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COMPOSITE MATERIALS CONSISTING
OF FERROMAGNETIC NANOPARTICLES IN INORGANIC MATRIX

Nanoparticles exhibit unique physical properties due to surface or quantum-size effects. Particular attention has been focused on magnetic nanoparticles and substantial progress has been done in this field. This is mainly due to the advances in the processing methods and development of characterization techniques. Substantial achievements in that field enabled fabrication of composite systems consisting of metallic particles embedded in various organic or inorganic matrices. Ferromagnetic composites, consisting of Co, Ni and Fe_3C nanocrystallites stabilised in an inorganic matrix, were prepared by the procedure including formation of appropriate metal acrylamide complex, followed by frontal polymerization and pyrolysis of the polymer at various temperatures. The pyrolysis products were in a form of coarse powder particles having irregular shape and size. These particles contained randomly distributed nanocrystallites having various composition and size from few to tens of nanometres, depending on the starting monomer and pyrolysis temperature. Application of this procedure stabilizes the nanostructure and enables processing of spherical nanoparticles within a narrow window of sizes. The ferromagnetic properties of the systems were confirmed by magnetic measurements. The magnetic parameters depend on the chemical composition and pyrolysis temperature.

Keywords: magnetic nanocomposites, ferromagnetic nanoparticles

MATERIAŁY KOMPOZYTOWE ZAWIERAJĄCE NANOCZĄSTKI FERROMAGNETYCZNE
W OSNOWIE NIEORGANICZNEJ

Nanocząstki wykazują unikalne własności fizyczne ze względu na ich dużą powierzchnię właściwą oraz efekty związane z rozmiarami nanometrycznymi. Szczególną uwagę skupiają nanocząstki magnetyczne i na tym polu osiągnięto znaczący postęp. Dzieje się tak z uwagi na rozwój metod wytwarzania materiałów oraz technik ich charakteryzacji. Istotne osiągnięcia na tym polu pozwalają na otrzymywanie układów kompozytowych, zawierających cząstki metali osadzonych w różnych, organicznych lub nieorganicznych, osnowach. Kompozyty ferromagnetyczne zawierające Co, Ni i Fe_3C, stabilizowane w osnowie nieorganicznej, były wytworzone w procesie obejmującym syntezę kompleksów akryloamidowych odpowiednich metali, następującą po niej polimeryzację frontalną oraz pirolizę polimerów w kilku temperaturach. Produkty pirolizy otrzymano w postaci ziaren proszku o nieregularnym kształcie i wielkości. Cząstki te zawierały przypadkowo zdyspergowane nanokrystality, różniące się składem oraz rozmiarami (od kilku do kilkudziesięciu nanometrów), zależnymi od składu wyjściowego monomeru oraz temperatury pirolizy. Zastosowanie tej metody zapewnia stabilizację nanostruktury i pozwala na wytwarzanie sferycznych nanocząstek o wąskim zakresie rozmiarów. Własności ferromagnetyczne kompozytów potwierdzono za pomocą pomiarów magnetycznych. Własności te zależą od składu chemicznego i temperatury pirolizy.

Słowa kluczowe: nanokompozyty magnetyczne, nanocząstki ferromagnetyczne

INTRODUCTION

Processing of composites containing nanodispersed particles focuses continuously substantial scientific and technological interest. Individual nanoparticles exhibit unique physical properties resulting from size effects and highly developed surface. Such materials can exhibit either superparamagnetic or ferromagnetic properties. The former can find medical applications, in targeted drug delivery therapy and as contrast in NMR body screening, whereas the latter is aimed at high den-sity magnetic recording systems. A significant problem arising in the preparation and application of the nanoparticles is their stabilization. Among the methods ensuring stabilization and conservation of the physicochemical properties is synthesis in a polymer matrix. Frontal polymerisation, which enables conversion of monomer to polymer in localized reaction zone, was first mentioned in 1970s [1, 2]. Currently application of frontal polymerisation and study of its kinetics and

dynamics is widely exploited [3-6]. Among the advantages of frontal polymerisation one can mention: high reaction rate, short reaction time, low energy consumption and the possibility of conducting polymerisation in ecologically friendly way, without addition of solvent. The frontal regime is formed and stabilized by the chemical heat release and its transfer by heat conductivity.

