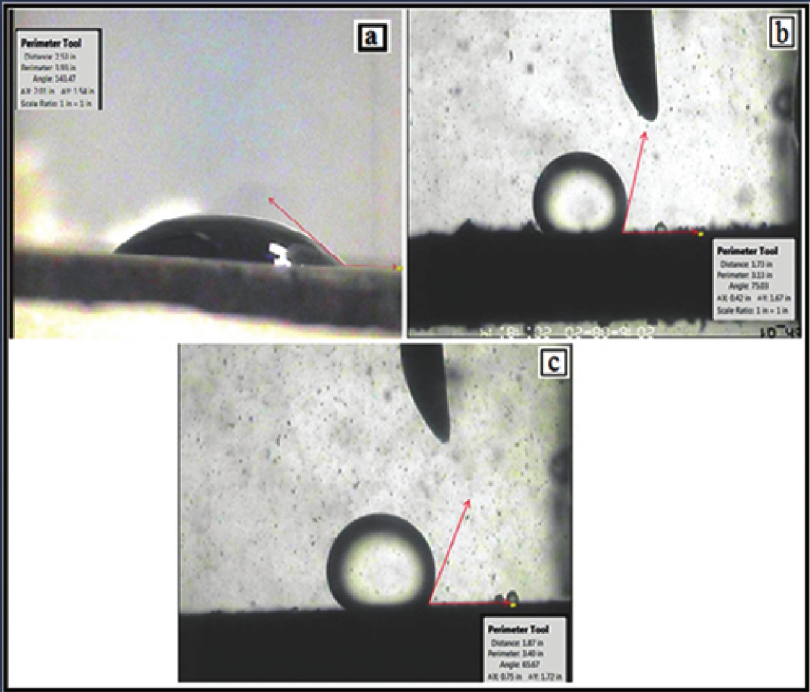


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Advanced Ceramics Progress (ISSN 2423-7477) (e-ISSN 2423-7485)

Web Site: www.acerp.ir, E-mail: office@acerp.ir

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An Overview of Cobalt Ferrite Core-Shell Nanoparticles for Magnetic Hyperthermia Applications

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PAPER INFO

Paper history:

Received 14 August 2019
Accepted in revised form 15 February 2020

Keywords:

Hyperthermia
Cobalt Ferrite
Rare-earth Elements
Surface Modification

ABSTRACT

Cobalt ferrite nanoparticles (CoFe_2O_4) are well known for some distinctive characteristics such as high magnetic permeability and coercive force, good saturation magnetization, excellent physical, and chemical stability, which make them so attractive for magnetic storage, magnetic resonance imaging (MRI), drug delivery, optical-magnetic equipment, radar absorbing materials (RAM), and magnetic hyperthermia applications. According to these particularities, cobalt ferrite-based core-shell nanoparticles have been reviewed focusing on hyperthermia applications. Promoting anisotropic constant and magnetic permeability, increasing the chemical and physical stability of nanoparticles, the proper distribution of particles in aquatic environments to prevent agglomeration, sedimentation, and obstruction in a specific position, as well as enhancing biocompatibility and avoiding the disadvantages, are essential for better efficiency in hyperthermia aspect. For this purpose, the synthesis of magnetic nanoparticles of cobalt ferrite with preferentially smaller sizes, as well as a narrower range of particle size distribution, is the primary objective of the synthesis process. Hence, it is important to identify the influence of effective parameters on the size and shape of nanoparticles, the substitution mechanisms of rare-earth elements, and changing the structure and behavior of the magnetic properties by these elements and finally, the thermal properties. Moreover, surface modifications and coating are other significant parameters in hyperthermia field that are investigated to achieve a suitable and stable distribution in aqueous media, and how they behave against the magnetic field.

1. INTRODUCTION

Metallic oxide nanoparticles are very much attractive due to their unique optical, electronic, and magnetic properties. Cobalt ferrite nanoparticles (CoFe_2O_4) with spinel structure have high magnetic permeability, high coercive force (greater than 50 KOe), good saturation magnetization (M_s) (80 emu.g^{-1}), mechanical hardness, and excellent stability of physical and chemical properties. Therefore, this material is a suitable candidate for high-density magnetic storage, magnetic fluid technology, drug delivery, magnetic resonance imaging (MRI), magnetic hyperthermia (MH) for killing cancerous cells, and radar absorbing materials (RAM) applications [1]. It should be noted that the magnetite iron oxide nanoparticles (Fe_3O_4) are the most commonly used materials due to their lower toxicity, magnetic properties, relatively easy

synthesis, and stability in many colloidal environments [2]. On the other hand, Fe_3O_4 has a high M_s and low anisotropic constant (K), and its practical application causes some kinds of aches and pains that are difficult to control. This problem can be solved through using complex magnetic oxides, whose physical, chemical, and magnetic properties can be modified with a variety of elements [3]. Hence, its anisotropic constant and magnetic permeability are modified by cationic substitution [3,4]. One of the substituted elements is cobalt. This element improves the thermal properties for the sake of enhanced anisotropic magnetic constant, chemical, and physical stability [5]. Furthermore, cobalt ferrite nanoparticles have special spatial and stronger linkages of albumin proteins compared to magnetite. Therefore, cobalt ferrite nanoparticles are considered as the best candidate that meet all expected conditions [3].

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The other thing about magnetic nanoparticles is the high ratio of the surface to the volume of the particles, which tends to accumulate and absorb plasma proteins during use. Besides, magnetic nanoparticles are mainly collected in the liver due to hydrophobic surfaces. In fact, unmodified nanoparticles in the bloodstream system are rapidly flooded. It is essential to extend the flow time of nanoparticles and reduce peptidase to improve the use of magnetic nanoparticles in various biological applications. Additionally, biocompatibility will decrease due to the presence of cobalt. Therefore, cobalt ferrite nanoparticle coatings are used to prevent possible damages to biocompatibility provide chemical and physical stability and appropriate distribution of particles in the fluid system. The surface modification of magnetic nanoparticles with a variety of coatings and surface modifiers, such as hydrophilic polymeric compounds, significantly prolongs the time of nanoparticle circulation in the blood through reducing or eliminating Protein adsorption [3,6].

Regarding biological applications, nanoparticles should (1) be less than 100nm (in some references up to 200nm) with a narrow size distribution, so that particles exhibit uniformity in physical and chemical properties; (2) have high saturation magnetization; and (3) require a special surface modification to improve their biocompatibility, and allow them to release at a specific position [3,6,7].

Therefore, the synthesis and coating of spinel cobalt ferrites are desirable for multiple applications including magnetic hyperthermia. It is important to study the parameters affecting powder synthesis and their mechanism of action to achieve optimal properties. Moreover, the type of shell applied to the nanoparticle and how it forms on the surface of nanoparticles will be considered to the final properties of the product. Accordingly, the magnetic hyperthermia and the mechanisms and factors influencing hyperthermia are initially discussed. Cobalt ferrite core-shell nanoparticles are then studied. In this paper, the mechanism of action and the effects of various rare-earth elements on the structure, as well as the magnetic properties of cobalt ferrite and its thermal properties, are comprehensively discussed due to the importance of the doping in the structure and their effects on the properties. The polymer coating of nanoparticles is also investigated with an emphasis on experimental papers.

2. MAGNETIC HYPERTHERMIA

Magnetic materials are used in a variety of applications, including computers, electronics, chemical and mineral industries, automotive, etc. [8-

9]. In addition, magnetic nanoparticles produce high thermal energy at different magnetic fields in the medical scope. Local heat in the biologic tissues stops the growth of the tumors and destroys them. Also, these materials can also be used in diagnostic applications such as magnetic resonance imaging (MRI) and drug delivery to the removal of cancerous cells [10]. This issue is discussed considering the application of magnetic nanoparticles in magnetic hyperthermia.

The term hyperthermia is used to explain a therapeutic approach in which a defective and cancerous tissue is subjected to a heat treatment that is higher than the normal physiological temperature (about 37°C) [11-13]. In conventional hyperthermia, heat may be generated by various sources such as microwave, supersonic, or radio waves. The hyperthermia of magnetic particles, known as MH, employs magnetic nanoparticles against an alternating magnetic field (AC). According to the published reports of Cristiano Blanco Andujar (2016), Hatami (2018), Alison E. Deatsch (2014), and M. Dalal (2018), this method is originally introduced by Gilchrist et al (1957) with the localized heat of lymph nodes by magnetic nanoparticles. Since then, many researchers have considered it in the development of MH and MNPs as heat agents [11-14].

This method is considered as an alternative and attractive treatment for cancer due to the lack of side effects compared with other therapies such as chemotherapy and radiotherapy. Most of the known hyperthermia methods suffer from certain limitations in the tumor or the control of the exact amount of thermal energy, or that the entire body is under heat and still challenging for specific tissues and tends to significant heat around tissue or inadequate heat. In contrast, it is possible to achieve a beneficial therapeutic effect with the lowest concentration of magnetic nanoparticles in magnetic hyperthermia due to the high specific absorption rate (SAR) from an optimal combination of destructive magnetic nanoscale materials [10].

Magnetic nanoparticles in sustained colloidal suspensions can be released without invasive properties through a variety of drug release pathways. After release, these particles can be heated with an alternating magnetic field at frequencies that have no negative effect on healthy tissue. This action creates sufficient heat in deep tissues along with the release of negligible energy in the path. Also, magnetic nanoparticles may be directed to some surfaces with the external magnetic field. Direction and substitution of nanoparticles in a particular tissue are also available using a suitable chemical agent. Also, it has been shown that magnetic nanoparticles are selectively collected in certain types of tumors. Finally, as noted above, magnetic nanoparticles are

used for drug delivery and for hyperthermia. Therefore, multifaceted treatment is possible [13-14]. The rules governing magnetic nanoparticles for hyperthermia are investigated to properly understand the magnetic hyperthermia. The capacity of a material for producing heat under the influence of an AC magnetic field with a specific absorption rate (SAR) or specific loss power (SLP) is defined as Equation (1):

$$SAR = \left(\frac{\Delta T}{\Delta t}\right) \left(\frac{C}{mFe}\right) \quad (1)$$

C is the heat capacity of the liquid per unit mass, mFe is the concentration of the colloid solution (g.l⁻¹ of iron), and $\Delta T/\Delta t$ is the increase of the measured temperature relative to the time. The SAR value is widely used to describe the ability of heat production of a system. However, the SAR value cannot be directly compared for a given sample of different experiments because it depends on the field and frequency of the applied magnetic field. As a result, intrinsic loss power (ILP) is proposed to normalize the SAR value using an alternative parameter, which allows direct comparison of the results from different groups as an independent parameter (Equation 2):

$$ILP = P/(\rho H^2 f) = SAR/(H^2 f) \quad (2)$$

P is the volumetric power dissipation $P = \mu_0 \pi \chi''(f) f H^2$, $\chi''(f)$ is the imaginary part of the magnetic susceptibility, ρ is the magnetic field density, H is the magnetic field strength, and f is the frequency [11]. In magnetic hyperthermia, three independent mechanisms including Neel relaxation, Brownian relaxation, and hysteresis loss have been identified. Each of them depends strongly on the size, shape, crystalline anisotropy, and agglomeration of the nanoparticles [11,13]. It has been shown that the heat-related to the hysteresis loss results from the displacement of the domain walls, which occur in magnetic particles larger than 100nm; it is necessary to explain that the two characteristics of coercivity and remanence strongly depend on the volume of particles that suddenly disappear for smaller particles. In particular, coercivity is defined as $H_c = (2K/M_s)[1 - (V_c/V)^{1/2}]$ for $V > V_c$, so that V_c is the critical volume of the particle, and the relaxation mechanisms are dominate below it.

In the hysteresis magnetic behavior, the energy lost in each cycle P can be obtained from the multiple of the surface area under curve A at the frequency (Equation 3). A is determined by the coercive force and a remanence magnetization of the nanoparticle:

$$P = \mu_0 f \oint H dM = A f \quad (3)$$

No hysteresis is observed when superparamagnetic particles are exposed to the magnetic field, which means there is no heat dissipation through this

mechanism. Therefore, thermal losses predominate by relaxation mechanisms [11]. In this case, heating is created by rotating the magnetic moment of each particle against an energy barrier. If the conditions are such that this spin causes the whole particle to rotate, the particles are placed under the Brownian mechanism, and thermal energy is released through shear stress in the fluid medium. In any case, if the moment spins while the particle stays constant, the particle is in the Neel state, and the thermal energy inside the crystal is dissipated by rearrangement of the bipolar atomic momentum [13].

At the Neel relaxation mechanism, the characteristic time to return to the equilibrium is defined as [11]:

$$\tau_N = \tau_0 e^{(KV/k_B T)} \quad (4)$$

Where τ_N is the Neel relaxation time, τ_0 is the exponential parameter ($\tau_0 = 10^{-9} - 10^{-3} s^{-1}$), K is the effective anisotropy constant, V is the volume of nanoparticles, K_B is Boltzmann constant, and T is the temperature ($K_B T$ is thermal energy). This time is modified by Brownie [13] as follow:

$$\tau_N = \tau_0 (\pi k T / KV)^{0.5} e^{(KV/k_B T)} \quad (5)$$

V is the volume of the particle and K is an anisotropy constant.

In the Brownian motion, which causes the magnetic field to rotate the nanoparticle physically in the fluid and thus, to the shear friction, Brownian relaxation time strongly depends on the viscosity of the solution η and the hydrodynamic volume of the particle (V_H), and is expressed via the following equation [11,13]:

$$\tau_B = (3\eta V_H / kT) \quad (6)$$

In general, the dynamic volume of the particle (V_H) is greater than the particle size due to the interaction of the liquid or the adsorbed modifiers [11,13].

The Neel and Brownian mechanisms may occur in parallel and simultaneously; therefore, the effective relaxation time (τ) of the system is given as Equation 7 [11,13]:

$$1/\tau = 1/\tau_B + 1/\tau_N \quad (7)$$

As described above, the size of the nanoparticles determines the main mechanism. The Brown mechanism is predominant in low viscosity conditions for large nanoparticles, while the Neel mechanism is dominant in systems with smaller nanoparticles in viscous solutions [11,13]. However, the phenomenon, which is dominant in relaxation time, is heavily dependent on the anisotropy constant of the nanoparticle, the mainly magnetocrystalline anisotropy, and morphology effects [11]. Moreover, the concentration of nanoparticles in the suspension is one of the parameters that influence the production of heat. Generally, the magnetic relaxation time is

reduced and the thermal performance is affected by increasing the concentration of nanoparticles in both Brownian and Neel mechanisms [11, 13].

2.1. The effective factors on magnetic hyperthermia

One of the remarkable points in magnetic hyperthermia is to ensure that the nanoparticle magnetic array is reversible in a medium-range magnetic field ($H_0 < 100\text{-}200\text{Oe}$), since assuming the use of a strong magnetic field requires a sufficiently large electric current generation, which may be dangerous in clinical treatment [10].

Several factors influence the heat generated by a group of magnetic nanoparticles. These variables are discussed as extrinsic and intrinsic parameters [11,13].

The heat generated from magnetic nanoparticles is not only related to the structure and composition of nanoparticles (intrinsic parameters), but also the frequency and intensity of the magnetic field (H) applied (extrinsic parameters). SAR values enhance with increasing frequency and/or applied field. Most SAR values have reported at a frequency of 300-700kHz and a range of 10 to 30KA⁻¹ for the applied field. However, it is still unclear whether these values are safe at the clinical treatments. The Brizovic criterion published Atkins and Brizovic (1988) reported a safety margin to avoid eddy current effects for magnetic hyperthermia. The H_f should be smaller than $4.85 \times 10^8 \text{A.ms}^{-1}$, which have been considered as a consensus standard for all the researchers and further studies have not been reported [11,13].

The role of the frequency in SAR is considerably more complicated than the field amplitude. However, its effect is subtle and delicate in the range of frequencies raised. Therefore, this issue has not been the focus of hyperthermia studies [13].

Intrinsic factors are also important in addition to external parameters that influence the function of magnetic hyperthermia. The first in this field is the type/composition of materials. In fact, magnetic properties such as saturation magnetization, coercive force, and anisotropic magnetocrystalline constant, which have been linked to hyperthermia in previous relationships, depend greatly on the type of composition and size. On this basis, the influence of rare-earth metals on the structure and magnetic properties of ferrites have attracted the attention of many researchers. However, in section 3.1, the mechanism of the substitution elements operation in the structure and effect on magnetic properties, the role of different elements and their effect on the size and magnetic properties are discussed briefly.

In fact, different elements have different electron arrangements and ionic radii. These doped elements fall into tetrahedral or octahedral spaces by

incorporating elements into the structure of ferrite, depending on the atomic arrangement, ionic radius, and even, doped element concentration. This can also cause changes in the magnetic moment of the material in addition to changing the lattice parameter of the structure and size of the particle [9]. Studies have shown that changes in saturation magnetization by chemical composition can be justified by the exchange reactions between the cations distributed in octahedral and tetrahedral sites [15].

On the other hand, the particle size parameter is one of the most important factors affecting magnetic properties. Changing the size of the particle can change the magnetic domains. Also, changes in magnetic domains can have a significant effect on magnetic properties such as M_s , H_c , and SAR. A ferromagnetic material that has a significant coercive force can be converted to a superparamagnetic material with a H_c near zero by reducing the particle size.

Regarding the investigation of the effect of particle size on saturation magnetization, it should be noted that the greater the surface area of a particle to its volume ratio (the smaller the particle size), the less saturation magnetization is predicted to occur because the spins on the surface of the particles have many perturbations. Therefore, when the effects of these surface perturbations can be mitigated the M_s further increases. Therefore, the saturation magnetization also increases as the particle size increases [16,17]. The coercive force will increase as the grain size decreases. This is because as the grain reduces, the volume fraction of defects will increase, and as a result, the domain walls would be changed harder and the H_c will increase. Equation 8 expresses the relation between H_c and D [18-20]:

$$H_c = a + b/D \quad (8)$$

Where H_c is the coercive force, a and b are the constant numbers and D is the particle size.

On the other hand, the coercive field depends on the anisotropic magnetocrystalline and the distribution of cations in the interstitials. For instance, high anisotropic magnetocrystalline in cobalt ferrite is mainly due to the presence of cobalt ions in octahedral sites, while this ion is placed in octahedral sites with the substitution of an element like Gd and cobalt ions move to tetrahedral sites, reducing the K [15].

There is also a relationship between saturation magnetization, coercive force, and anisotropic magnetocrystalline known as Wuhlforth theory (Equation 9) [21-23]. This relationship well indicates the direct correlation of the H_c and K , and their inverse ratio to the M_s . As it was stated, there will be a decrease in the M_s and an increase in the H_c along particle size reduction and vice versa:

$$H_c = 0.98K/M_s \quad (9)$$

Where H_C is the coercive force, K is the anisotropic magnetocrystalline, and M_S is the saturation magnetization.

