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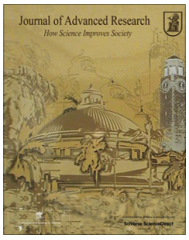

ORIGINAL ARTICLE

Effect of P_2O_5 and MnO_2 on crystallization of magnetic glass ceramics

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ABSTRACT

This work pointed out the effect of adding P_2O_5 and/or MnO_2 on the crystallization behavior of magnetic glass ceramic in the system Fe_2O_3·ZnO·CaO·SiO_2·B_2O_3. The differential thermal analysis of the quenched samples revealed decrease in the thermal effects by adding P_2O_5 and/or MnO_2 to the base sample. The X-ray diffraction patterns show the development of nanometric magnetite crystals in a glassy matrix. Heat treatment at 800 °C for 2 h, under reducing atmosphere, caused an increase in the amount of the crystallized magnetite with the appearance of minor hematite and Ca_2SiO_4. The transmission electron microscope revealed a crystallite size in the range 10–30 nm. Magnetic hysteresis cycles were analyzed with a maximum applied field of 25 kOe at room temperature. The prepared magnetic glass ceramics are expected to be useful for localized treatment of cancer.

Introduction

Hyperthermia destroys cancer cells by raising the tumor temperature to a "high fever" range, similar to the way that the body naturally uses to combat other forms of disease [1]. Generally, tumors are more easily heated than the surrounding normal tissues, since blood vessels and nervous systems are poorly developed in the tumor, and cancer cells are easily killed by heat treatment, since oxygen supply via the blood vessels is not sufficient in the tumor. Hence hyperthermia is expected to be a most useful treatment for cancer with no side effects [2]. On the contrary, these temperatures are safe for surrounding healthy tissues with normal and efficient blood cooling systems [2].

Bioactive ferromagnetic glass–ceramics are expected to be useful as thermoseeds for hyperthermia treatment of cancer, especially deep-seated cancers such as bone tumors. When ferromagnetic glass–ceramics are implanted around tumors in granular form, they are bonded to each other so as not to be moved by forming biologically active bone-like apatite on them [3], and stably fixed around the tumors if they are located near bones. Moreover, when they are placed under an alternating magnetic field, they generally heat effectively cancer cells to be necrotized by magnetic hysteresis loss. After heating, they can also reinforced weakened timorous bone by bonding to bone.

Several materials that generate heat by hysteresis loss have been developed [4–9]. Among them, bioactive ferro and ferrimagnetic glass–ceramics have been investigated [10–13].

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Preparation of magnetite-containing glass ceramics has been reported by several workers [2,14,15]. It is known that heat generation depends mainly on the magnetic properties of the implant, the magnetic field parameters and the characteristics of the tissue [16].

Bretcanu et al. [16] prepared ferrimagnetic bioglass–ceramics containing 45 wt% of magnetite revealing a saturation magnetization of 34 emu/g and a coercive force of 85 Oe. The estimated heat generation of this glass–ceramic using a magnetic field of 40 kA/m and a frequency of 440 kHz was 25 W/g. The previous material showed a bioactive behavior after 2 weeks of soaking in a simulated body fluid. Ebisawa et al., in 1997 [2] prepared glass ceramic contains 36% magnetite, in a matrix of $CaO{\cdot}SiO_2$ based glass, and β-wollastonite which showed ferrimagnetisms and no bioactivity [17].

Kuwashita et al. [18] prepare zinc-iron ferrite ($Zn_xFe_{3-x}O_4$) in a $CaO–SiO_2$ glassy matrix by heat-treatment under 95 CO_2 + 5H_2 atmosphere. The prepared material showed a large amount of heat generation of 12.4 W g^{-1} under conditions of 300 Oe and 100 kHz.

Wu et al. [19] found that, Zn ions play an important role in the human body, as reported to be involved in bone metabolism and can stimulate bone formation and increase bone protein, calcium content, and alkaline phosphates activity in humans and animals. They crystallize hardystonite ($Ca_2ZnSi_2O_7$) which might be biocompatible and used as biomaterials [19].

