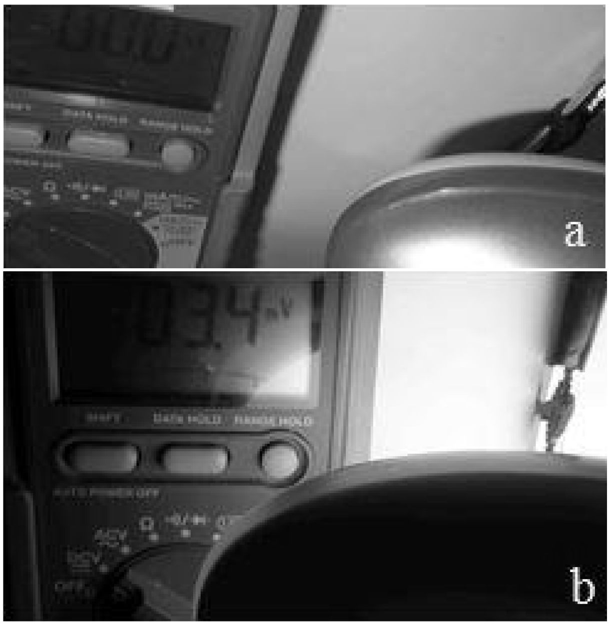


Fig. 1. Gd-paraffin sample: a) Gd-paraffin sample in an open circuit configuration held by steel electrodes; a fluorescent lamp switched of – voltage: 0 [V]; b) Gd-paraffin sample illuminated by the fluorescent lamp – voltage: 3.4 [mV].

As it is visible in Fig. 1 the photovoltaic effect was measured by the multi-meter in a configuration "open circuit". Holders of Gd – paraffin element were made of steel and copper. For an induction of the photovoltaic effect a fluorescent lamp with power 27 [W] was used. Depend on a concentration of Gd particles in the paraffin matrix and a kind of electrodes the composite material presented different voltage values which never excided 5 [mV]. Also it was observed that when the composite material was irradiated perpendicular to its surface the voltage was lower than in parallel case, it means, when the junction: metal holder – composite material was irradiated directly the induced voltage was bigger. It suggests the key role of the junction in the photovoltaic effect. An explanation of the phenomenon could be a creation of Schottky barrier in a composite material – metallic electrode junction where the Gd – paraffin mixture plays role of semiconductor. In a system: metal – semiconductor, a characteristic of the junction dependent on work functions of components. If the work function of a semiconductor is smaller than that of a conductor, this forms a diode junction. In an opposite situation, only a linear (ohmic) junction is created which does not present rectifying properties. This kind of the photoelectric phenomenon, based on the semiconductor – metal junction, has a long history dating back to the nineteenth century [11]. The result suggests that Gd particles – paraffin mixture, in a relevant ratio, could behave like semiconductor. The semiconductor behavior suggests an existence of a band gap which eliminates hypothesis that Gd particles in the paraffin matrix touch each other directly. Assuming that Gd particles contact among each other through thin film of paraffin, enough thin, according to Poole-Frenkel effect [12], to allow electrons to diffuse from one Gd particle to another, when they obtain enough energy (Fig. 2).

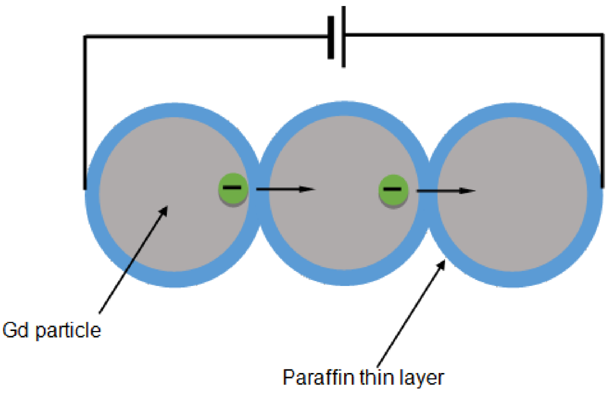


Fig. 2. Scheme of electron conduction Gd – paraffin composite material. Particles of gadolinium are close to each other and covered by thin film of paraffin which allows diffusion of electron from one Gd particle to another.

In the classical semiconductor existence of donors or acceptor of electron are necessary to obtain photoelectric effect. In the novel material Gd particles could be play role of donors or acceptors or both. It is obvious that metal nanoparticles exhibit different optical, magnetic and electrical properties from bulk materials [13–15]. Existence of surface plasmon effect [16] could explain the appearance of donors and acceptors in the Gd – paraffin semiconductor. Under influence of light surface electrons collects on one side of the particle. Depends on a light phase a maximum of electron density moves around the particle. Different length of light causes the surface plasmon resonance for different size of particles [17].

The hypothesis explaining the origin of donors and acceptors in the Gd-paraffin material assumes when surface plasmons are in-phase on neighbouring particles they create some kind of capacitor (Fig. 3).