On the other hand, as obvious in Equation 6, Brownian relaxation time is proportional to fluid viscosity. In extremely viscous environments, its relaxation time is longer and heating is dominated by the Neel mechanism. It has been empirically proved that the mechanism governing the heat dissipation in small nanoparticles is the Neel mechanism, while Brownian motion plays an important role for larger nanoparticles [11].

Determining the mechanism for heat generation is largely dependent on the size of the particles. The hysteresis loss in large particles (>100nm) predominates [11,13], but these sizes of particles are too large for many clinical treatments. These particles do not form a stable colloidal system and do not easily penetrate and dissipate in tumors; Also, large particles may activate the mechanisms of bacterial defense in the body [13]. In smaller particles, the hysteresis loss is negligible. In this range, the relaxation times of the Neel and Brownie are proposed as a suitable mechanism for particles. Generally, the Brownian relaxation time is important in larger particles in this area and the Neel relaxation time is noticeable in smaller particles. However, exactly where this division occurs is strongly dependent on the anisotropy constant of the particle [11,13].

To optimize the hyperthermia system of a particle, magnetic anisotropy control of the particles is critical. In general, magnetic anisotropy may exist from two distinct sources: crystalline anisotropy and shape anisotropy. It is possible to some extent control magnetic anisotropy by choosing the crystalline structure and the shape of the nanoparticles [11,13]. Anisotropy may be increased by substitution of other transition metals such as cobalt, manganese, or nickel in the inverse spinel structure [11].

As evident in Equation 5, any change in the anisotropy constant can be compensated by the corresponding change in the volume of the particle (V) in a system under the mechanism of the Neel. Regardless of this, it is clear that poor control of anisotropy is a major obstacle to the effective optimization of nanoparticle systems for hyperthermia treatments. It is worth noting that hysteresis is also affected by anisotropy since anisotropy is attributed to the coercivity of the sample [13].

In high concentration solutions, magnetic anisotropy is more complicated than single-particle behavior. In these solutions, the interaction between adjacent particles may stimulate the formation of a chain, which then creates an axial anisotropy along the chain that is independent of the anisotropy of single-particles. In a study by Dennis, this kind of particle

interaction significantly increased SAR in dextran-coated iron oxide nanoparticles. Generally, concentration dependence is created due to interdimensional bipolar interactions. As the concentration increases, the distance between the particles decreases and increases the bipolar interaction, thus changing the magnetic response of the magnetic fluid. This interaction directly affects the relaxation time of Neel and is the dominant mechanism in the hyperthermia studies. However, numerous contradictory models describe the effects of these bipolar interactions on the relaxation time [13]. These types of particle interactions are rarely well studied in hyperthermia nanoparticles, although they may have a significant effect on SAR [11,13].

3. COBALT FERRITE-BASED CORE-SHELL NANOPARTICLES

Various materials are thought to be hyperthermia agents due to different thermal sources in the field of hyperthermia, most notably nanoparticles include; gold, silicon, palladium, cobalt, carbon base nanoparticles, iron oxide, and substituted iron oxide nanoparticles with other elements [24]. Some materials can act as hyperthermia agents in different heating sources. Ferrite core-shell nanoparticles are the most important materials among the materials highlighted for this purpose. The nanocomposite material has both the advantages of minerals cores (including hardness, thermal stability, etc.) in the core-shell nanoparticles based on the cobalt ferrite core and organic shell, and the benefit of organic shells (including, flexibility, dielectric, toughness, process ability, etc.). Therefore, the final properties of the nanocomposite is a combination of the properties of organic and inorganic materials [25].

A wide range of magnetic nanoscale materials has been reported for using in hyperthermia. Many core-shell nanoparticles have been investigated and their results have been extracted in terms of parameters such as temperature, SAR, frequency, field, time, type of cancer treated the thickness of the shell and core, and the synthesis method. Table 1 shows the SAR value and temperature for different core-shell nanoparticles prepared in various synthesis methods. In summary, iron oxide is the most common material for magnetic hyperthermia, which has attracted the most attention so far due to its biocompatibility. The preparation methods of such particles are varied. The most common approach for synthesizing these materials is known as the co-precipitation method that benefits from iron salts. This process gives ultrafine powder with a narrow size distribution. Also, it is a simple method and takes less time to do [2,4,26-28].

TABLE 1. The SAR value and temperature for different ferrite core-shell nanoparticles prepared via various synthesis methods

core	shell	Temp.(°C)	SAR (w/g)	Synthesis method	Ref.
Zn-Mn and Zn-Co ferrites	maghemite, dimercaptosuccinic acid (DMSA), MnFe_2O_4		799	hydrothermal coprecipitation of aqueous solutions	[26, 29-34]
CoFe_2O_4	$\text{Zn}_{0.4}\text{Fe}_{2.6}\text{O}_4$		10,600		[16]
$\text{Zn}_{0.4}\text{Co}_{0.6}\text{Fe}_2\text{O}_4$	$\text{Zn}_{0.4}\text{Mn}_{0.6}\text{Fe}_2\text{O}_4$		3866		[16]
MnFe_2O_4	CoFe_2O_4		3034		[16]
CoFe_2O_4	MnFe_2O_4		2274.12		[16]
$(\text{Mn}_x\text{Fe}_{1-x})\text{Fe}_2\text{O}_4$ (MFO)	SiO_2 , mPEG, dimercaptosuccinic acid (DMSA)		1635	co-precipitation	[33, 34, 35]
MWCNTs	$\text{Zn}_{0.54}\text{Co}_{0.46}\text{Cr}_{0.6}\text{Fe}_{1.4}\text{O}_4$	42.7	1372	coprecipitation	[26]
$\text{Zn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$	MnFe_2O_4	39-47	530	chemical synthesis	[34]
MnFe_2O_4 and CoFe_2O_4	oleylamine, dimercaptosuccinic acid (DMSA), DEG and polyacrylic acid		525	solvothermal	[30, 32, 33, 35, 36]
Mn doped iron oxide	DEG and polyacrylic acid		390	chemical route	[36]
$\text{Zn}_{0.47}\text{Mn}_{0.53}\text{Fe}_2\text{O}_4$ SPION	ligand (TRAIL)	37-43	347.3	thermal decomposition	[37]
$\text{Li}_{0.31}\text{Zn}_{0.38}\text{Fe}_{2.31}\text{O}_4$, (LZFO)-RGO		42–45	300	sol-gel	[26, 37]
$\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Co}_{0.3}\text{Fe}_2\text{O}_4$	MWCNT, MnFe_2O_4		200	co- precipitation	[6, 14, 30, 32, 34, 38]
manganese-ferrite nanoparticles	dimercaptosuccinic acid (DMSA)	50	128		[33]
$\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$	Poly(ethyleneglycol)	$\Delta T=10^\circ\text{C}$	92	mechanical milling and subsequent sintering, high-temperature polyol method	[12, 39, 40]
Fe_3O_4 , $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$		40	92	sol-gel autocombustion technique	[40]
MgFe_2O_4		50	85		[6, 31, 41]
$\text{Co}_{0.2}\text{Fe}_{0.8}\text{Fe}_2\text{O}_4$	dextran, MnFe_2O_4		78	co-prcipitation	[4, 6, 26, 30, 34, 38]
$\text{Zn}_{0.9}\text{Fe}_{2.1}\text{O}_4$	MnFe_2O_4	38.6	36		[6, 30, 31, 34]
$\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Fe}_2\text{O}_4$	Poly(ethyleneglycol)	42	33.47	high-temperature polyol method	[40]
$\text{Fe}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$	hydrophobic oleic acid, and hydrophilic poly(acrylic acid)	$\Delta T=10^\circ\text{C}$	22.4	solvothermal	[4, 41]
$\text{Fe}_2\text{O}_3:\text{CuO}:\text{ZnO}:\text{MgO}$	gold	42.5–43	21.27		[38]
CoFe_2O_4	ZnO , MnFe_2O_4		9.6	heat-up method	[25, 31, 34, 38]
$\text{Mn}_{0.75}[(\text{Zn or Co})_{0.25}\text{Fe}_2\text{O}_4]$	citric acid, dimercaptosuccinic acid (DMSA), MnFe_2O_4 , PEG-phospholipid and a cyclic tripeptide of arginine-glycine-aspartic acid (RGD)		4.5	hydrothermal	[6, 12, 30, 32- 34, 36, 37, 42-44]

cobalt ferrite magnetic nano-articles (MNPs)	folic acid	37 and 44	1	co-precipitation	[28, 45]
$Zn_{0.54}Co_{0.46}Cr_{0.6}Fe_{1.4}O_4$		45.7	0.774		[32- 34, 37, 43, 44 , 46, 47]
$Zn_{0.4}Fe_{2.6}O_4$	nanothin SiO_2 layer, PEG-phospholipid and a cyclic tripeptide of arginine-glycine-aspartic acid (RGD)	44.9 °C		FSP, in situ	[6, 12, 29, 32-34, 37, 43, 44 ,48]
$Mn_{0.5}Zn_{0.5}Fe_2O_4$	PEG coating, ligand (TRAIL), dimercaptosuccinic acid (DMSA), PEG-phospholipid and a cyclic tripeptide of arginine-glycine-aspartic acid (RGD), DEG and polyacrylic acid	40.5 ± 0.3 , 37-43		thermal decomposition	[32- 34, 36, 37, 43, 44]
Mg doping in γ - Fe_2O_3 ($Mg_{x-c}Fe_2O_3$)		99-184		thermally decomposition synthesis	[4, 6, 31, 41]
$CoFe_2O_4$	SiO_2 , PEG	42		hydrothermal approach, pechini method	[7, 12, 30]
$Cu_{0.3}Zn_{0.2}Mg_{0.5}Fe_2O_4$		43		thermal treatment technique	[31, 41]
$Ce_xFe_{3-x}O_4$		42		single step microwave refluxing technique	[49]
$CoFe_{2-x}La_xO_4$ ($x = 0.0; 0.2$ and 0.5)	oleic acid (OA) & ethylenediamine triacetate trisodium salt	58.8, 51.7 and 56.8		coprecipitation	[2]
$MgFe_2O_4/ZrO_2$ composites		50-120		citrate gel technique	[50]
Mn-Zn ferrite MNCs	PEG-phospholipid and a cyclic tripeptide of arginine-glycine-aspartic acid (RGD)	43~44		thermal decomposition	[44]
cubic spinel cobalt ferrites		50		co-recipitation	[28]
3D-printed b-tricalcium phosphate bioceramic scaffold	Fe_3O_4 nanoparticles/graphene oxide nanocomposite layers	50–80		3D scaffolds of beta-TCP= printing device, Fe_3O_4/GO nanocomposites = in situ forming	[51]
mesoporous bioactive glass/ polycaprolactone MBG/PCL) scaffolds	Fe_3O_4	80	4.7	MBG powders (Si/Ca/P molar ratio 80/15/5)= sol gel, Fe_3O_4 nanoparticles= coprecipitation, Preparation of $Fe_3O_4/MBG/PCL$ scaffolds= by 3D printing	
$ZrFe_2O_5$			0.026	mechanical milling process and Sintering process at 1100°C	[50]
$La_{0.73}Sr_{0.27}MnO_3$ (LSMO)	LSMO nanoparticles were coated with a bilayer surfactant(first layer; oleic acid and SDS; second layer: PNIPAAm and Aam chains)	45–60	27.3, 28.8 and 20.1	citrate gel method	[52]
Fe_3O_4 , $Zn_{0.4}Co_{0.6}Fe_2O_4$, $MnFe_2O_4$ (core), $CoFe_2O_4$	SiO_2 , $Zn_{0.4}Mn_{0.6}Fe_2O_4$, $CoFe_2O_4$ (shell), $Zn_{0.4}Fe_{2.6}O_4$				[7]

It can be seen from the table that various core-shell nanoparticles have been studied. It can be indicated

that the highest SAR value in most of the core-shell composite compounds belong to the cobalt ferritic

nanoparticles, and most efforts have been relatively focused on the development of these types of compounds. Cobalt ferrite nanoparticles have a relatively high saturation magnetization as well as significant thermal effects. These materials have higher SAR values (up to $720 \text{ W} \cdot \text{g}^{-1}$ and sometimes even much more) than all data reported for iron oxide in recent studies. Since less attention has been paid to these particles compared to iron oxide, the control methods of their size, shape, and size distribution have not yet fully developed. Therefore, the potential for higher heat production is anticipated. One of the factors affecting the properties of ferrite materials, as seen from the above table, is the presence of substituted elements that are present in the structure. Therefore, understanding how to influence these elements will be very helpful. On the other hand, the application of particles containing cobalt, nickel, or other magnetic elements has been somewhat limited due to the complexity of synthesis and reduced biocompatibility, and magnetic nanoparticles are often coated with a mainly polymeric shell or modified with surface treatments to achieve a stable distribution for environmental reasons. There are pieces of evidence that such coatings can greatly affect heating efficiency [13,28,53]. Therefore, the mechanism of the elements substitution and their effect on the properties is discussed in the first step, and then, the coating of these nanoparticles by the polymer shell is described.

3.1. Mechanism of action of doped elements within the structure and influence on magnetic properties

Cations operation within the structure will be discussed to understand the behavior of metal cations within the ferrite structure as the substituted elements regarding the parameters and mechanisms affecting magnetic hyperthermia. The metal elements have different mass, atomic number atomic and ion radii as well as different valences because of their position in the periodic table. Magnetic moments will arise from the presence of an element within the structure due to the electron spin related to each element [9].

It is known that the magnetite structure has the inverse spinel-type, and the iron element is from group VIIIB and the periodic type $4s3d4p (d^6s^2)$. In this structure, Fe^{2+} occupies the octahedral position, and half of the Fe^{3+} sits in the octahedral space and the other half is located in the tetrahedron site. Therefore, when Fe^{2+} forms, two electrons belong to the 4s electrons are removed, but all the electrons of the 3d level remain. Since four unpaired electrons are in the 3d, the strength of the Fe^{2+} bipolar field is equal to four Bohr magneton. When Fe^{3+} ions are formed, all 4s electrons and one of the 3d electrons are

eliminated, so the 5 Bohr magneton will be generated.

The ions in the tetrahedral site of the magnetite are in opposition to the applied field so that their magnetic moment is opposite to the magnetic field, but they amplify the field in the octahedral spaces. As a result, Fe^{3+} ions in the tetrahedral sites neutralize Fe^{3+} ions in the octahedral positions. The Fe^{2+} ions in the octahedral spaces do not contradict any ions, and therefore, strengthens the magnetic field.

Therefore, the magnetic moment per unit volume and the amount of saturation flux density (B_{sat}) for magnetite can be calculated in terms of cation distribution in tetrahedral and octahedral spaces. In a single cell, the total magnetic moment is equivalent to four Bohr magneton resulted from Fe^{2+} ions because the magnetic moments of iron Fe^{3+} eliminate each other. In the overall network cell (spinel structure), there are 8 cells, so the total magnetic moment is 32 Bohr magneton. Regarding the network parameter ($8.37 \times 10^{-8} \text{ cm}$) for a magnetite cell, the magnitude of Bohr magneton per unit volume (saturation magnetization) is $10^{22} \text{ magnetons} \cdot \text{cm}^{-3}$ ($5.1 \times 10^5 \text{ A} \cdot \text{m}^{-1}$). As a result, the amount of saturation flux density (B_{sat}) is according to Equation 10 [9]:

$$B_{\text{sat}} = \mu_0 \times M_s = (4\pi \times 10^{-7}) (5.1 \times 10^5) = 0.64 \text{ Tesla} \quad (10)$$

Now, the amount of the Bohr magneton derived from the substitution varies in the system if all or a part of these elements with two or three valences are replaced by other cations with different valences, considering the fact that the electron balance of the elements is different. Therefore, the amount of saturation magnetization and flux density would also be different.

Cobalt ferrite (CoFe_2O_4) is the same as magnetite with an inverse spinel structure, in which oxygen ions lie in cubic positions. The tetrahedral sites are filled with Fe^{3+} cations, and Co^{2+} and Fe^{3+} cations with different ratios are located in octahedral spaces. Magnetic properties of ferrites are usually dependent on the nature and mode of distribution of cations in the tetrahedral and octahedral sites. The exchange of cation distribution causes a change in magnetic moments and then, alters the M_s and H_C . Moreover, magnetic moments can be affected by the replacement of different cations in the spinel structure, as expressed in the magnetite case. Rare-earth elements are good candidates for substitution in cobalt ferrite structure because these elements have large magnetic moments, magnetocrystalline anisotropy, and magnetostriction at low temperatures due to the nature of 4f electrons. In rare-earth elements, electrons of the 4f layer are unpaired and have spin-orbit couplings in angular momentum. Hence, various studies have been done to investigate

the effect of rare-earth elements on the magnetic properties of cobalt ferrite. According to the results of these types of research, the substitution of rare-earth ions leads to the migration of cobalt ions from octahedral sites to tetrahedral spaces. As a result, the amount of saturation magnetization and coercive field will also change [54].

Zhou *et al.* [55] investigated the effect of doping the structure of cobalt ferrite with some rare-earth elements such as Y, Lu, Yb, Tm, Sm, and La. According to the X-ray diffraction pattern, the spinel structures were synthesized with lattice parameters in the range of 8.376 to 8.430°Å. There were also no additional peaks arising from rare-earth elements. These observations mean that the added elements are entirely in the spinel structure. Another important point is the decreasing peak intensity and increasing the width of the peaks by increasing dopants elements. This can be attributed to reducing the crystallinity of spinel ferrites. Rare-earth elements prevent the complete crystallization of ferrites due to the high ionic radius. They examine the changes in saturation magnetization and coercive field through the addition of rare-earth elements (Table 2). Accordingly, they reported the amount of saturation magnetization has decreased substantially by adding these elements, which is the reason for decreasing the crystallization. However, the addition of Lu element in contrast to other elements leads to an increase in saturation magnetization. It can be seen from Table 2

that the coercive field and saturation magnetization decreases with increasing the rare-earth elements, and Ho has greatly reduced the amount of coercive field. In general, the changes arising from the presence of rare-earth elements in the structure of manganese cobalt ferrite are attributed to the presence of the 4f layer [55].