In the current study the nanocomposites containing Co, Ni and Fe_3C nanoparticles were prepared by frontal polymerisation of acrylamide (AAm) monomer and subsequent pyrolysis of the polymer. Structure and magnetic properties of the nanocomposites were evaluated and discussed. For the nanocomposite material is formed in the course of pyrolysis, the first two stages, monomer formation and frontal polymerisation, are not discussed in this paper.

EXPERIMENTAL

The acrylamide metal complexes (MeAAm) (Me = = Co, Ni, Fe) were obtained by substitution reaction of inorganic hydrate by acrylamide. Frontal polymerization was carried out at atmospheric pressure in self-generated atmosphere. The nanocomposites were formed by further pyrolysis at a temperature range 643÷1073 K. Structure of the material, after all stages of preparation, was studied by X-ray diffraction (Philips X-pert, Cu-K$_\alpha$). Microstructure was analysed using High Resolution Electron Microscope JEOL JEM 3010. The hysteresis loops were recorded at a temperature 300 K, in external magnetic field ±1.1 T.

RESULTS AND DISCUSSION

Structure and microstructure

All the pyrolysis products were in a form of coarse, irregular powder particles exhibiting broad size distribution, ranging from 50 to 500 μm and having high porosity with pores size within a range 5÷50 μm (Fig. 1). The magnetic nanocrystallites were distributed within the volume of the powder particles.
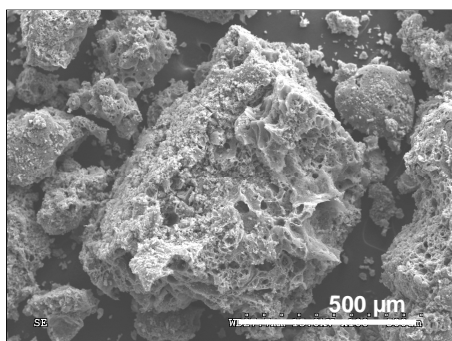

Fig. 1. SEM microstructures of powder particles obtained by pyrolysis of frontally polymerised monomer

Rys. 1. Mikrostruktury SEM proszków otrzymanych przez pirolizę polimerów wytworzonych w procesie frontalnej polimeryzacji

Co containing polymer after pyrolysis

After pyrolysis the distinct crystalline reflections, which appeared in the pattern, matched well the characteristic lines of metallic cobalt (Fig. 2). The broad spectra suggested nanocrystalline structure. In fact the crystallites were very fine and their size depended on the pyrolysis temperature. The Scherrer assessment gave the mean crystallite size 7 and 20 nm, for the samples thermolysed at temperatures 873 and 1073 K, respectively. The higher pyrolysis temperature resulted also in the formation of a (CoC_x) layer on the surface of the crystallites.
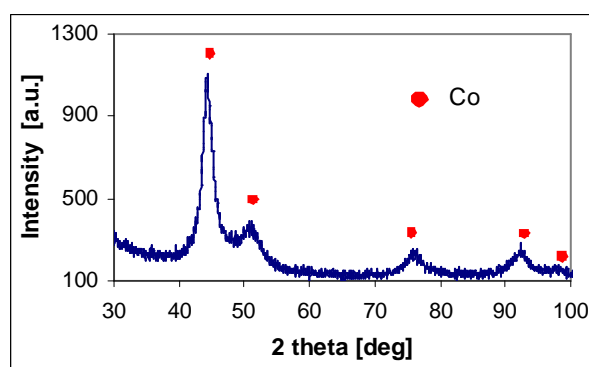

Fig. 2. X-ray patterns of the pyrolysed polymer containing Co. Pyrolysis temperature 873 K

Rys. 2. Dyfrakcja rentgenowska pirolizowanego polimeru zawierającego Co. Temperatura pirolizy 873 K

The TEM images (Fig. 3) proved that the crystallites obtained at the pyrolysis temperature 873 K had uniform, close to 7 nm, size which well corresponds to the value obtained from the X-ray pattern. Increase of the pyrolysis temperature resulted in coarsening of the microstructure and agglomeration of the nanoparticles.
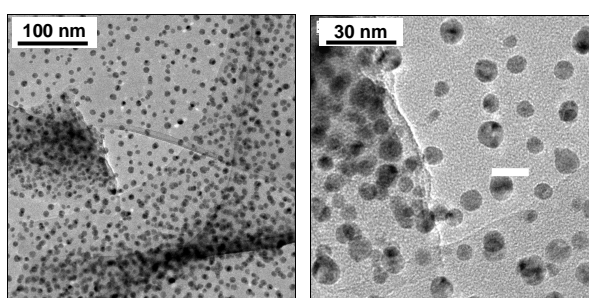

Fig. 3. TEM microstructures of nanocomposites containing Co nanocrystallites. Pyrolysis temperature 873 K

Rys. 3. Mikrostruktury TEM nanokompozytów zawierających Co. Temperatura pirolizy 873 K

Fe containing polymer after pyrolysis

The X-ray phase analysis revealed that the pyrolysed material contained nanocrystallites of iron carbide (Fe_3C) (Fig. 4). This was also confirmed by Mössbauer spectroscopy [7], and TEM observations (Fig. 5). The particles for the pyrolysed iron containing polymer were coarser than for the Co containing polymer.