From all the above mentioned materials manganese zinc ferrite (Mn–$ZnFe_2O_4$) have special importance due to its high initial permeability, saturation magnetization and relatively lower eddy current loss compared to alloy cores [20], moreover Mn–Zn ferrites are very important in biomedicine as magnetic carriers, such as in bioseparation, enzyme and protein immobilization [21].

This work aimed at preparation and characterization of magnetic glass ceramic in the $Fe_2O_3{\cdot}ZnO{\cdot}CaO{\cdot}SiO_2{\cdot}B_2O_3$ system containing P_2O_5 and MnO_2. The influence of adding different addition from P_2O_5 and/or MnO_2 on sequence of crystallization, amount and crystal size of the developed ferrite and microstructure were studied.

P_2O_5 was added to study its effect as nucleating agents on the crystallization of magnetite, while MnO_2 were added to study the effect of replacing Fe^{2+} by Mn^{2+}, in the magnetite crystals, on the crystallization process.

Experimental

Theoretical considerations on designing glass ceramic composition

In previous work [22], the authors succeed to precipitate ~60% nanoparticles magnetite in two different systems, $Fe_2O_3{\cdot}CaO{\cdot}ZnO{\cdot}SiO_2{\cdot}B_2O_3$ and $Fe_2O_3{\cdot}CaO{\cdot}SiO_2{\cdot}B_2O_3$. The results showed that, crystallization of large amount of nanoparticles of magnetite in the presence of Zn ions; consequently the saturation magnetization was increased to reach 52.13 emu/g. In order to improve the amount and nano-crystallite size of magnetite, we got before in the Zn-containing sample, different oxides such as TiO_2, Na_2O and P_2O_5 were added to this composition. The results showed that, addition of the P_2O_5 was greatly enhancing the amount and nano-crystallite size of magnetite.

Preparation of glasses

The chemical compositions of the examined glasses are shown in Table 1. About 100 g powder mixtures of our compositions were prepared from reagent grades of CaO as Ca_2CO_3, SiO_2, Fe_2O_3, ZnO and B_2O_3 as H_3BO_3. Different amounts of MnO_2 (0.5–40 gm) as $MnCO_3$ and/or P_2O_5 (3–10 gm) as $NH_4H_2PO_4$ were added over 100% batch composition.

Our target was to obtain a glass–ceramic, not a ceramic material, so a melting step was necessary. Based on their compositions, the batches were melted in a platinum crucible at 1350–1400 °C for 2 h in an electric furnace, with occasional swirling every 30 min to ensure homogenization. As the amount of P_2O_5 and/or MnO_2 increased the melting temperatures decreased. The glass melted at 1400 °C was poured onto a stainless steel plate at room temperature and pressed into a plate 1–2 mm thick by another cold steel plate. An additional sample was poured at 1450 °C to study the effect of increasing temperature on the crystallization of magnetite.

Crystallization of glasses

The samples were thermally examined using Differential Thermal Analysis (DTA). According to the DTA results the obtained samples were covered with active carbon powders, to apply a reducing atmosphere preventing ferrous ions from oxidation, and heated up to various temperatures at a rate of 10 °C min in a SiC electric furnace for crystallization. It was noticed that the synthesis parameters (such as temperature, time, heating rate, and atmosphere) play a fundamental role for magnetite crystallization.

Characterization

The quenched samples were subjected to powder X-ray diffraction using Ni-filled Cu Kα radiation for determining the types and contents of the precipitated crystalline phases. The average crystallite size of magnetite in the heat treated and untreated samples for the most intense peaks (220, 311, 400, 511 and 440) was determined from the XRD using Debye–Scherrer formula: $D = k\lambda/B\cos\Theta$, where D is particle size, k is constant, λ for Cu is 1.54 Å, B is full half wide and $2\theta = 4°$. The microstructures of prepared samples were studied using TEM. The sample was crushed and sonically suspended in ethanol and few drops of the suspended solution were placed on an amorphous carbon film held by copper microgrid mesh and then observed under transmission electron microscope.

Results and discussion

Characterization

Fig. 1 shows thermal behavior of samples under investigation. All curves show a glass transformation temperature (Tg) typical of an amorphous phase in the range of 634–675 °C and exothermic peak in the range of 700–892 °C. The transformation temperature is accompanied by absorption of the heat