Pervaiz *et al.* [56] and Sodaee *et al.* [15] investigated the effect of adding Gd on the magnetic properties of cobalt ferrite in separate studies. The results showed that the M_s and H_C were reduced by increasing Gd and the area of the hysteresis loop decreased significantly. Changes in M_s by chemical composition are explained by the exchange reactions between cations distributed in octahedral and tetrahedral spaces. These exchange reactions depend on the length and angle of the bonding, this cation goes to the octahedral and replaces some of the Fe^{3+} ions by adding Gd^{3+} . This behavior is because Gd^{3+} ions have a very high ionic radius and their probability of being present in tetrahedral is very low. Since the magnetic moments arising from 4f layer's electrons of the rare-earth elements including gadolinium ions originate at temperatures lower than 40K, and these elements exhibit non-magnetic behavior at room temperature, their presence instead of iron ions reduces magnetism in octahedral positions. As a result, the material's M_s decreases [15,56].

TABLE 2. Effect of rare-earth elements on magnetic properties of manganese cobalt ferrite

Elements	Mn-Co ferrite Without element	La	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Atomic Number	-	57	59	60	62	63	64	65	66	67	68	69	70	71
M_s (emu.g ⁻¹)	32.9	30.2	31	30.5	27.5	31.1	32	29.1	29	28.5	28.8	29	32.1	34.5
Bohr magneton (μ_B)		0	3.5	3.5	1	0	8	10	11	10.8	9.5	7.5	4.5	0
H_C (Oe)	340	215	21	195	225	295	280	250	210	155	160	190	215	235

According to Sodaee *et al.* results, Gd increased the crystallite size from 21.2 to 42.4nm. This is due to the replacement of Gd cations instead of Fe in the spinel structure because the ionic radius of gadolinium is 1.07°Å, while the iron ionic radius is 0.67°Å. For this reason, the strain rate of the network has increased with the replacement of Gd instead of iron. On the other hand, H_C depends on grain size and crystalline defects. The larger the size of the grain, the lower the locking of the wall domain, due to the reduction of

the grain boundary fraction. Therefore, the coercive field is also decreased with increasing Gd [15].

Another point is that the coercive field depends on the anisotropy constant and cation distribution in interstitial locations. Strong anisotropy in cobalt ferrite is mainly due to the presence of cobalt ions in octahedral positions. Cobalt ions migrate to tetrahedral sites and reduce anisotropy constant by the replacement of Gd ions in octahedral locations. As a result, macro spins are more easily returned to the previous location, and then, H_C is reduced [15].

In the study of Xavier *et al.* [57], the effect of samarium on the structural and magnetic properties of cobalt ferrite were also investigated. The crystallite size increased from 11.26 to 16.53nm with an increase of Sm^{3+} as 0.25 molar, which is attributed to the higher ionic radius of the samarium. Saturation magnetization and coercive field were also decreased from 52.24emu.g^{-1} to 32.55emu.g^{-1} and from 1379.2Oe to 814.73Oe, respectively. The reason for these changes is the same as explained for other rare-earth elements.

Naik and Salker [58] investigated the effect of temperature on the magnetic properties of cobalt ferrite in the presence of Dy and Gd elements at room temperature (300K) and very low temperature (5K). They observed when the temperature dropped from 300K to 5K, the M_s increased from 73.84emu.g^{-1} to 79.69emu.g^{-1} for cobalt ferrite; 70.29emu.g^{-1} to 79.35emu.g^{-1} for Dy presence in cobalt ferrite; and 60.85emu.g^{-1} to 71.02emu.g^{-1} for gadolinium cobalt ferrite. Moreover, the coercive field for Co-ferrite, Co-Dy ferrite, and Co-Gd ferrite changed from 1.326KOe to 13.939KOe, 1.435KOe to 10.149KOe, and 1.215KOe to 15.602KOe, respectively. The reason for this phenomenon is attributed to the magnetic moments activation of the Dy and Gd ions at temperatures below 40K. It is also observed that the M_s in the cobalt ferrite doped by Dy is much higher than the Gd doped cobalt ferrite. This is related to the higher magnetic moments in Dy ions. The effect of adding yttrium ion (Y^{3+}) on the structural and magnetic properties of cobalt ferrite nanoparticles was investigated by Alves *et al.* [20]. They showed the increasing the ion Y^{3+} up to 0.04 mole, and the grain size decreased from 35.32nm to 16.05nm. Saturation magnetization is also reduced from 69emu.g^{-1} to 33emu.g^{-1} . This is while the coercive field increased from 1.1KOe to 1.9KOe. The decrease in M_s can be attributed to the non-magnetic Y^{3+} substitution. This behavior is similar to that mentioned for other rare-earth elements discussed in this report. Increasing the H_C can be justified by increasing the amount of Y^{3+} , which causes a smaller grain size. As the grain size is smaller, the defective volume fraction and grain boundary will be greater. Then, changing the magnetic domain walls becomes harder, and H_C increases.

Motavallian *et al.* [4] synthesized $\text{Cd}_x\text{Co}_{1-x}\text{Zr}_{0.05}\text{Fe}_{1.95}$ ($0.0 \leq x \leq 0.3$) and CoFe_2O_4 nanocrystals via Pechini method with average particle sizes in the order of 32-40nm. X-ray diffraction analysis showed only the presence of a cubic spinel phase, and the lattice parameter increased with increasing cadmium substitution in the cobalt ferrite structure (from 8.3348°A for CoFe_2O_4 to 8.3975°A for $\text{Cd}_{0.3}\text{Co}_{0.7}\text{Zr}_{0.05}\text{Fe}_{1.95}$). The observed change in the lattice parameter is justified by the fact that the ionic radius of Cd^{2+} ion (0.97°A) is greater than that for

Co^{2+} ion (0.745°A). Also, the crystallite size of the spinel structure decreased by increasing the amount of cadmium from 40nm to 32nm. Saturation magnetization increased with increasing cadmium up to 0.1 due to the migration of Fe^{3+} ions to octahedral positions, and thus, the reduction of iron ions in tetrahedron spaces. With increasing cadmium, more than 0.1 molar, reduced M_s was observed as 57.33emu.g^{-1} for $\text{Cd}_{0.3}\text{Co}_{0.7}\text{Zr}_{0.05}\text{Fe}_{1.95}$, which was attributed to the effect of spin tilting in octahedral spaces.

Pilati *et al.* [29] synthesized Zn-Mn and Zn-Co ferrite nanoparticles by the hydrothermal method of Fe^{3+} , Zn^{2+} , and Co^{2+} solutions (0.5mol.L^{-1}) in a strongly alkaline environment at 100°C under vigorous stirring. XRD patterns confirmed the cubic spinel structure of the samples. The size of the cubic cell changed with Zn for both samples. Both Zn-Co and Zn-Mn ferrite nanoparticles showed a decrease in crystallite size by increasing the Zn ratio, and this decrease was higher for Zn-Mn ferrites. The distance between atomic Mn-O is greater than that of Zn-O, which leads to a further reduction of the cubic cell. Therefore, the size of the nanoparticles is smaller.

The saturation magnetization of synthetic nanoparticles was investigated at room temperature (300K) and lower temperature (5K). An increase in saturation magnetization from 65emu.g^{-1} to 87emu.g^{-1} was seen for Zn-Mn ferrite nanoparticles, with an increase of Zn up to 0.4 moles at 5k. Afterward, this property decreased to 80emu.g^{-1} by increasing 0.6 mole zinc. The observed magnetization decrease is attributed to the weak interaction of rapid changes in octahedral-tetrahedral positions arising from increased zinc concentration in tetrahedron sites. This trend is also observed for Zn-Co nanoparticles. Although, saturation magnetization for Zn-Mn nanoparticles at 300K shows a decreasing trend from 50emu.g^{-1} for 0.1 mole zinc to 30emu.g^{-1} for 0.6 mole. Saturation magnetization changes for Zn-Co nanoparticles are different from Zn-Mn ferrites at this temperature. Saturation magnetization is 40emu.g^{-1} for 0.1 mole zinc. This value decreases to 30emu.g^{-1} for 0.2 mole Zn, and then increases to 40emu.g^{-1} for 0.4 mole, and again decreases to 30emu.g^{-1} at 0.4 mole.

Considering the magnetic properties of nanoparticles, it was found that the replacement of Zn alters anisotropic constant of nanoparticles in different forms. Magnetic anisotropy of nanoparticles based on Zn-Co ferrite varies strongly from $K_{ef} = 2.5 \times 10^5 \text{J.m}^{-3}$ (low zinc content) to $K_{ef} = 5.3 \times 10^4 \text{J.m}^{-3}$ (high Zn content), whereas the anisotropy of nanoparticles based on the Zn-Mn ferrite changes less than 40% for any Zn value ($0.9 - 1.4 \times 10^4 \text{J.m}^{-3}$). These differences were related to the thermo-magnetic behavior of nanoparticles as a function of their Zn content. The relaxation time (τ_c) values decreased

compared with other iron oxides, especially magnetite as a function of Zn content for both samples have. Reducing τ_c in hyperthermia is very interesting in preventing excessive heat in the biological environment [29].

The SAR results of the samples were evaluated as a function of zinc value. In Zn-Co ferrite nanoparticles, the samples with low content of Zn have the best performance for heat generation ($\text{SPA}=1230\text{w.g}^{-1}$ for $x=0.18$) and the SPA reaches zero for more Zn. In this type of specimen with a negligible variation of magnetic anisotropy, this mode is related to a decrease in nanoparticle diameter and saturation magnetization at 300K [29]. It is observed that these nanoparticles provide the same amount of SPA as similar ferrites. The increase in Zn value decreases fast interaction and induces power absorption. Therefore, these nanoparticles are a good candidate for MH behaviors in a more secure and safer strategy because they help prevent excessive heat generation and damage healthy tissues.

It has already been stated that the performance of the nanoparticles in heat generation is influenced by the diameter of the nanoparticles, the magnetic anisotropy constant, and saturation magnetization. The magnetic moment is strongly coupled to the anisotropy field and preferential relaxations through the mechanical rotation for nanoparticles with high anisotropy constant. Increasing the viscosity of the fluid environment disrupts Brownian's rotation and reduces heat production efficiency. Also, higher SPA values are attributed to larger amounts of M_s , which is associated with a less anisotropy barrier induced by increasing zinc content [29].

In a similar study, Dalal *et al.* [14] synthesized $\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Co}_{0.3}\text{Fe}_2\text{O}_4$, $\text{Ni}_{0.4}\text{Zn}_{0.4}\text{Co}_{0.2}\text{Fe}_2\text{O}_4$, and $\text{Ni}_{0.3}\text{Zn}_{0.4}\text{Co}_{0.2}\text{Cu}_{0.1}\text{Fe}_2\text{O}_4$ nanoparticles via co-precipitation method. Synthesized nanoparticles were added to the MWCNT matrix to achieve radar absorption properties and to study the SAR characteristic for cancer treatment under alternating current (AC). Through the studied nanoparticles, $\text{Ni}_{0.4}\text{Zn}_{0.4}\text{Co}_{0.2}\text{Fe}_2\text{O}_4$ with crystallite sizes as much as 34.7nm showed a maximum SAR as 200w.g^{-1} value. The high M_s ($\sim 84\text{emu.g}^{-1}$) was obtained at room temperature [14].

3.2. Coating of nanoparticles by a polymer shell

Magnetic nanoparticles are highly sensitive to oxidation and agglomeration due to their high surface area and are reactive in chemical reactions. Under environmental conditions, the surface of nanoparticles undergoes rapid oxidation, resulting in the formation of a thin layer of oxide, which changes the properties of the particle. The natural agglomeration of nanoparticles in the form of larger

clusters is another problem that such particles face. The encapsulation process has been proposed to maintain magnetic properties and to protect against oxidation and agglomeration. Nanoparticle encapsulation has been successfully carried out using carbon, silica, precious metals, metal oxides, organic polymers, and surface modifiers [7,53].

The surface modification of magnetic nanoparticles plays a vital role in the application of these materials. The surface coating improves not only the colloid stability of nanoparticles, but also enhances biocompatibility, bio-safety, and SLP. Hence, the design of multipurpose biocompatible magnetic nanoparticles with upgraded magnetic properties and SLP values is possible by applying coatings [4,5]. Generally, electrostatic or chain repulsion is used to distribute nanoparticles, which keeps them stable. Modifiers or polymers chemically bind nanoparticles or physically absorb them to create single or double layers that generate repulsive forces (mainly repulsive chains) for balancing Vander walls gravity and magnetic forces of nanoparticles. Therefore, with magnetic repulsion and magnetic particles remain stable in suspension [53].

Sun and Murray reported the synthesis of cobalt nanoparticles in the presence of an organic surface modifier such as oleic acid, lauric acid, trioctylphosphonic acid, and pyridine. Among the organic surface modifiers, oleic acid is an organic sealant that can bind to heavy metal surfaces through the carboxyl group. This acid has been widely used in the synthesis of colloidal nanoparticles for a large number of metals. Recently, Lu *et al.* compared several surface modifiers (stearic acid, oleic acid, and ealidic acid) to synthesize cobalt magnetic nanoparticles to investigate the difference between their ability to control the particle size, distribution, and oxidation stability of nanoparticles. They found that the poor performance of stearic acid on nanoparticles stability was attributed largely to its linear composition. Unlike the oleic acid or ealidic acid, there is no double bond of $\text{C}=\text{C}$ in the stearic acid chain. They claimed that the interaction of the dual bond between olefinic acid contributes to the formation of a dense layer on the surface of cobalt nanoparticles. The sharing of binary links between adjacent molecules results in the hardness of the coating layers. There is a formation probability of magnetic gels through polymerization and cross-linking of binary bonds during solvent evaporation due to the presence of dual bonding in olefinic acid [53].

So far, most studies have focused on the development of surface-modifying coatings, which recently have attracted more attention to polymers that make magnetic nanoparticles stable. Polymers can produce more repulsive forces than surface modifiers. In resources, both synthetic and natural polymers are

used to cover magnetic nanoparticles. The most common natural polymers are dextran, chitosan, starch, gum arabic, and gelatin. Also, the most usual synthetic polymers are polyethylene glycol (PEG), polyvinyl alcohol (PVA), polylactide acid (PLA), alginate, polyacrylic acid (PAA), and polymethylmethacrylate (PMMA) [53].

Hatamie *et al.* used polyethylene glycol (PEG) to modify the surface of the synthesized cobalt ferrite nanoparticles prepared via the hydrothermal method. The average particle size of this method was 30nm. The M_s and H_C of synthesized nanoparticle were 41.3 emu.g^{-1} and 2284Oe, respectively, which changed to 29.8 emu.g^{-1} and 2324Oe with PEG coating, respectively. It can be seen that the saturation magnetization decreases and the coercive force increases with surface treatment. Moreover, the maximum SLP was 31.8 w.g^{-1} for nanoparticles coated with polyethylene glycol for $0.0025 \text{ gr.mL}^{-1}$ at 350kHz. The temperature of the coated nanoparticle after 10 minutes was 42°C [12].

Linh *et al.* synthesized core-shell structure from $\text{Co}_{0.2}\text{Fe}_{0.8}\text{Fe}_2\text{O}_4$ nanoparticles coated with dextran via coprecipitation method using an ultrasound chemical process. The mean crystallite size was obtained as $10.5 \pm 0.7 \text{ nm}$ using the Scherer equation. The average diameter of the uncoated particles was measured as much as $11.8 \pm 1.5 \text{ nm}$, while this number for dextran-coated particles was obtained as $50 \pm 5 \text{ nm}$. This value is suitable for in vivo applications. The magnetization of both samples did not saturate due to the dead layers with paramagnetic properties on the surface of the magnetic nanoparticles. The M_s values of 53 and 48.5 emu.g^{-1} were obtained for uncoated and coated nanoparticles, respectively. Clearly, the M_s decreased by 4.8% after surface coating. This was attributed to the presence of paramagnetic polymer coatings. Additionally, the H_C value for both samples was 116Oe. The highest SAR value for magnetic fluid exposed to the 300Oe field intensity was 78 w.g^{-1} [5].

In another study by Gharibshahian *et al.* [7], cobalt ferrite nanoparticles and $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ core-shell nanoparticles were prepared using the Pechini method. They synthesized nanoparticles in an electric furnace and microwave. It was observed that synthesized nanoparticles in the microwave were smaller particles than those prepared in an electric furnace (14nm in comparison with 35.06nm). The M_s value for coated particles was equal to 36.25 emu.g^{-1} , while it obtained as much as 64.5 emu.g^{-1} for uncoated particles synthesized in the microwave, and 71.51 emu.g^{-1} for uncoated powders prepared in an electric furnace. Also, the lower H_C and smaller remnant magnetization (almost zero) and more biocompatibility were observed for silica-coated particles, which makes them suitable for most of the medical applications, such as drug delivery,

hyperthermia therapy for cancer cells, cancer cell imaging, and MRI in the diagnosis of cancer.

Salunkhe *et al.* [3] synthesized cobalt ferrite nanoparticles via coprecipitation method and applied oleic acid (OA) and oleic acid- polyethylene glycol acid (OA-PEG) coatings on the particles. The crystallite diameter of the uncoated (CIO) and coated (CIO-OA-PEG) nanoparticles was calculated using the Scherer equation as 10 and 12nm, respectively. The lattice parameter for the uncoated and coated samples was about 0.8377 and 0.8376nm, respectively. There was no significant difference in the lattice parameters, indicating that the crystalline structure is not affected by the OA-PEG coating. TEM images showed uncoated particles were agglomerated, while coated particles were well distributed in the solution. Bipolar interactions in magnetic nanoparticles cause agglomeration of uncoated particles. Reduction in bipolar interactions between magnetic nanoparticles is necessary because it affects SAR. Upgrading SAR or maximizing thermal power often depends on optimal density, which ultimately influenced by the power of bipolar/bipolar interactions. Optimizing the mentioned properties is often important to focus on increasing the density of particles in the tumor through novel targeting designs. Bipolar-dipole interactions can be reduced by the physical and chemical adsorption of the polymer on the nanoparticle surfaces. The increased distribution after the OA-PEG coating is attributed to the presence of dead layers on nanoparticles, which reduces bipolar interactions between particles.

4. CONCLUSION

Magnetic nanoparticles have a high utility in detecting and treating cancer due to their special magnetic properties. For this reason, advanced magnetic hyperthermia has progressed tremendously during the last decade. The present research shows that the type of magnetic nanoparticles had a great effect on hyperthermia performance. Accordingly, it seems that cobalt ferrites were good materials for synthesizing and performing hyperthermia operations based on the extracted data from various papers on the heating of different nanoparticles and their comparison with each other, as well as the suggestions of other authors. The structural and magnetic properties of substituted spinel ferrites depended heavily on the type of substituted elements and their concentration, and these properties could be altered by modifying the size and shape of the nanoparticles, and the chemical composition. Accordingly, the ratio of the raw materials, the type of dopant, the temperature, and time required for optimal nanoparticle synthesis were the factors

affecting the structural properties of the nanoparticles, phase formation, density, and lattice parameter.