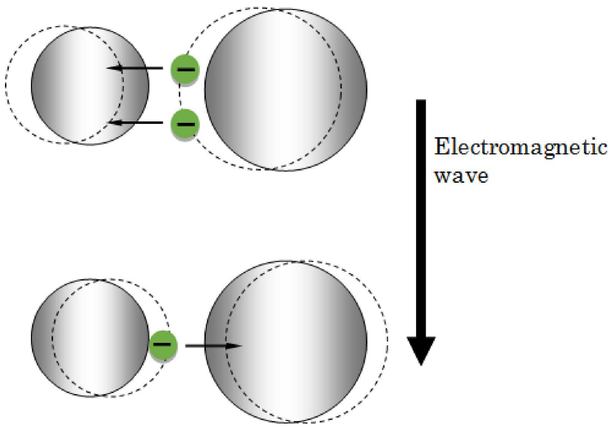
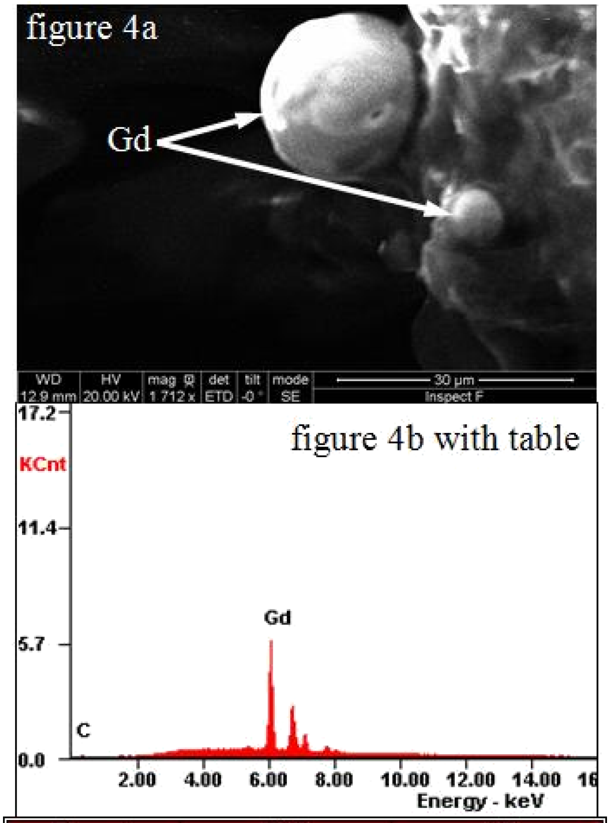


Fig. 3. Donors and acceptors creation hypothesis.

Diameters of neighbouring particles are different but densities of charge on both particles are equal constant for both direction of electric field. Consequently absolute electric charge on neighbouring surfaces are different. From both surfaces can diffuse this same percentage of electrons for both directions of electric field creating exceed or lack of electrons on these surfaces. After some time electric field between neighbouring particles stops further movement of electric charge from one particle to next one and some Gd particles could be treated as donors and others as acceptors of electron. The hypothesis could be confirmed or disproved by future research of surface plasmons of Gd nanoparticles.

Next step of the experiment was a test of a stability of the composite material. To avoid any contamination from reactive gas such as oxygen, the Gd/paraffin composite received a special preparation. In order to insulate efficiently the particles in the composite, the surface of the composite material was covered by a small quantity of toluene in a glass vessel. Toluene was used to dissolve paraffin on the surface of the composite, which sealed entirely the surface of the composite material. Then the composite material was stored on an office wall shelf. After seven months, the paraffin was molten again at 90 [°C] and the Gd particles were collected by the permanent magnet in order to analyze them by SEM as described before.

The SEM micrograph in Fig. 4a shows two Gd micrometersized particles embedded in the paraffin. The EDX spectrum given in Fig. 4b does not revealed any peak corresponding to oxygen, which should be found near 0.6 [keV] if oxygen were present at the surface of the particles. The values of the analyzed compositions have been reported in table in Fig. 4b below the EDX graph. Also electrical, magnetic and photoelectric properties did not change during the seven month period. These results indicated that the composition of the Gd particles embedded in paraffin is stable during a long period of time and does not lose its properties.



Element	Wt%	At%
CK	00.99	11.53
GdL	99.01	88.47
Matrix	Correction	ZAF

Fig. 4. The results of the experiment: Fig. 4a – SEM image of Gd microparticles in paraffin after seven months after creation; Fig. 4b – EDX analysis performed for the gadolinium particle with a table of compositional analysis of Gd. The spectrum shows mainly gadolinium with a small doping of carbon without any trace of oxygen peak, which should be located between carbon and gadolinium peaks, at energy of 0.5 [eV]. All 4 peaks on right side of gadolinium peak belong also to Gd.

Conclusions

This AC electric arc technique of Gd particles production using paraffin as medium seems to be promising for further industrial applications of Gd in the form of particles seems it can hinder oxidation. Magnetic, electrical and photovoltaic properties of the composite material and its high stability could be used in many branches of industry. Gadolinium has the highest neutron cross-section, paraffin is an effective neutron moderator [18–21] so the new composite material: paraffin – Gd multiscale particles should have unique properties, which could be used in new applications of nuclear technique, new types of reactor construction, in nuclear medicine or in a new nuclear weapon creation.

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