The stoichiometry of the nanocrystallites was found to match iron carbide (Fe_3C).
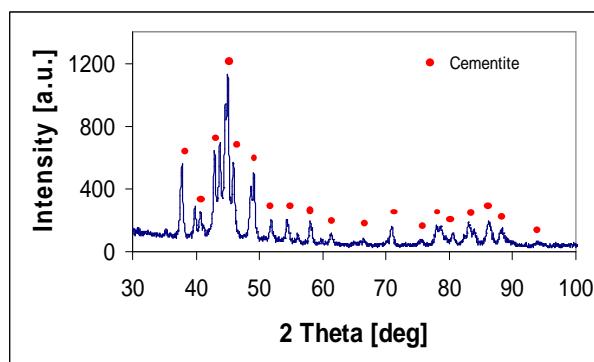

Fig. 4. X-ray pattern of the pyrolysed material containing iron carbide. Pyrolysis temperature 873 K

Rys. 4. Dyfrakcja rentgenowska pirolizowanego materiału zawierającego węglik żelaza. Temperatura pirolizy 873 K

The iron carbide crystallites, obtained by the pyrolysis of iron containing polymer, were partly agglomerated and had broad range of sizes, from 10 up to 80 nm. Closer look at their surface shows few nanometres thick amorphous surface layer. The EDS analysis of the amorphous matrix revealed the presence of carbon, nitrogen and oxygen atoms in it.
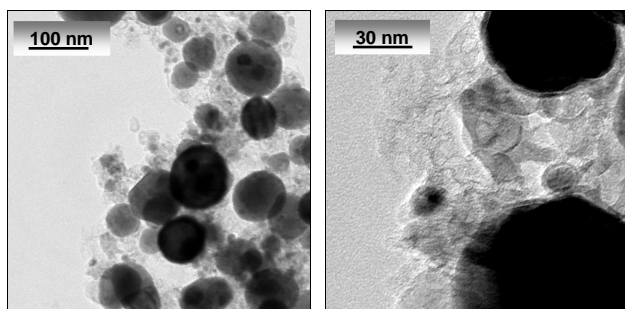

Fig. 5. TEM microstructures of nanocomposites containing iron carbide nanocrystallites. Pyrolysis temperature 873 K

Rys. 5. Mikrostruktury TEM nanokompozytów zawierających węglik żelaza. Temperatura pirolizy 873 K

Ni containing polymer after pyrolysis

X-ray phase analysis performed for this material showed the presence of nanocrystallites of pure Ni (Fig. 6). Measurement of the lattice parameters do not detect any carbon dissolved. The TEM observations fully confirmed the diffraction results. For the polymer pyrolysed at 643 K Ni nanocrystallites, having pretty uniform size in the range 9÷15 nm, were found (Fig. 7).

One can nottice that for nickel and cobalt containing polymers, nanocrystallites of pure metals were obtained, whereas for iron containing polymer iron carbide was produced. This was attributed to the thermodynamics of the process, where the free energy for the carbide formation is much lower for iron than that for cobalt and nickel.
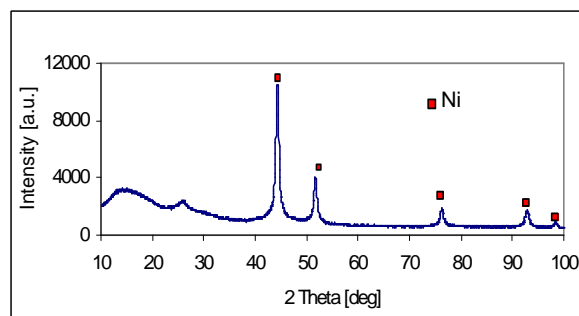

Fig. 6. X-ray pattern of the pyrolysed material containing nickel. Pyrolysis temperature 643 K