The use of rare-earth elements and the simultaneous substitution of these elements into the structure of cobalt ferrite had an important effect on the structural and magnetic properties of the nanoparticles as well as the thermal effects of nanoparticles to control the magnetic properties. Furthermore, nanoparticle biocompatibility with physiological conditions, especially biocompatible coatings such as dextran, chitosan, or PEG seemed to be necessary for the proper distribution of nanoparticles, as well as the prevention of agglomeration and particle bonding. There are many methods for controlled synthesis of nanoparticles for hyperthermia applications and SAR enhancement. Finally, further investigations are needed to improve the uniformity and to synthesize nanoparticles with a narrower size distribution of nanoparticles. Additionally, mass fraction and agglomerations of nanoparticles are the other important parameters that affect the relaxation time and SAR.

5. ACKNOWLEDGEMENTS

The authors would like to thank the Department of Materials Engineering, Babol Noshirvani University of Technology.

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An Investigation into the Effects of Composition and BaF₂ Content on the Structure and Crystallization Behavior of SiO₂-Al₂O₃-K₂O-BaF₂ Oxyfluoride Glasses

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PAPER INFO

Paper history:

Received 31 August 2019
Accepted in revised form 8 February 2020

Keywords:

Optical Glass
Oxyfluoride
Barium Fluoride

ABSTRACT

Nowadays, oxyfluoride glasses have received much attention from photonic researchers as they benefit from the advantages of both oxide and fluoride glasses (low phonon energy in parallel with high mechanical and chemical durability). The purpose of this paper was to study the different glass compositions in SiO₂-Al₂O₃-K₂O-BaF₂ system and investigate the BaF₂ effects on their crystallization behavior and structure. Therefore, various chemical compositions with different amounts of BaF₂ (20, 30, and 40mol%) were chosen and melted in alumina crucibles at 1450°C. The sample could not melt with the lowest percentage of BaF₂. On the other hand, the glass composition containing the highest amount of BaF₂ was not able to show high transparency due to the phase separation that occurred in it. Finally, the sample with a 30mole ratio of BaF₂ was chosen as the optimized sample due to the favorable transparency. XRD patterns showed that the samples were amorphous and it somehow proved the low transparency in the presence of higher amounts of BaF₂ arose from phase separation than the unwanted crystallization. According to the DTA results, the crystallization peak of the fluoride phase decreased from 693°C to 678°C by increasing the content of BaF₂. FT-IR spectra approved the oxyfluoride structure of the glasses. Higher BaF₂ content increased the absorption of peaks in FT-IR spectra since it results in a more discontinuous structure. Fluorine loss was higher for the glass containing the highest amount of BaF₂ due to the lower amount of Al₂O₃ in its composition.

1. INTRODUCTION

Importance of rare-earth (RE) ions doped materials is due to their potential applications such as optical fibers, amplifiers, optical storages, solar cells, etc. [1, 2]. The most essential parameter in the preparation of a luminescence material is actually choosing an optimal host. Candidate host material should have high optical transparency, low phonon energy, and favorable solubility of rare-earth ions [2]. Oxide glasses are used as hosts of RE ions since they have high transparency, mechanical strength, chemical stability, and easy fabrication procedure. However, they suffer from high phonon energies (more than 1000cm⁻¹), which lead to non-radiative relaxation of excited-RE ions [3]. On the other hand, fluoride materials do not have the limitation of high phonon energy, but the lack of mechanical and

chemical durability makes their preparation and application under ambient atmosphere too difficult [4]. Therefore, oxyfluoride glass-ceramics, which were invented in 1993 by Ohwaki and Wang [5], achieved a very high interest of researchers. In these new materials, RE ions enter the fluoride nanocrystals that have low phonon energy, and consequently, exhibit more intensive luminescence emissions than other glassy materials. Moreover, embedding these fluoride nanocrystals in an oxide glass matrix based on Al₂O₃-SiO₂ overcomes the above-mentioned problems for pure fluoride materials [6]. Among the different oxyfluoride glass-ceramics introduced until now, systems containing MF₂ (M=Ba, Ca, Sr) nanocrystals have been studied more. It is due to their low cost and non-toxic raw materials. Further, MF₂ nanocrystals have high

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solubility of RE ions and give a better matching of refractive index with aluminosilicate glass [7].

The majority of studies are devoted to the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaF}_2$ system and there are only a few types of research about systems containing BaF_2 nanocrystals. Whereas, BaF_2 has less phonon energy than CaF_2 , offers a more extended IR transmittance window, and achieves transmission up to $9\mu\text{m}$ [8]. Hence, it is tried to study $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-BaF}_2$ glass and glass ceramic system in the present paper. For this purpose, different chemical compositions with various amounts of BaF_2 were chosen and the effects of these changes on transparency, structure, and crystallization behavior of prepared glasses were investigated.

2. EXPERIMENTAL PROCEDURE

Three chemical compositions containing different amounts of BaF_2 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ in $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-BaF}_2$ system were selected (Table 1). According to these compositions, high purity materials were weighted, mixed, and completely homogenized. That is worth to say that, K_2O is a flux agent. Sb_2O_3 and As_2O_3 were added to batches as refining agents to prepare bubble-free samples. 50g of batches were melted in covered alumina crucibles at 1450°C for 1 hour. Melted glasses were poured on preheated stainless steel molds to give them disc-like shapes. To diminish the internal stress of samples, annealing at 550°C for 1 hour was carried out.

TABLE 1. Different chemical compositions of glasses in $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-BaF}_2$ system (mole ratio)

Composition Sample code	$\text{SiO}_2/\text{Al}_2\text{O}_3$	SiO_2	Al_2O_3	BaF_2	K_2O
GBF40	3	45	15	40	5
GBF30	2.5	50	20	30	5
GBF20	2.2	55	25	20	5

XRD analysis was used to study the amorphous nature of glasses and identifying the precipitated crystalline phases in heat-treated samples (taken by Philip Xpert-MMD system). Differential thermal analysis (DTA) curves were plotted with the rate of $10^\circ\text{C.min}^{-1}$ to measure crystallization peak temperatures of samples using DTG-60AH Shimadzu equipment. the ASTM C169-16 standard method was used. The glasses were mixed with sodium hydroxide granules through the grinding method to obtain the fluorine loss amount in glasses. The obtained mixtures were melted in covered

alumina crucibles at 900°C . the achieved melts poured to 500ml polyethylene beaker containing 90°C -distilled water. A total ionic strength adjustment buffer (TISAB) solution was used to adjust ionic strength and minimize the undesirable fluoride coordinating ability of impurities. The TISAB solution was prepared with 57ml of glacial acetic acid, 58.0g of sodium chloride, and 12.0g of sodium citrate in 500ml of distilled water under constant agitation. The pH of the solution was adjusted to 6.0–6.5 with $\text{NaOH } 6\text{mol.l}^{-1}$ and the addition of water continued till completing the volume to 1l. The solution was kept in polyethylene flasks. Standard NaF solution prepared by dissolution of fluorides in distilled water for obtaining calibration curves. The potentiometric determination was performed with a fluoride ion-selective and a reference electrode (saturated calomel electrode) using the Orion dual star model of Thermo fisher company's equipment. Each millivolt (mV) measurement was made after stirring the solution for 2min and then leaving it for 4min. Then the fluorine amount (g.ml^{-1}) was obtained according to the calibration curves. Finally, the lost amount of fluorine was calculated by differences of fluorine content in the chemical composition of samples and their measured fluorine content [9].

UV-Vis-NIR spectra of samples, recorded by UV-Vis Shimadzu 1700 spectrophotometer, were used to investigate the effect of chemical composition and BaF_2 content on the transparency of glasses. FT-IR analysis was performed to obtain some structural information about samples (using FT-IR Tensor 27 Brucker device).

3. RESULTS AND DISCUSSION

3.1. Results of Melting

After melt/shaping process at 1450°C for 1 hour, sample GBF20 did not melt and it remained as an unmelted powder in the crucible. It is attributed to the high amounts of SiO_2 and Al_2O_3 , and consequently, lower percentage of BaF_2 in its composition, which elevates its refractoriness degree. Other samples were melted successfully, whereas, sample GBF40 containing the highest content of BaF_2 , demonstrated phase separation during the melt/quenching process. Therefore, sample GBF40 was less transparent than GBF30 (Figure 1). The resulted phase separation is ascribed to the high content of fluoride ions in sample GBF40. It is reported that anions like F^- and Cl^- can increase the phase separation in glasses [10]. Therefore, partially substitution of oxygen by fluorine breaks down the glass network and its viscosity decreases, and consequently phase separation speeds up in glass [11].



Figure 1. The image of disc-like shaped and polished GBF40 and GBF30 samples

3.2. DTA Results

Figure 2 presents the DTA curves of samples. For both GBF40 and GBF30 samples, two exothermic peaks are observable. The presence of two exothermic peaks is DTA curves, which are reported by other researchers too [12-14]. The first peak (at 693°C and 678°C for GBF30 and GBF40 samples, respectively) is attributed to the crystallization of the BaF₂ phase, which is in agreement with other reports with small differences [12-16]. The diversity of the peak temperature of the BaF₂ crystallization in various references is sparked off the different chemical composition, additives, and dopants used for preparing samples. Furthermore, the second exothermic peak is appeared due to the crystallization of the glassy matrix [12], which is not discussed in many types of research [14-17].

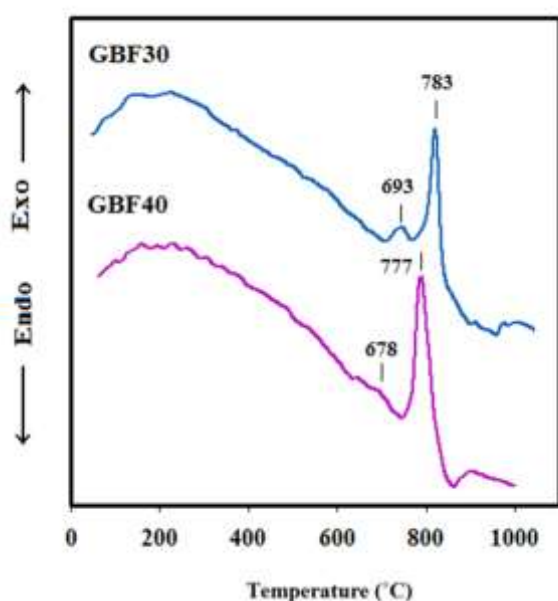


Figure 2. DTA cures of GBF40 and GBF30 samples

The lower peak temperature of the crystallization of BaF₂ in GBF40 (678°C) in comparison with GBF30

(693°C) could be attributed to the phase separation in this sample, which has a high amount of BaF₂. It is clarified that the addition of fluorine ions to the glass structure introduces nonbridging oxygens. Hereby, the viscosity of the glass decreases, which facilitates the mobility of ions, which provokes the phase separation and crystallization, consequently [11]. On the other hand, the crystallization mechanism of oxyfluoride glasses is a diffusion-controlled process; hence, adding higher amounts of glass network modifier agents (here the fluorides) results in readily movement and diffusion of ions, and consequently, lower crystallization temperatures [18,19].

The peak temperature of the glassy matrix is higher for the GBF30 sample (783°C) and XRD results prove that the precipitated crystalline phase at second peak temperatures is BaAl₂Si₂O₈ (Figure 3(c)).

3.3. XRD Patterns of Glassy and Crystallized Samples

As shown in Figure 3(a), there is no observable peak in XRD patterns of glass samples. The absence of peaks in the XRD pattern of GBF40 sample, somewhat approves that the smoky non-transparent regions in this glass is due to the phase separation and not related to unwanted crystallization. No crystalline peak was observed in GBF30. Moreover, two amorphous humps are distinguishable in the XRD results of both samples. This implies that two separate crystalline phases can precipitate each of the glasses and it is in agreement with the existence of two exothermic peaks in DTA curves.

In Figure 3(b) patterns of heat-treated glasses at first and second exothermic peaks of DTA curves, are presented. If both samples experience the heat treatment at their first peak temperature of their DTA results, BaF₂ nanocrystals would be the only precipitated crystalline phase, while heat-treating at second peak temperatures results in crystallization of two different crystalline phases, i. e., BaF₂, and BaAl₂Si₂O₈ (Figure 3(c)). Based on XRD results and using Scherrer equation (Equation 1), the mean crystal size of BaF₂ nanocrystals was calculated and it was 10nm for GBF30 and 16nm for GBF40.

$$D = 0.9\lambda / \beta \cos\theta \quad (1)$$

According to Bocker et. al. [20], when BaF₂ crystals appear in the glassy matrix, SiO₂-Al₂O₃ rich layers surround these crystals. Therefore, to grow the size of crystals, ions diffuse the SiO₂-Al₂O₃ rich layers. When the fluoride ion, which is considered as barrier layers. The amount should be high enough to keep viscosity low to allow ions as a consequence, in sample GBF40 higher BaF₂ percentage results in larger BaF₂ crystals than GBF30.

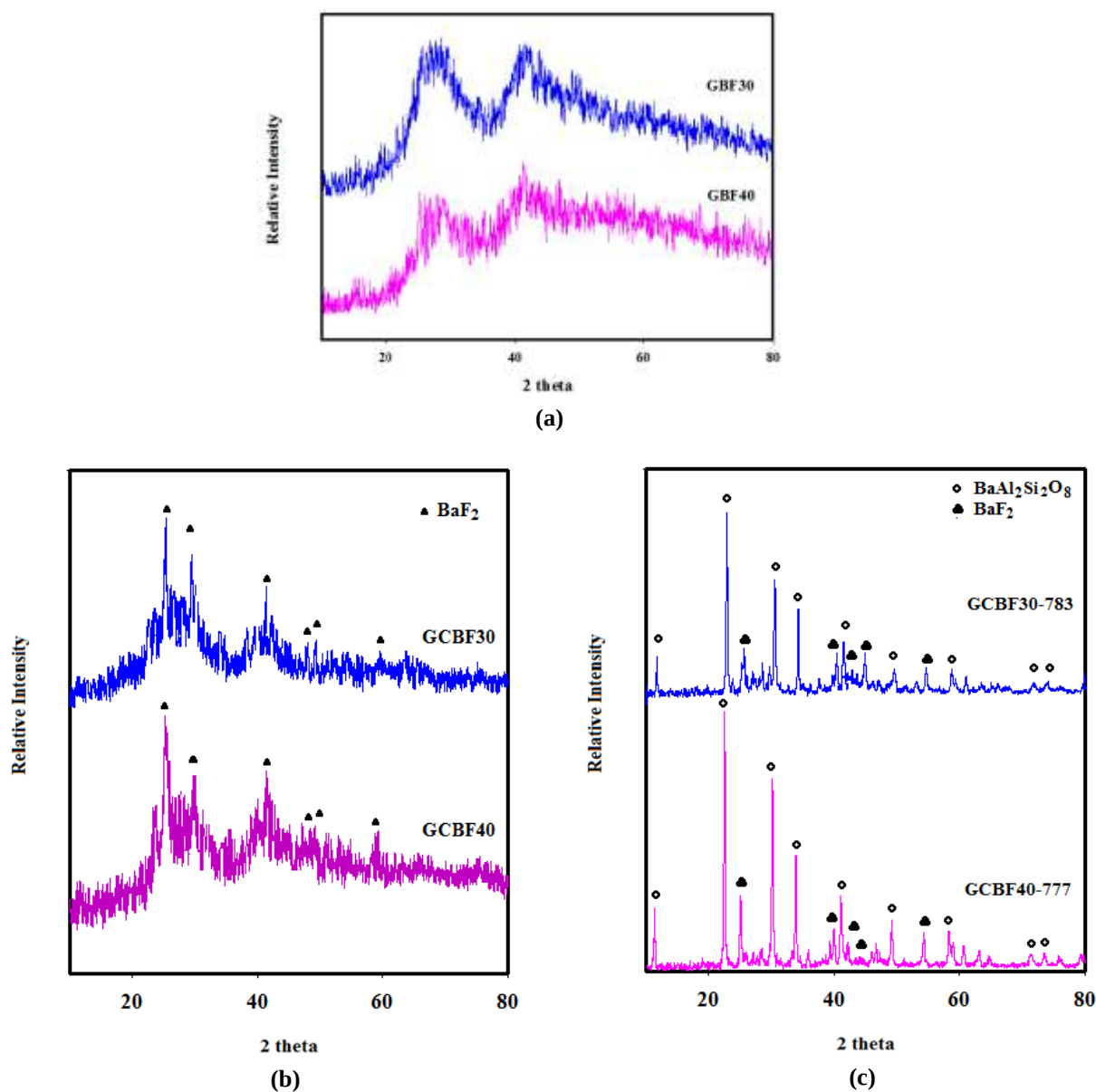


Figure 3. XRD patterns of (a) glassy samples and glass-ceramic samples heat-treated at (b) first and (c) second exothermic peak temperatures according to DTA curves

3.4. UV-Vis-NIR Spectra and Structural Study

UV-Vis-NIR transmission spectra of glasses are shown in Figure 4. There is a sharp increase in absorption at wavelengths close to the band-gap that manifests itself as an absorption edge. This outcome demonstrates the amorphous nature of these compounds. Generally, the absorption edge of glasses is affected by the strength of oxygen binding and the number of non-bridging oxygens in the glass network. The addition of glass

modifiers and network breaking agents, like fluoride ions, causes breaking oxygen bonds. In this way, the number of non-bridging oxygens (NBO) grows and the absorption characteristics change. As BaF_2 content increases, the NBOs increase and then, the bond edge should move to lower energies, which is observable in Figure 4. However, the inordinate red shifting of absorption edge of GBF40 is due to the phase separation within its network and based on Rayleigh and Mie scattering effect [21].

That is worth to notice that, both samples have high transmissions without decrement (approximately higher than 90%) in the UV-Vis-NIR region up to 2500nm.

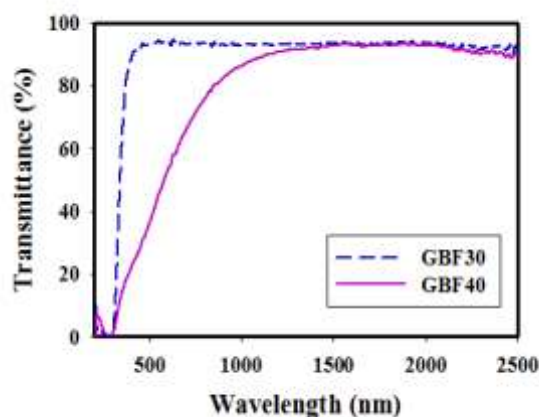


Figure 4. UV-Vis-NIR spectra of GBF40 and GBF30 samples

FT-IR spectra of samples are presented in Figure 5. Peaks placed at 445, 700, and 985 cm^{-1} are ascribed to bending, symmetric stretching, and asymmetric stretching vibrations of Si-O-Si bonds, respectively [22, 23], which imply the silicate-like structure of glasses. Besides, the absorption peak at 587 cm^{-1} is due to the presence of Ba-F bonds in samples [24]. Therefore, the oxyfluoride structure of the studied samples is somewhat proved.

In oxyfluoride glasses, fluorides behave in three ways: (1) as network modifier agents (2) stay as free fluoride ions (3) bond with cations such as Ca^{2+} or Al^{3+} . Each of these roles is taken based on the content of modifying oxides in glass [25]. It is also proved that if oxide content increase, fluorides would not exist as Si-F bonds and F⁻ ions would have a high tendency to bond Al^{3+} cations rather than Si^{4+} , which results in peaks at 1460, 1741, and 1640 cm^{-1} in FT-IR spectra and no evidence of Si-F bond (which usually places at 945 cm^{-1} [26]) is observable [27-29].

Si^{4+} cations are replaced by Al^{3+} and form peaks at 1160 cm^{-1} , which overlaps with the peak of asymmetric-stretching Si-O-Si bonds [30].

It is obvious in Figure 5 that the transmittance of overall FT-IR spectrum changes for varying amounts of BaF_2 in the glass composition. In fact, the glass network gets weaker in the case of higher BaF_2 content and thus, the absorption of the whole spectrum increases [31]. In spite of the absorption of silicate bonds, fluorine-based bonds, i.e., Ba-F, and Al-F, do not demonstrate a very significant sharpening for the GBF40 sample. As discussed above, fluoride ions bond to Al^{3+} and Ba^{2+} cations. Bonding to Al^{3+} reduces fluorine loss in

oxyfluoride glasses [9]. In sample GBF40, Al_2O_3 amount is higher than that of GBF30. Therefore, the lower Al^{3+} ions per fluoride anions causes higher fluorine loss, and consequently, the intensity of fluoride-based bonds does not change as it was expected. Fluorine loss analysis also confirms this claim. In other words, fluorine loss in GBF40 is 38% while it is only 25% for GBF30.

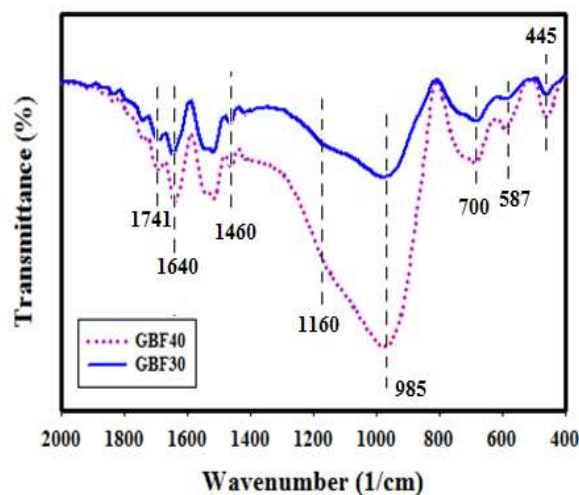


Figure 5. FT-IR spectra of GBF40 and GBF30 samples

4. CONCLUSIONS

- 1- According to DTA results, the crystallization temperature for GBF30 glass (693 $^{\circ}\text{C}$) was higher than the GBF40 (678 $^{\circ}\text{C}$) sample, which implies the more depolymerization of glass network in presence of higher fluoride content.
- 2- The only precipitated crystalline phase at the first peak temperature of both samples was BaF_2 .
- 3- Due to the Rayleigh and Mie scattering effect of phase-separated parts in the GBF40, band edge shifts to higher wavelengths.
- 4- Owing to the lower amount of Al_2O_3 in GBF40, higher fluorine loss occurred in comparison with GBF30 sample.

5. ACKNOWLEDGEMENTS

We would like to show our gratitude to Farhad Ghanbari, the chemistry service laboratory assistant of University of Tabriz for assistance with spectroscopic studies.

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The Impact of Current Density of Electroplating on Microstructure and Mechanical Properties of Ni-ZrO₂-TiO₂ Composite Coating

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PAPER INFO

Paper history:

Received 15 December 2019
Accepted in revised form 03 February 2020

Keywords:

Composite Coating
TiO₂
ZrO₂
Current Density
Abrasive Resistance

ABSTRACT

Metallic composite coatings with ceramic particles can be used to improve the mechanical and corrosion properties of steel. In the present research, Ni-ZrO₂-TiO₂ composite coating was fabricated on AISI 430 stainless steel through the electrodeposition method. The effect of the current density of electroplating (15, 17, 20, and 23 mA.cm⁻²) was investigated on the microstructure and mechanical behavior of coated steel. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to study the morphology and phases. Micro-hardness was measured by the Wickers method, and wear behavior was evaluated by the pin-on-disk test. The results showed that the deposition of TiO₂ and ZrO₂ ceramic particles in the composite coating increased and then decreased by increasing the applied current density up to 20 mA.cm⁻². Similar trends were observed for the variations in hardness and wear resistance of the composite coating. According to the results, the use of Ni-ZrO₂-TiO₂ composite coating on AISI 430 stainless steel improved the mechanical properties.

1. INTRODUCTION

Composite coatings are deposited on various steel substrates to improve the properties such as corrosion and wear resistance. Stainless steel is among the most widely used types of steel in various industries, and therefore, a great deal of research has been done on the coating of stainless steel [1,2].

Metal-based composite coatings are fabricated throughout both electroplating and electroless method. Neutral particles (TiO₂, ZrO₂, SiO₂, SiC, Al₂O₃, etc.) that are suspended in an electric bath can be coincidentally deposited during electroplating. The obtained composite coatings will have higher physical and mechanical properties, such as higher wear and corrosion resistance than pure metal coatings [3].

Since in the composite coatings the properties of the matrix and the secondary particles are combined, special properties such as good strength at high temperature, high thermal conductivity, and low thermal expansion coefficient are obtained [4].

In a study by Hong et al., it was reported that factors such as the concentration of particles in the plating bath, the applied current density, and the pH of the plating bath affect the amount of particle deposition in the coating, the crystalline size, and the mechanical properties of the coating considering the microstructure. Wang et al. investigated the effect of cathodic current density on the weight percent of TiO₂ particles when the particle concentration in the electrolyte is 30 g.L⁻¹. Their results showed that the weight percent of TiO₂ particles initially increased with increasing cathodic current density until it reached the maximum value as much as 5A.dm⁻². As the current density increases, the amount of TiO₂ particles decreases [5].

Qu studied the effect of current density on the amount of CeO₂ particles deposited on Ni-CeO₂ composite coatings. Their results showed that the amount of CeO₂ particles decreased as the current density increased [6]. Titanium oxide is one of the most important particles due to the low thermal expansion coefficient, favorable mechanical properties, and excellent chemical stability at all temperatures as reinforcement to nickel-

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phosphorus coatings [7]. Saravanan et al. [8] showed that titania particles have a great impact on the growth process and the phase structure of the nickel-phosphorus coating, which increases the corrosion resistance. They also showed that adding more amounts of alumina would increase the porosity of the coating and reduce the corrosion resistance.

The reactive element and its oxides can greatly reduce the oxidation rate and increase the resistance of the alloy to cracking [9]. This is commonly known as the reactive element effect, and reactive elements are added to the surface by ion implantation or to the surface as oxide when added as metal alloying elements, oxide dispersion [10,11]. Zirconium is the common reactive element used in composite coatings. Studies have shown that coatings with ZrO_2 significantly reduce the oxidation rate of stainless steel and increase the performance of SOFC interconnects [12].

Laszczyńska et al. [13] investigated the effect of ZrO_2 on the characterization of electrodeposited Ni-Mo- ZrO_2 composite coatings. They reported that ZrO_2 oxide modified the structure and adhesion of Ni-Mo coating [13]. In the recent research by Khoran et al. [14], they investigated the addition of TiO_2 oxide on the microstructure and oxidation behavior of Ni- TiO_2 composite coating. Their studies showed that the addition of TiO_2 to nickel coating decreased in grain size and improvement of oxidation behavior [14]. In another study, Saiedpour et al. [15] investigated the effect of ZrO_2 particles on oxidation and electrical behavior of Co coatings electroplated on ferritic stainless steel interconnect. Their results showed that the addition of ZrO_2 to cobalt coating improved the structure and oxidation behavior of the steel [15].

According to previous studies and a survey of the literature, no Ni- ZrO_2 - TiO_2 coating has been fabricated on AISI 430 steel substrate so far. The presence of titanium oxide and zirconium oxide is expected to improve the mechanical properties of the coating.

In the present study, Ni- ZrO_2 - TiO_2 composite coating was deposited on AISI 430 steel substrate by the electrodeposition method. Then, the effect of applied current density on microstructure and mechanical properties were investigated. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to determine the microstructure. Finally, a pin on the disk test was performed to evaluate the wear behavior of these coatings.

2. EXPERIMENTAL PROCEDURES

In this study, AISI 430 stainless steel with the chemical composition was used that is given in Table 1. Samples with dimensions of 2mm×10mm×10mm were used as the substrate for coating and pure nickel sheet (purity above 99%) with dimensions as much as 20mm ×20

were used as the anode. Pre-plating preparation of the samples was performed according to the ASTM B254 standard by first polishing the steel plates with abrasives 400, 600, 800, 1200, and 2500.

TABLE 1. Chemical composition of AISI 430 stainless steel (wt%)

Element	Concentration (wt. %)
C	0.12
Cr	17.10
Mn	0.92
Si	0.50
P	0.02
S	0.023
Fe	Bal

The samples were placed in an acetone solution for 10 minutes after washing with distilled water. Then, they were washed again with distilled water and finally etched in 10% sulfuric acid solution for 90 seconds and washed with distilled water after extraction. The samples were placed in the coating bath immediately after preparation. The composition of the bath and the electroplating conditions for the Ni- ZrO_2 - TiO_2 composite coating are presented in Table 2.

In this operation, the bath components were first weighed by a digital scale (GF-300 model), and then, added to a 100 ml beaker by adding distilled water. ALFA-HS860 magnetic stirrer was used to mix the materials. The PROVA 8000 power supply was used to generate power. The pH of the solution was adjusted using sulfuric acid or sodium hydroxide and the pH meter of model AZ 8686 was used to control it. Samples were plated at Watts bath at current densities as much as 15, 17, 20, and 23 mA.cm⁻². The samples were washed with distilled water and dried using a dryer after plating. Microscopic analysis of the samples was carried out using a Scanning Electron Microscope Model Cam Scan MV 2300 equipped with EDS analysis. The morphology of the samples was investigated by SEM at a voltage as much as 20KV.

Phases were identified using a Philips X-ray diffraction device with Cu K α radiation ($\lambda=0.1542$ nm). The XRD patterns of the samples were analyzed using X-Pert software.

Two methods were applied to check the wear resistance of the coated samples. In the first method, each sample was weighed before and after the abrasion test by a scale of four decimal places. The wear behavior of Ni- ZrO_2 - TiO_2 composite coating was studied by the pin-on-disk wear. The wear test was performed by the pin-on-disk method with a distance of 100 and a disk rotation speed as much as 0.03 m.s⁻¹. The mass change of the samples before and after the wear test was measured using a scale

of four decimal places. The friction coefficient results were analyzed using CDT125 software. All wear tests were done based on ASTM G 99-17 and previous studies [8].

Microhardness of the samples was determined using a Shimadzu hardness tester and applied force as much as 50g for 10s.

TABLE 2. Composition and bath conditions for Ni-ZrO₂-TiO₂ composite coating

Coating Mixtures		Electrodeposition Parameters/Materials	
NiSO ₄ .6H ₂ O	280.00 g/L	Current density	15, 17, 20, 23 mA.cm ⁻²
NiCl ₂ .6H ₂ O	40.00 g/L	pH	3.5
H ₃ BO ₃	40.00 g/L	Plating time	20 min
CoSO ₄ .7H ₂ O	6 g/L	Plating temperature	50±5 °C
ZrO ₂	3, 5, 7, 9 g/L	Cathode	AISI 430 stainless steel
TiO ₂	3, 5, 7, 9 g/L	Anode	Nickel plate

3. RESULTS AND DISCUSSION

3.1. Influence of Current Density on Structure

3.1.1. Deposition of ZrO₂ and TiO₂ Particles

Figure 1 shows the impact of current density on the deposition of ZrO₂ and TiO₂ particles in Ni-ZrO₂-TiO₂ composite coating at concentrations of 5 g.L⁻¹ ZrO₂ and 7 g.L⁻¹ TiO₂, and pH as much as 3.5. As can be seen the deposition is increased by increasing the current density up to 20 mA.cm⁻² due to the increased mobility of the ZrO₂ and TiO₂ particles. The maximum particle deposition amount was obtained at the current density as much as 20 mA.cm⁻². The electrophoretic force for moving of ZrO₂ and TiO₂ particles toward the cathode is low at low current densities, resulting in lower particle deposition at low densities.

According to the Guglielmi model [11,14], the particle inclusion in metal matrix from an electroplating solution occurs in two consecutive steps of adsorption, including the "loose adsorption" and "strong adsorption of the particles. The first step is a loose physical adsorption of the particles on the cathode with a high degree of coverage and without the discharge of electro-active ions adsorb on the particles. The fractional coverage follows a Langmuir adsorption isotherm. The second step is the strong electrochemical adsorption of the particles caused by the applied electrochemical field, which is accompanied by the discharge of electro-active ions. Both steps take place at the same time all over the cathode surface. If a particle is strongly adsorbed on the

cathode, it will be embedded in the growing metal layer by the electrodeposition of free solvated electro-active ions from the plating bath.

As stated by the Guglielmi model, the particle movement increases with increasing current density. This increase in particle movement causes the ZrO₂ and TiO₂ particles to leave the surface before the second stage adsorption is completed and the particle deposition decreases. Particles recede is due to the high activity of ZrO₂ and TiO₂.

This is due to the high activity of the particles of ZrO₂ and TiO₂ [16]. The nickel ions dissolved in the anode are transported faster than the ZrO₂ and TiO₂ particles traveling with mechanical turbulence at densities higher than the optimum current density (20 mA.cm⁻²), which, thus, reduces the particle deposition of ZrO₂ and TiO₂ in the coating. In the coating [17], the increase in current density causes the release of hydrogen on the cathode surface, which forms the hydrogen bubbles. These bubbles prevent the deposition of particles on the cathode surface and reduce the amount of Co absorption [18].

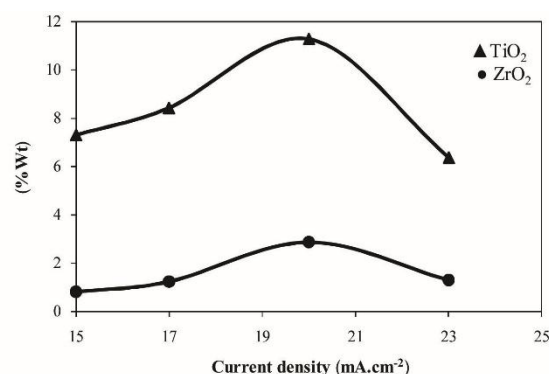


Figure 1. Particle deposition value as a function of current density at concentrations of 5 g.L⁻¹ ZrO₂ and 7 g.L⁻¹ TiO₂ and pH as much as 3.5

3.1.2. Surface Morphology

Figure 2 shows the effect of current density on the morphology of Ni-ZrO₂-TiO₂ composite coatings. As can be seen the content of ZrO₂ and TiO₂ particles in the coating increases by increasing the current density from 15 to 20 mA.cm⁻². There is a drop in the deposition of both particles at current densities more than 20 mA.cm⁻². The decrease in a deposition is due to the release of hydrogen at high current density.

The XRD results of the Ni-ZrO₂-TiO₂ composite coating at different current densities at the concentration as much as 5 g.L⁻¹ ZrO₂ and 7 g.L⁻¹ TiO₂ in the electrolyte and pH=3.5 are shown in Fig. 3. As can be seen, the available phases are Ni (JCPDS, Card No. 001-1266), ZrO₂ (JCPDS, Card No. 014-0534), and TiO₂ (JCPDS, Card No. 021-1236). However, the observed peaks of Fe

(JCPDS, Card No. 003-1050) are related to the substrate.

It is obvious that the grain size decreases with increasing current density. Figure 2a shows the SEM image of a sample electroplated at a current density as much as 15 mA.cm^{-2} . As shown, the coating is not uniform and some agglomeration is observed. At the current density as much as 17 mA.cm^{-2} , the irregularity of the coating is less and the coating is more uniform than the obtained value at the current density as much as 15 mA.cm^{-2} . The coating obtained at a density as much as 20 mA.cm^{-2} is uniform without cracking and agglomeration. The coating is not uniform at $i=23 \text{ mA.cm}^{-2}$ and the agglomeration is observed in some places.

Maud software was employed to investigate the effect of current density on phase formations based on the

XRD patterns. The amount of precipitated ZrO_2 and TiO_2 was calculated by Maud software. The outputs of the Maud software were consistent with the results of SEM images and XRD analysis. As can be seen the number of ceramic particles ZrO_2 and TiO_2 to the current density as much as 20 mA.cm^{-2} increased by increasing the current density. The SEM images also show that the grain size decreased and the structure was fine by increasing the concentration of ceramic particles ZrO_2 and TiO_2 up to the current density as much as 20 mA.cm^{-2} . As the current density increases, the peak intensity of the ZrO_2 and TiO_2 phases increases up to 20 mA.cm^{-2} , indicating an increase in the deposition of these particles in the composite coating. This was also observed in other studies [16,17].