Rys. 6. Dyfrakcja rentgenowska pirolizowanego materiału zawierającego nikiel. Temperatura pirolizy 643 K
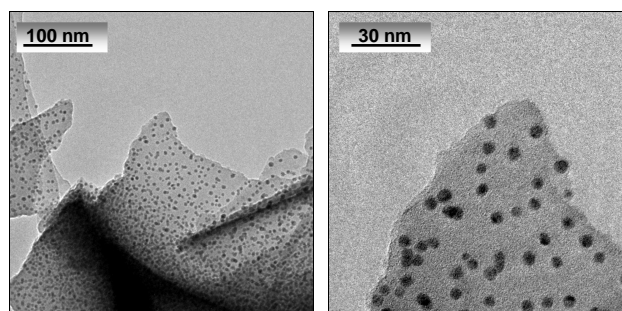

Fig. 7. TEM microstructures of nanocomposites containing nickel nanocrystallites. Pyrolysis temperature 643 K

Rys. 7. Mikrostruktury TEM nanokompozytów zawierających Ni. Temperatura pirolizy 643 K

Magnetic properties

Room temperature hysteresis loops for the three nanocomposites studied are shown in Figure 8. The loops are closed and symmetrical versus origin of the coordinate system. Shape of the loops evidences ferromagnetic character of the material. No evidence of superparamagnetism was seen.
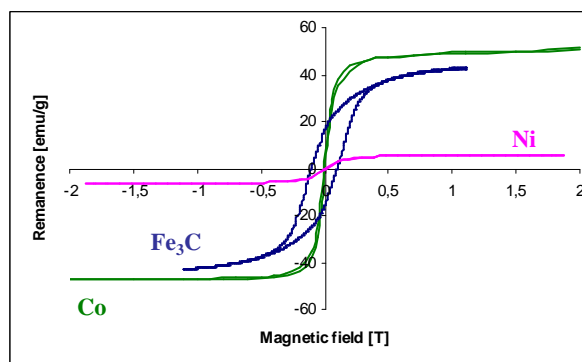

Fig. 8. Room temperature hysteresis loops for the nanocomposites containing Co, Ni and Fe_3C

Rys. 8. Pętle histerezy w temperaturze pokojowej dla kompozytów zawierających Co, Ni i Fe_3C

The magnetic properties of these materials differ substantially, which is due to their different chemical composition and volume fraction of the magnetic phase

in the carbon matrix. The saturation magnetization of the nanocomposites containing cobalt, iron carbide and nickel is 50, 40 and 6 emu/g, respectively. The coercivity depends purely on the chemical composition of the nanocrystallites. Lower H_c present pure metals (Co – $H_c = 0.006$ T, Ni – $H_c = 0.0095$ T) whereas substantially higher coercivity is represented by the intermetallic compound Fe_3C ($H_c = 0.06$ T).

CONCLUSIONS

Cobalt, nickel and Fe_3C nanoparticles were prepared by frontal polymerisation and pyrolysis of acrylamide metal nitrate complexes. The material composition and particle size depend on both the starting acrylamide type and pyrolysis temperature. Application of this procedure stabilizes the nanostructure and enables processing of spherical nanoparticles within a narrow window of sizes. The nanocomposites exhibit ferromagnetic properties.

The particles produced exhibit ferromagnetic properties. Their magnetic properties depend on the chemical composition and pyrolysis temperature.

REFERENCES

[1] Maksimov E.I., Dokl. Akad. Nauk SSSR 1970, 191, 1091.
[2] Chechilo N.M., Khvilitskij R.Ya, Enikolopyan N.S., Dokl. Akad. Nauk SSSR 1972, 204, 1180.
[3] Pojman J.A., Willis J., Fortenberry D. et al., J. Polym. Sci., Part A: Polym. Chem. 1995, 33, 643.
[4] Ivanov V.V., Stegno E.V., Melnikov V.P., Pushacheva L.M., J. Polym. Sci., Part A: Polym. Chem. 2002, 40, 1017.
[5] Goldfeder P.M., Volpert V.A., Math. Probl. Eng. 1999, 5, 139.
[6] Goldfeder M., Volpert V.A., Ilyashenko V.M. et. al., J. Phys. Chem. 1997, B 101, 3474.
[7] Sówka E., Leonowicz M., Pomogailo A.D., Dzhardimalieva G.I., Kaźmierczak J., Ślawska-Waniewska A., Kopcewicz M., J. Magn. Magn. Mater (in print).