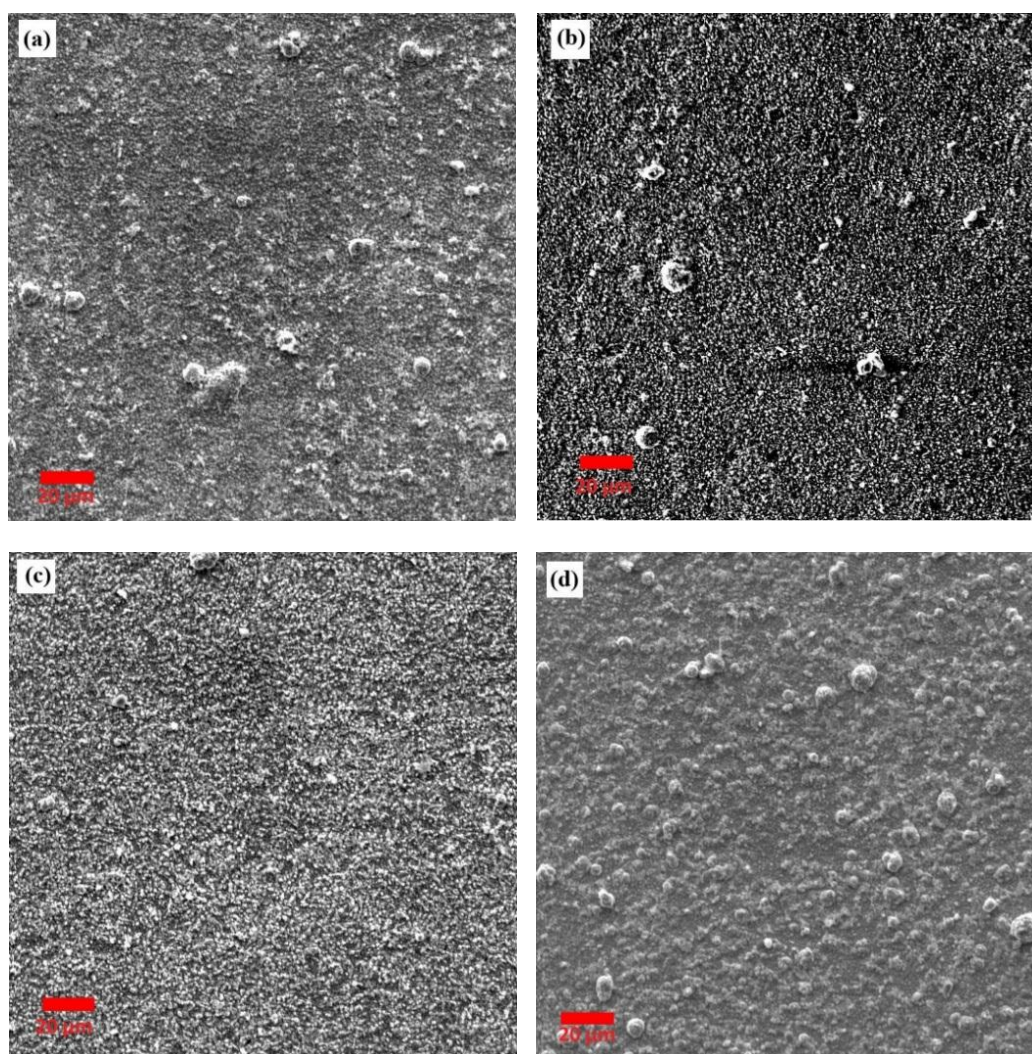


Figure 2. Surface morphology of Ni-ZrO₂-TiO₂ coating deposited under different current densities. a) 15 mA.cm^{-2} , b) 17 mA.cm^{-2} , c) 20 mA.cm^{-2} , and d) 23 mA.cm^{-2}

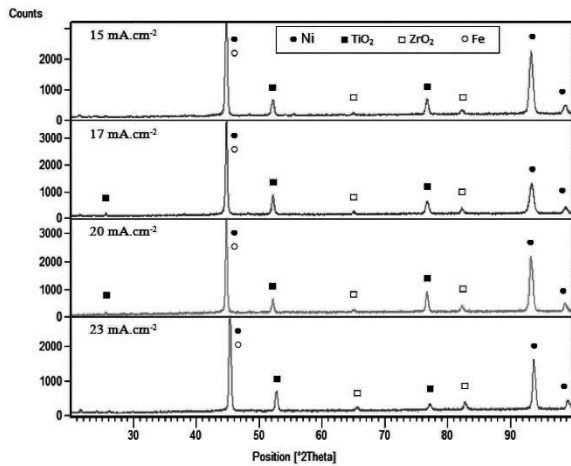


Figure 3. XRD results of Ni-ZrO₂-TiO₂ composite coating at different current densities

3.1.3. Grain Size

The grain size was calculated by the Williamson Hall equation using Equation (1) and Sigma Plot software [17, 18]:

$$\beta \cos \theta = (0.9 \times \lambda) / d + 2 \sin \theta \quad (1)$$

where λ is the x-ray wavelength in angstrom (1.5406 Å), d is the crystallite size, β is the maximum peak width at half the height of the peak, θ is the bragg angle corresponding to the peak, and A is a constant (usually one).

Fig. 4 shows the effect of current density on the grain size of Ni-ZrO₂-TiO₂ composite coating at the concentration as much as 5 g.L⁻¹ ZrO₂ and 7 g.L⁻¹ TiO₂ in the electrolyte and pH=3.5. As can be seen the grain size decreases by increasing current density from 15mA.cm⁻² to 20 mA.cm⁻². Increasing the current density above 20 mA.cm⁻² increases the grain size. The obtained grain size at the current density as much as 20 mA.cm⁻² is about 17nm.

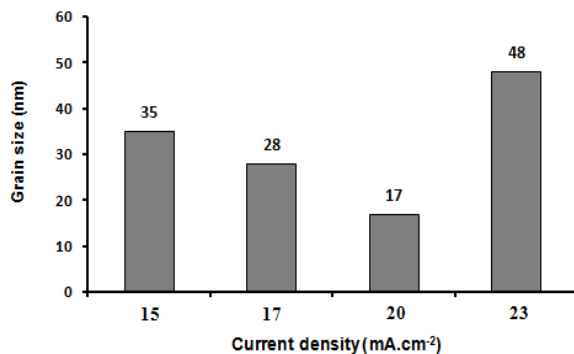


Figure 4. The Influence of current density on the grain size of Ni-ZrO₂-TiO₂ composite coating

According to Equation 2, the nucleation rate increases by increasing current density overvoltage increases and according to equation 3 with increasing overvoltage. The grain size decreases with increasing nucleation rate. Also according to equation 4 the critical radius of nucleation decreases by increasing overvoltage [5,7]:

$$\eta = a + b \log i \quad (2)$$

$$j = K1 \exp[-bs\varepsilon^2/zekT\eta] \quad (3)$$

$$r = s\varepsilon/z\eta \quad (4)$$

In Equation (2) η is the overvoltage, a and b are constant, and i is the current density.

In equations (3) and (4), j is the nucleation rate, b is the geometrical factors of the cluster shape, s is the area occupied by an atom, ε is the specific edge energy, z is the ion capacity, e is Electron flux, k_1 is constant and k is Boltzmann constant.

In electrochemistry, overvoltage is the potential difference (voltage) between the determined thermodynamically reduction potential of half-reaction and the potential at which the redox event is experimentally observed [18,19]. The term is directly related to a cell's voltage efficiency. In an electrolytic cell, the existence of overvoltage implies the cell requires more energy than thermodynamically expected to drive a reaction.

In fact, J was given by Equation (2) according to the classical theories on electrochemical phase formation and growth, the two dimensional (2D) nucleation rate. Regarding crystallization theory, crystallization in an electrodeposition process usually involves two steps. The first step is about the discharge of nickel ions and the generation of nickel atom. There are two scenarios in the second step, (i) the incorporation of nickel atom into the crystal and crystal growth, and (ii) the formation of the new nucleus when the rate of crystal growth may not be sufficient to cater for a generation of atoms. It has been proved that r is a function of the overvoltage in the critical radius of the surface nucleus [19-21].

On the other hand, the number of nucleation sites is increased with increasing particle deposition on the cathode surface, resulting in smaller grain size. The movement of particles and ions increase by increasing the current density up to 23 mA.cm⁻². Therefore, prior to completing the second step according to Guglielmi's theory, they receded due to the high activity of ZrO₂ and TiO₂ as soon as they deposited. The amount of particles has reduced, the number of nucleation sites has decreased, and the previously formed nuclei have grown and resulted in more coarse grains [10].

3.2. The Impact of Current Density on Mechanical Properties

3.2.1 Microhardness of Coating

Figure 5 shows the microhardness of the coatings as a function of applied current density at concentrations as much as 5 g.L⁻¹ ZrO₂ and 7 g.L⁻¹ TiO₂, and pH=3.5. As shown, the microhardness increases and reaches its maximum value at 20 mA.cm⁻² by increasing the applied current density, which is 284.03 Vickers. Increasing the current density above 20 results in a decrease in microhardness. The microhardness reduces to 135.4 Vickers at the current density as much as 23 mA.cm⁻².

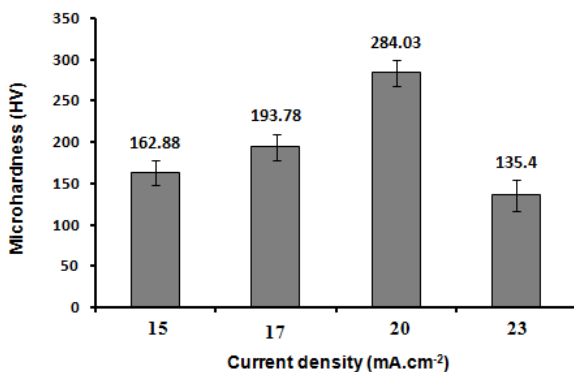


Figure 5. Microhardness changes as a function of current density at concentrations 5 g.L⁻¹ ZrO₂ and 7 g.L⁻¹ TiO₂, and pH=3.5

One of the mechanisms that increase the microhardness of the composite is the Orowan mechanism. In the Orowan equation (relation 5), λ is the distance between scattered particles, G is shear stress, and b is burgers vector. The smaller the distance between the scattered particles, the greater the shear strength. As a result, an increase in dispersed particles decreases the value of λ , which increases σ . This increase in stress increases the amount of microhardness (Equation 5).

$$\sigma = 2Gb/\lambda \quad (5)$$

High current density levels are not suitable for deposition and coating properties [20].

3.2.2. Coefficient of Friction

Figure 6 shows the effect of the concentration of ZrO₂ and TiO₂ particles on the kinetic friction coefficient of Ni-ZrO₂-TiO₂ composite coating. μ_k is the kinetic friction coefficient that opposes the range of relative motion. The kinetic friction coefficient decreases with increasing the current density up to 20 mA.cm⁻². This decrease is due to the high-deposited amounts of ZrO₂ and TiO₂ particles on the Ni-ZrO₂-TiO₂ composite coating at a current density as much as 20 mA.cm⁻². At

the mentioned density, the highest amount of ZrO₂ and TiO₂ particles are obtained by the uniform distribution. As a result, the coating is fine-grained and has the highest microhardness. The presence of particles in the coating reduces the contact area between the pin and the coating surface, and reduces the coefficient of friction. The coefficient of friction increases by increasing current density to 23 mA.cm⁻² due to the decrease in particle deposition [21].

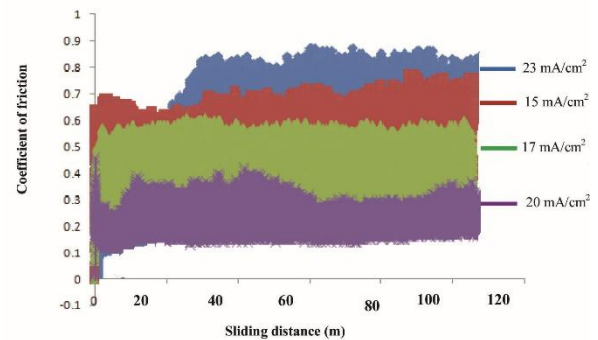


Figure 6. Influence of current density on kinetic friction coefficient at 100m

3.2.3. Wear Resistance

Figure 7 shows the weight loss of Ni-ZrO₂-TiO₂ composite coating based on current density. The weight of the samples decreases by increasing the current density up to 20 mA.cm⁻². The lowest weight loss at the current density as much as 20 mA.cm⁻² is 0.2 mg. This procedure follows Archard's Law (Equation 6) [22]:

$$W = k(P_n L)/H \quad (6)$$

Where W is the sample weight loss after wear test, k is coefficient of wear, P_n is normal pressure in wear test, L is the distance traveled in wear test, and H is the hardness of the sample.

According to Archard's interface, the weight loss of the sample under abrasion is directly related to the sample pressure and slips distance, which is inversely related to the hardness of the sample under abrasion. Thus, the weight loss of the sample decreased with increasing the microhardness.

Another reason is the Hall-Patch mechanism, which is based on grain size. The highest microhardness was observed at the current density as much as 20 mA.cm⁻². The microhardness and wear resistance decreases with increasing the distance from each side as the grain size increases and the deposition rate of ZrO₂ and TiO₂ particles decreases.

Another reason is that according to the Orowan equation, the particles in the coating prevent the plastic deformation of the coating by preventing the

deformation of the particles. This is due to the dispersion of the particles in the coating, and consequently, increasing the microhardness and wear resistance [23].

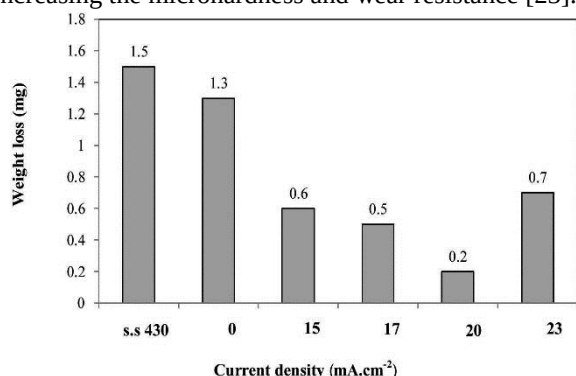


Figure 7. The Influence of current density on the weight loss of Ni-ZrO₂-TiO₂ composite coating

4. CONCLUSION

The Ni-ZrO₂-TiO₂ composite coating was fabricated on AISI 430 stainless steel at different current densities as much as 15, 17, 20, and 23 mA.cm⁻², and the following results were obtained:

1. Their deposition amount was increased by increasing the current density up to 20 mA.cm⁻² due to the increased mobility of the ZrO₂ and TiO₂ particles. The maximum particle deposition value was obtained at the current density as much as 20 mA.cm⁻².
2. The number of nucleation sites increased with increasing particle deposition on the cathode surface and the grain size was decreased as the number of nucleation sites increased.
3. The lowest kinetic friction coefficient was obtained for the coated samples at the current density as much as 20 mA.cm⁻². This was due to the highest deposition of ZrO₂ and TiO₂ particles on the Ni-ZrO₂-TiO₂ composite coating at a current density as much as 20 mA.cm⁻².
4. The wear resistance was increased by increasing the current density of coating up to 20 mA.cm⁻². Wear resistance was increased by increasing the microhardness due to the increase in ceramic particles of ZrO₂ and TiO₂.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial supports given by the University of Shahid Bahonar of Kerman.

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Crude Oil Interfacial Tension Reduction and Reservoir Wettability Alteration with Graphite or Activated Carbon/Silica Nanohybrid Pickering Emulsions

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PAPER INFO

Paper history:

Received 16 July 2019
Accepted in revised form 8 February 2020

Keywords:

Pickering Emulsion
Nanohybrid
Graphite
Activated Carbon
Silica
Chemical Enhanced Oil Recovery (C-EOR)

ABSTRACT

In this research, two carbon structures silica nanohybrids Pickering emulsions were prepared. Graphite and activated carbon were carbon allotropes with different morphologies of laminar and spherical, respectively. The effect of carbon morphology investigated on the related silica nanohybrids Pickering emulsions for C-EOR. Therefore, nanohybrids were prepared with graphite and activated carbon through the sol-gel method based on different weight percents and two different methods. X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), and Thermal Gravimetric Analysis (TGA) used to characterize the synthesized samples. Pickering emulsions of these nanohybrids were prepared by utilizing octane as oil model, suitable anionic surfactants and an alcoholic co-surfactant with pH=7 at room temperature using distilled water. The apparent stability of Pickering emulsion studied over a period of one month. The results of analyses indicated that graphite/silica nanohybrids Pickering emulsions had superior properties for C-EOR in comparison to activated carbon/silica nanohybrids Pickering emulsions. It concluded that laminar morphology is more significant than the spherical morphology of carbon structure for the mentioned purpose. According to emulsion phase morphology, the optical microscopic images showed that the best samples were 70% graphite/silica (method 2) and 50% activated carbon/silica (method 2). The results of contact angle measurement represented that the 70% graphite/silica nanohybrid (method 2) is more effective on the stone reservoir improvement, which can change the wettability from oil-wet to water-wet. Nanofluid of 70% graphite/silica nanohybrid (method 2) could reduce interfacial tension.

1. INTRODUCTION

S. Pickering discovered Pickering emulsion, which referred to as emulsion, stabilized by solid particles in 1907 [1]. Solid particles adsorbed onto the interface between the two phases [2]. The particles tend to stabilize O/W or W/O emulsions depending on whether they are more hydrophilic or hydrophobic, respectively. Effective parameters such as the particle size and the surface wettability are key factors in controlling emulsion properties [3]. Pristine carbon structures have amphiphobic nature. Therefore, they are accumulated at the water/oil interface rather than dispersing in any of the bulk phases. Silica particles have also extensively investigated regarding oil-in-water Pickering emulsions as hydrophilic emulsifiers [4].

The oxidation process causes the dispersion of graphite oxide sheets in water and other polar solvents because of functional groups such as carboxyl, epoxy and

hydroxyl in the edges [5-8]. The activated carbon is a form of carbon with low pore volumes, which increases the available surface area for adsorption or chemical reactions [9-15]. In this research, two carbon structures silica nanohybrids are prepared. Graphite silica nanohybrid shows better Pickering emulsion properties for C-EOR in comparison with similar silica nanohybrids prepared with activated carbon. According to the results of contact angle and interfacial tension measurement, 70% graphite/silica nanohybrid (method 2) is more effective to improve the stone reservoir wettability alteration from oil-wet to water-wet and reduce the interfacial tension.

2. MATERIALS AND METHODS

Graphite and activated carbon (commercial grade) obtained from the Nanotechnology Research Center of

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Research Institute of Petroleum Industry (RIPI). Commercial sodium silicate solution ($\text{SiO}_2/\text{Na}_2\text{O}=3.35$) was used as the precursor for silica structure. Sodium dodecylbenzene sulfonic acid (SDBS), 2-propanol and n-octane purchased from Merck Chemical Company, which used without further purification.

Morphology evaluation of the as-prepared nanohybrids performed with Field Emission Scanning Electron Microscopy (FE-SEM) by a Holland Phillips XL30 microscope. A Holland Philips X-ray powder diffraction ($\text{Cu K}\alpha$, $\lambda=1.5406\text{\AA}$) was used to record XRD patterns of the samples at a scanning speed of 2°min^{-1} from 20° to 80° . A Philips EM 208 FEG instrument operating at 90kV used to perform transmission Electron Microscopy (TEM). A Quantimet-570 microscope used to prepare optical microscopic images.

2.1. Functionalization of carbon structures

Carbon structures were acid-treated using concentrated HNO_3 . Thus, carbon structures (2g) first added to a mixture of distilled water (160ml) and nitric acid (140ml) and they allowed refluxing for 10h. The sample dried at 60°C after the filtration and neutralization with distilled water.

2.2. Synthesis of carbon structures/silica nanohybrid

2.2.1. Method 1: Addition of carbon structure in media before starting the synthesis of silica nanoparticles

Suitable amount of the functionalized carbon structure for 70wt%, 50wt%, and 10wt% nanohybrids were dispersed individually in 2.5% HCl solution (30ml) in ambient temperature. After this step, sodium silicate (2-3ml) added to the mixture. The solution washed with distilled water and then, dried at 60°C after mixing for about 5h.

2.2.2. Method 2: Addition of carbon structure during silica nanoparticles synthesis steps

Sodium silicate (2-3ml) first dissolved in 2.5% HCl (30ml) at ambient temperature. The suitable amount of the functionalized carbon structure for 70wt%, 50wt%, and 10wt % nanohybrids was then dispersed in 2.5% HCl solution (30ml) in ambient temperature. The solution washed with distilled water and then dried at 60°C after mixing about 5h.

2.3. Preparation of Pickering emulsions

Nanohybrid (0.05g) dissolved in distilled water (50ml) and then sonicated for 10 minutes in an ultrasonic bath.

Afterward, SDBS (0.15g), 2-propanol (3ml) and n-decane (3ml) added to the solution as the model oil and the mixture sonicated for 10 minutes again. The stability of Pickering emulsions of these nanohybrids studied over a period of one month.

3. RESULTS AND DISCUSSION

3.1. Modification of carbon structure

The hydrophilicity of carbon structure was enhanced by modification with nitric acid to produce O/W emulsion. The amount of oxygenated groups on the surface of the carbon structure related to the treatment time with HNO_3 . Oxygen containing groups (e.g., alcohols) are located on the surface and edges of graphite sheets as well as the surface of activated carbon.

3.2. Synthesis of carbon structures/silica nanohybrids

Nanohybrids determined by XRD, SEM, and TGA analyses with the most emulsion stability. Figures 1a, 1b, and 1c, show XRD patterns of silica nanoparticles, 70% graphite/silica nanohybrid (method 2) and 50% activated carbon/silica nanohybrid (method 2), respectively. As shown in Figure 1a, silica nanoparticles have amorphous structures with a broad peak at 24° [16]. Figure 1b shows that 70% graphite/silica nanohybrid (method 2) has a crystalline structure with two main peaks at 31° and 64° , indicating that the carbon phase dominates the silica phase. In addition, 50% activated carbon/silica nanohybrid (method 2) has an amorphous structure (Figure 1c).

Figures 2a, 2b, and 2c show the SEM images of silica nanoparticles, 70% graphite/silica nanohybrid (method 2) and 50% activated carbon/silica nanohybrids (method 2), respectively. As observed in Figure 2a, spherical silica nanoparticles have been formed with diameters as much as 50 nm. Figure 2b shows that spherical silica nanoparticles attached to graphite sheets with an average diameter of 40nm (calculated with the special software program. According to Figure 2c, silica nanoparticles are perched on activated carbon.

Figures 3a and 3b show thermal Gravimetric Analysis (TGA) results of 70% graphite/silica nanohybrid and 50% activated carbon/silica nanohybrid in a nitrogen atmosphere with $0.1^\circ\text{C.min}^{-1}$ temperature rate increase, respectively. The diagram drop at 100°C related to the moisture outflow from the sample. Carbon structures were degraded at about $260\text{--}270^\circ\text{C}$. The Silica nanoparticles remain stable even at 800°C due to their high thermal stability.

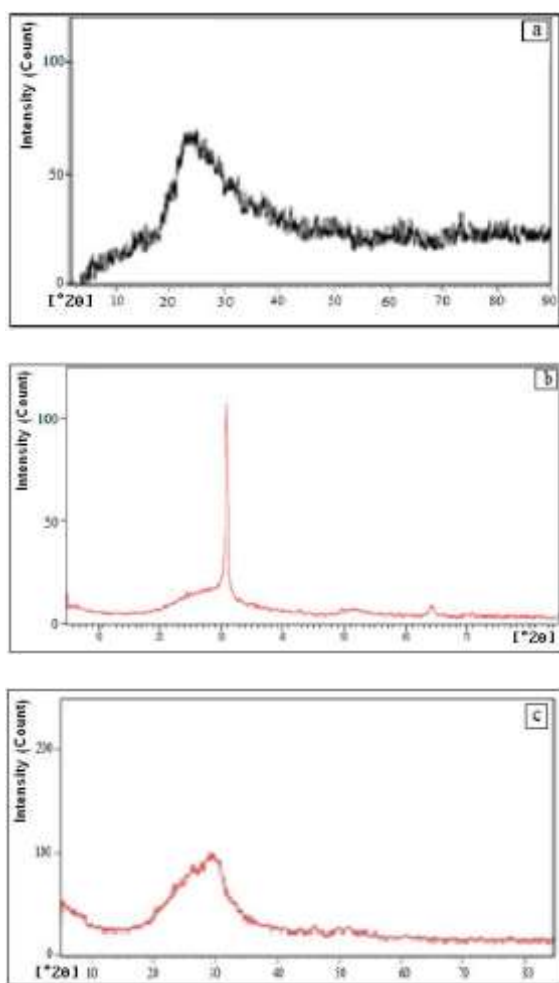


Figure 1. XRD patterns of (a) silica nanoparticles (b) 70% graphite/silica (method 2) (c) 50% activated carbon/silica (method 2)

This result suggests that the assemblies of silica nanoparticles have good stability on MWCNT which is attributed to the unique structure. Two kinds of binding forces may exist between the silica and MWCNT. Silica precursors would adsorb onto the walls of MWCNT during the sol-gel process due to the porous nature of MWCNT, and eventually the silica nanoparticles would physically anchor onto the MWCNT. On the other hand, as there are defects on the walls of MWCNT (e.g., hydroxyl group existing on the defects), some silica precursors would covalently bond to MWCNT. Nanohybrids prepared by the addition of a carbon compound during the silica nanoparticle preparation through the sol-gel method via two different mixing methods:

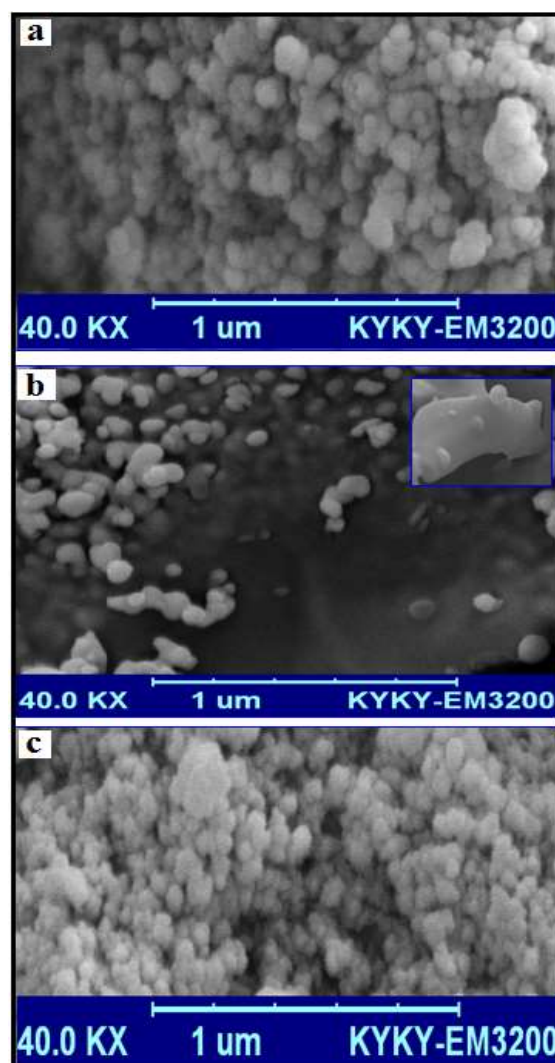


Figure 2. SEM images of (a) silica nanoparticles (b) 70% graphite/silica (method 2) (c) 50% activated carbon/silica (method 2)

bond to MWCNT. The OH groups act as the centers of molecular adsorption during their specific interaction with adsorbents capable of forming a hydrogen bonding with the OH groups or undergoing donor-acceptor interaction. On the SiO_2 surface, there also exist surface siloxane groups or $-\text{Si}-\text{O}-\text{Si}-$ bridges with oxygen atoms on the surface [11].

Method 1: Addition of carbon compound before the beginning of silica nanoparticle synthesis.

Method 2: Addition of carbon compound during the step of synthesizing silica nanoparticle.

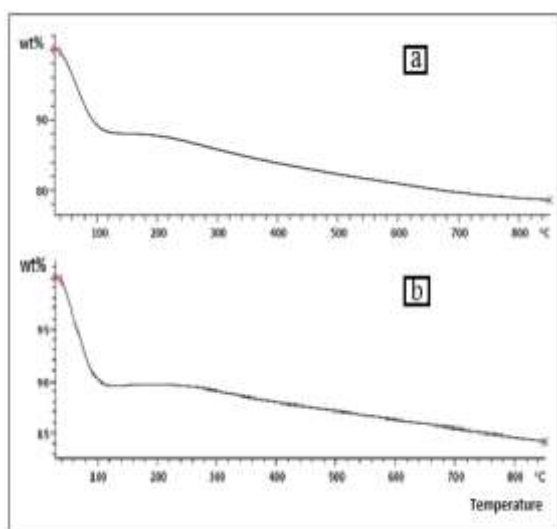


Figure 3. Thermal Gravimetric analysis (TGA) of (a) 70% graphite/silica (method 2) (b) 50% activated carbon/silica (method 2)

Figure 4 shows the schematic formation of Pickering emulsions of the as-prepared nanohybrids. Nanohybrids act as surfactants in oil recovery processes and they can reduce the interfacial tension (IFT) between oil and water. The emulsion stability of nanohybrids Pickering emulsions for one month, and the corresponding images have shown in Figure 5. The stability of graphite/silica and activated carbon/silica nanohybrids Pickering emulsions prepared after a month by two different methods are shown in Figures 5a and 5b, respectively.

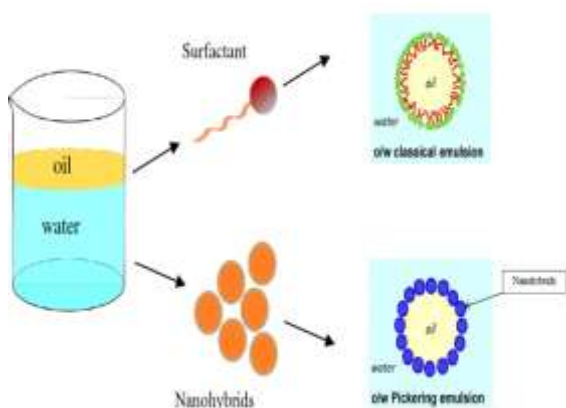


Figure 4. Schematic formation of the Pickering emulsion

Therefore, 70% graphite/silica Pickering emulsion were prepared by method 2 possesses the least precipitation

and the best stability (Figure 4a). Figure 4b shows the comparison between the emulsion stability of activated carbon/silica nanohybrids. As represented in the Figure, 70% and 50% activated carbon nanohybrid emulsions prepared by method 2 showed good stability. However, 50% activated carbon/silica had the lowest precipitation. Thus, the best stability achieved by Pickering emulsions including 70% graphite/silica nanohybrid and 50% activated carbon/silica nanohybrid prepared through method 2.

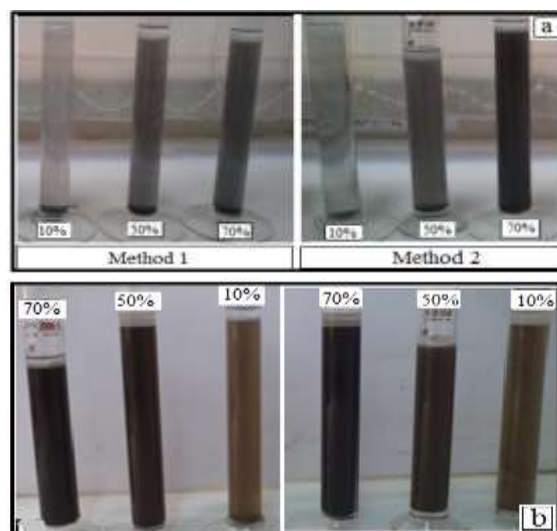


Figure 5. Nanohybrids Pickering emulsions of (a) graphite/silica (b) activated carbon/silica

Optical microscopic images of the nanohybrid Pickering emulsions have shown in Figure 6. As observed in Figure 6, 70% graphite/silica nanohybrid and 50% activated carbon/silica nanohybrid prepared by method 2 have small droplet size with spherical shape and solid particles have surrounded the droplets very well [17-19]. This can explain Pickering emulsion stability results derived for 70% graphite/silica nanohybrid. Moreover, 50% activated carbon/silica nanohybrid prepared by method 2 shows homogenously dispersed emulsion droplets with the smallest precipitation.

Figure 7 indicates that the contact angles for (a) water droplet and stone reservoir, (b) water droplet and stone reservoir with a layer of 50% activated carbon/silica nanohybrid (method 2) and (c) water droplet and stone reservoir with a layer of 70% graphite/silica nanohybrid (method 2) are 143.47, 75.03, and 65.67, respectively. As observed, the 70% graphite/silica nanohybrid (method 2) with the smallest contact angle is more hydrophilic and can better alter the carbonate reservoir rock wettability from oil-wet to water-wet.

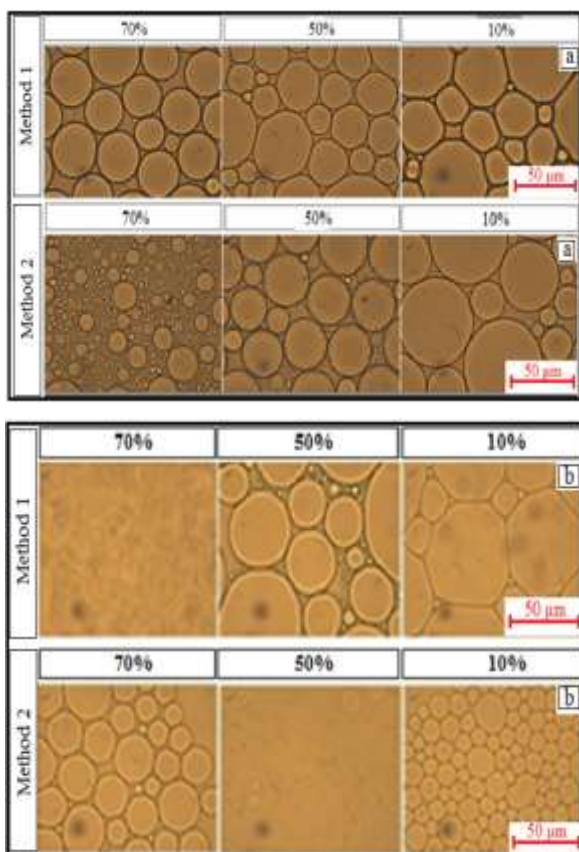


Figure 6. Emulsion phase optical microscopic images of (a) graphite/silica (b) activated carbon/silica

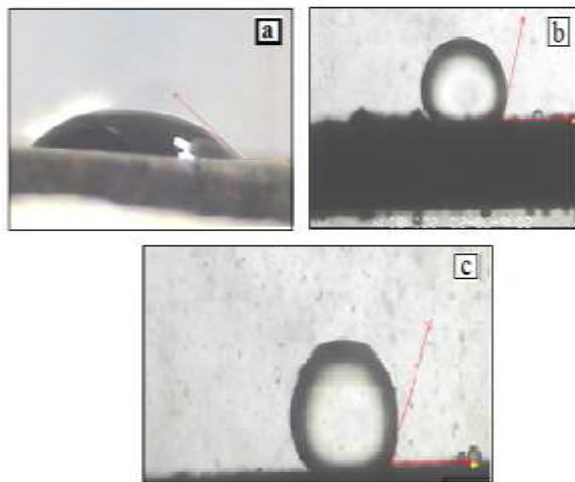


Figure 7. Contact angle between the water droplet and (a) carbonate rock reservoir (b) stone reservoir with a layer of 50% activated carbon/Silica Nanohybrid (c) stone reservoir with a layer of 70% graphite/silica Nanohybrid

The graphite layer structure can presumably be better spread on a stone reservoir compared with spherical activated carbon. Consequently, 70% graphite/silica

nanohybrid (method 2) is more effective in changing the stone reservoir wettability from oil-wet to water-wet.

As indicated by the interfacial tension results (Figure 8), the corresponding amount for injection droplet of (a) water, (b) 50% activated carbon/silica nanohybrid (method 2) and (c) 70% graphite/silica nanohybrid (method 2) are 53.90, 31.21, and 29.95 mN.m⁻¹, respectively.

The maximum amount corresponds to the injection of water, and the minimum amount is associated with the injection of nanofluid of 70% graphite/silica nanohybrid (method 2). Thus, 70% graphite/silica nanohybrid (method 2) Pickering emulsion shows the best properties in comparison with other nanohybrids investigated in this work, and therefore, it can be used in C-EOR.

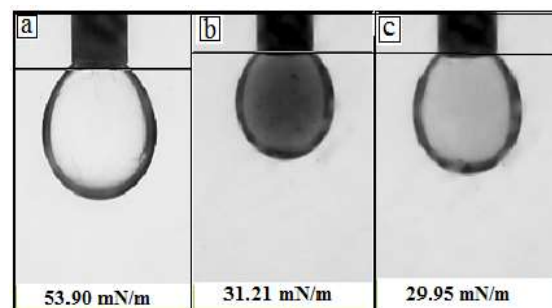


Figure 8. Interfacial Tension of (a) water, (b) 50% activated carbon/silica nanohybrid, (c) 70% graphite/silica nanohybrid

4. CONCLUSION

In this work, graphite and activated carbon nanohybrids with silica nanoparticles synthesized with different weight percentages via the sol-gel method. The corresponding nanohybrid Pickering emulsions were prepared using n-octane as the model oil, a suitable anionic surfactant (such as SDBS) and 2-propanol as an alcoholic co-surfactant at pH=7, and room temperature using distilled water. Further, the nanohybrids were prepared via two different approaches including the addition of carbon compound before the beginning of silica nanoparticle synthesis (Method 1) and addition of carbon compound during the step of synthesizing silica nanoparticle (Method 2). Optical microscopic images have been used to investigate emulsion phase morphology. The best samples were 70% graphite/silica and 50% activated/silica nanohybrids prepared by method 2, as indicated by comparison of the results. According to contact angle and interfacial tension measurement results, the 70% graphite/silica nanohybrid (method 2) was more effective on the improvement of the stone reservoir wettability alteration from oil-wet to water-

wet. The results show that 70% graphite/silica nanohybrid (method 2) Pickering emulsion was better than activated carbon/silica nanohybrids which can be applied in C-EOR.

ACKNOWLEDGMENT

This work was supported by Research Institute of Petroleum Industry (RIPI). The authors would like to express their thanks to the RIPI, Tehran, Iran for their financial support of this project.

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Addition of Alumina to Nanoporous Calcium Titanium Phosphate Glass-Ceramics and its Effects on Crystallization Behavior

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PAPER INFO

Paper history:

Received 28 November 2019

Accepted in revised form 7 March 2020

Keywords:

Phosphate Glass-Ceramics
Nanoporous
Crystallization
Alumina

ABSTRACT

Microporous Calcium Titanium Phosphate glass-ceramics have many uses in high-tech industries. For example, they have applications in catalysts industry. In this study, different molar percentages of alumina were added to a glass with P_2O_5 30, CaO 45, TiO_2 25 (mol%) composition. The samples were melted at 1350°C and crystallization heat treatment was performed on the glasses after cooling to make glass-ceramics. The Differential Thermal Analysis (DTA) was used to determine nucleation and crystallization temperature. The DTA curve of the sample had 4 molar% and alumina had the sharpest crystallization peak. The CP and CTP phases were the most crystalline phases in all samples. The soluble CP phase disappeared and the porous structure of the CPT crystals remained through the acid washing of the samples. The results showed that the addition of alumina decreased the crystallization temperature, time and temperature of crystallization, and also increased the average size of porosities (from 12 to 16 nm).

1. INTRODUCTION

Nanoporous glass-ceramics have advanced applications in various industries. They can be used in sensors [1], biomaterials [2], as well as immobilization of enzymes [3], catalysts [4], and lithium-ion batteries [5]. Calcium titanium phosphate (CTP) glass-ceramics are produced by glass heat treatment in the nominal composition of 45CaO-25TiO₂-35P₂O₅ [6]. They generally include different phases that can be referred to Nasicon-type CaTi₄(PO₄)₆ (CTP) crystals and some crystalline titanium and calcium phosphates (CP) phases. The porous material can eventually be obtained by removing these phases because the calcium phosphate phases in this ceramic glass are soluble in some acidic solutions, which can be eliminated by washing them in acid, [7]. For some applications, pores need to be controlled and resized. Some reports have shown that porosities can be resized by subsequent heat treatment. However, the surface chemistry of the pores has changed and may not be suitable for using this type of operation [8]. It has already been reported that porosities can be increased by adding cerium oxide [9]. In this study, it has been tried to increase the porosity size not sharply but moderately

and also, improve the glass in the glass. It was found that the crystallization could be improved and the pores eventually changed by adding alumina to the base glass. In this research, the crystallization behavior of ceramic glass has been investigated in the presence of alumina.

2. EXPERIMENTAL PROCEDURES

2.1. Preparation of Glass-Ceramics

The chemical composition of the base glass is 45CaO-25TiO₂-35P₂O₅ + 2Na₂O (mol%). The base glass was prepared according to Hosono's report [10]. The raw materials that were used to make the glass were reagent grade, CaCO₃ (Merck 102069), TiO₂ (Merck 100808), P₂O₅ (Merck 100540), and Al₂O₃ (Merck 106396). The first sample had 2mol% Al₂O₃ (Al2), the second had 4mol% Al₂O₃ (Al4), and the third had 6 mol% Al₂O₃ (Al6). The base glass (G) had no Al₂O₃. The batch of glass was first poured into an alumina plant to melt the glass and then, it transferred to an electric furnace. The furnace temperature was increased to 1450°C and the samples were kept at the maximum temperature for 2h. The melt was then poured into a pre-heated steel mold. The glass was kept at the maximum temperature for less

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than 2h to prevent corrosion by the molten glass. The crucible were shaken for 2 minutes before casting into the furnace to achieve a homogeneous melt. The glass samples were then transferred to another furnace at 600°C and allowed to cool in the furnace. The heat treatment should be performed on glass samples for the growth of crystals to make a glass-ceramic,. The crystalline glass samples were kept in the hydrochloric acid solution for one week after heat treatment to dissolve the dissolvable phase and leave the porous structure. The porous structure will be a porous glass-ceramic.

2.2. Nucleation and Crystallization

The nucleation heat treatment must be initially performed on the glass samples to produce glass - ceramic. This operation is consist of holding the samples at the appropriate nucleation temperature. Nucleation temperatures are typically selected between the glass temperature (T_g) and the dilatometry temperature (T_d) ($(T_g+T_d)/2$). The samples must first be kept at nucleation temperature at variable times and then subjected to the DTA test to determine the appropriate time for nucleation. After nucleation treatment, crystallization of the samples should be preformed at onset of the crystallization peak temperature where the crystallization begins (T_p-30). Then, samples crystallized at different temperatures subject to XRD analysis. Moreover, the samples should be crystallized at different period of times and the optimum crystalization time will be selected according to the amount of crystallinity .

2.3. Thermal Analyses

DTA technique (Shimadzu-DTG60AH) was used to study the thermal behavior of glass samples. The reference material in this technique was α - Al_2O_3 and the heat rise rate was set to 10°C.min⁻¹. The glass transition temperature (T_g) and the dilatometric temperature (T_d) were determined by considering the endothermic peak position in the DTA pattern [11]. The minimum temperatures at the endothermic peak, the dilatometric temperature, and the beginning of the endothermic peak were the glass transition temperatures. These temperatures were used to determine the phase separation range as well as the nucleation temperature. According to previous research, the DTA of the sample with the thinnest exothermic peak was identified as the best sample for nucleation [12].

2.4. XRD analysis

The phase analysis of the crystalline samples is performed using an XRD device. For this purpose, the samples were first powdered and tested using the XRD (Siemens-D500) at 20kV and in the 2θ ranges from 10°–60°.

2.5. Microstructure and Porosity Characterization

The samples were first polished, and then, etched in dilute hydrofluoric acid solution to investigate their microstructure. The etched samples were coated with gold using a sputtering device. Field Emission Electron Microscopy (FESEM) (Hitachi-S-4800) was then used to observe their microstructure. Moreover, porosity was determined through the BT method (Belsorp mini II).

3. RESULTS

3.1. Phase Separation

Fig. 1 shows the DTA results of the samples. The DTA exothermic peaks correspond to crystallization in glass samples. As can be observed in DTA traces, the sharpest exothermic peak with the lowest temperature belongs to the sample with 4% mol Al_2O_3 (Al4).

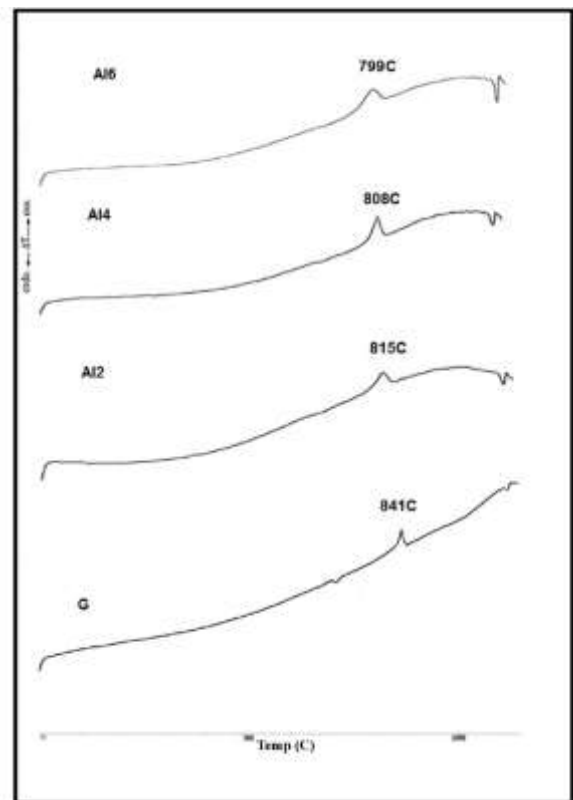


Figure 1. DTA traces of glass samples (G, Al2, Al4, and Al6)

According to the Ray and Day method [12], Al4 has the best crystallization behavior among the samples. Therefore, Al4 was suitable and selected for further studies. The base glass was crystallized according to the method of Hosono for comparison [6].

The phase separation was not observable in the glass samples even at very high magnifications by FESEM. Therefore, heat treatment was first performed at the

appropriate temperature range to encourage the phase separation process in the glass samples. It should be noted that there is a direct correlation between nucleation and phase separation in the glass-ceramics, i.e., first, there should be a phase separation in the glasses for good nucleation [9]. It was suggested that the nucleation needs a pretreatment for phase separation. The range of phase separation is between T_g and T_d . The mentioned temperatures as determined by DTA are summarized in Table 1.

TABLE 1. Glass transition (T_g) and dilatometric softening (T_d) and nucleation (T_n) temperatures of glass samples

Sample	Temperature (°C)				
	T_g	T_d	T_n	T_p	T_i
G (Base Glass)	~675	~705	690	841	1070
Al2	~668	~683	682	815	1072
Al4	~660	~675	668	808	1070
Al6	~653	~667	693	799	1071

Fig. 2 shows the DTA traces for the nucleated samples at different lengths of time.

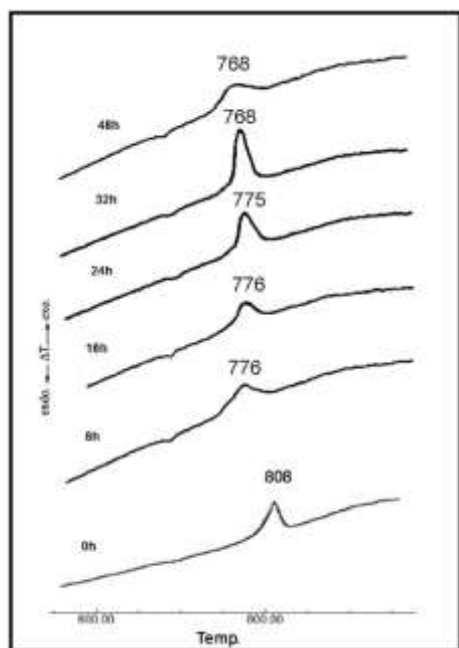


Figure 2. DTA traces for Al4 samples after nucleation heat treatment for different lengths of time (0, 8, 16, 24, and 32h)

The nucleation process was found to be effective since T_p decreased with increasing the nucleation time [7]. The T_p became wider and began to fade after 32 hours of nucleation. Therefore, it is concluded that 32 hours of nucleation is appropriate.

The microstructure of the samples was observed using FESEM to confirm the results of the DTA. Fig. 3 shows the FESEM images of the samples nucleated in different lengths of time. A sample containing 4% alumina (Al4), which had been nucleated for 32h, had a separated microstructure. This type of separation appears to be spinodal because it is more specific with longer holding time at the nucleation temperature. FESEM images of the base glass sample are shown in Fig. 3 (G32) after 32h of nucleation at 690°C for comparison. The appropriate temperature and time for nucleation of the base glass were previously reported by other researchers [7].

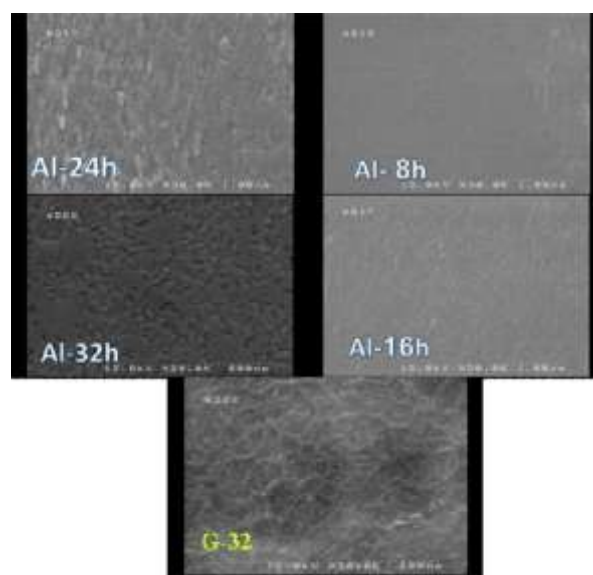


Figure 3. FESEM micrographs for the nucleation heat treatment of base glass (G) and Al4 for different lengths of time (8, 16, 24, and 32h)

3.2. Crystallization

The exothermic peaks in the DAT pattern usually reflect the crystallization in the glass samples. According to previous reports, the crystallization in this system is the bulk crystallization type [9]. Samples should, therefore, be crystallized in bulk. Glass parts were subjected to crystallization for this purpose. Interestingly, the glass changed color after crystallization operations, indicating the crystallization of glass samples.

The results showed that the optimum nucleation temperature was 668 and the optimum nucleation time was 32h. If the crystallization process is performed at the above-mentioned temperature peak (808°C), it will eventually lead to the formation of large crystals and coarse-grained microstructures. Therefore, the crystallization process should be carried out at lower temperatures. According to Fig. 1, it is clear that crystallization begins at a temperature of about 740°C.

The sample was subjected to crystallization between T_c and (T_c-30) to accurately determine the crystallization temperature, which appears to be the beginning of crystallization. For this purpose, the samples were first nucleated at 668 for 32h, and then, kept at different temperatures for 3h to get crystallized.

Fig. 4 shows the XRD patterns of some heat-treated samples according to the above program. Since glass-ceramic microstructure will ultimately determine the size of pores, it should be fine-grained as far as possible. For this purpose, the crystallization temperature should be set as low as possible. According to the XRD results, it is clear that the crystallization started at 755°C because it showed the peaks of its crystalline phases.

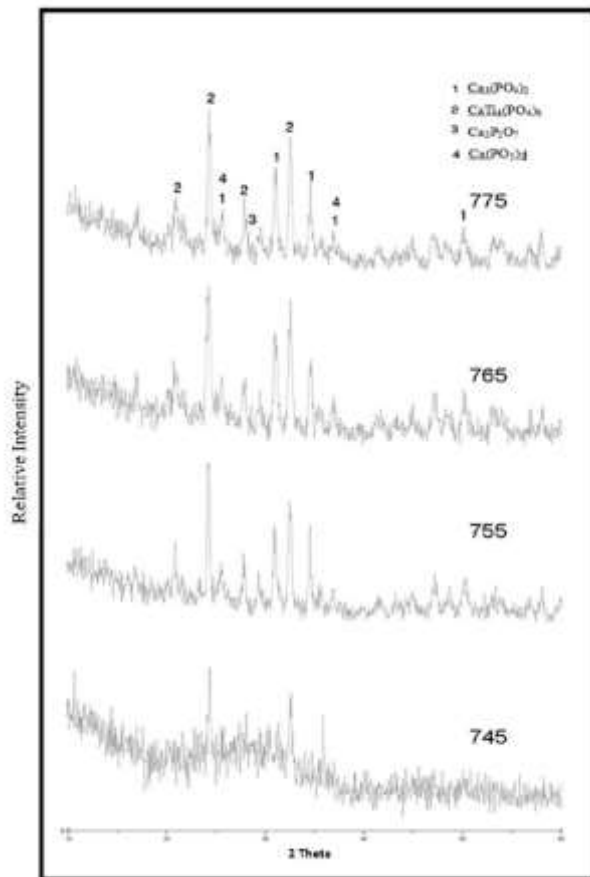


Figure 4. XRD patterns for samples heat-treated at different temperatures (745°C, 755°C, 765°C, 775°C) for 3h after nucleation at 668°C for 32h

Therefore, the temperature of 755°C was determined as the appropriate crystallization temperature. In addition, to determine the optimal nucleation time, the samples were first nucleated at 668°C for 32h, and then, crystallized at 755°C for various intervals.

Fig. 5 shows the XRD patterns of the samples. The XRD results show that the crystallization rate increases steadily from 45min to 48h. Looking closely at the results, it can be seen that the 24-hour XRD pattern is not significantly different from 48 hours. On the other hand, the FESEM results (Fig. 6) showed that the crystals grow larger from 24h to 48h. Therefore, a 24-hour crystallization time seems appropriate to prevent excessive growth of crystals.

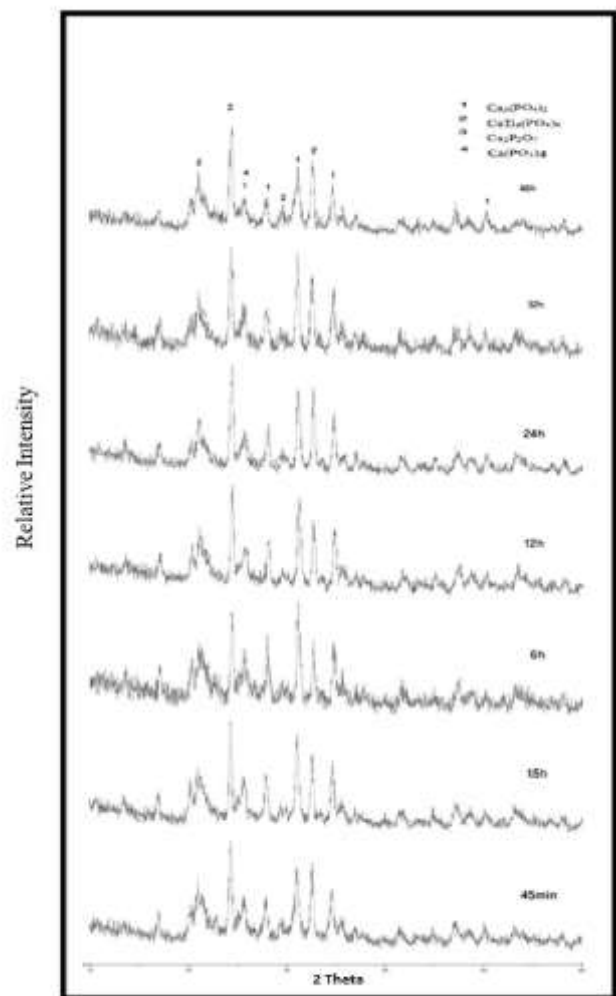


Figure 5. XRD patterns for nucleated samples at 668°C for 24h, and afterward, crystallized at 755°C for different lengths of time (45min, 1.5, 6, 12, 24, 32, and 48h)

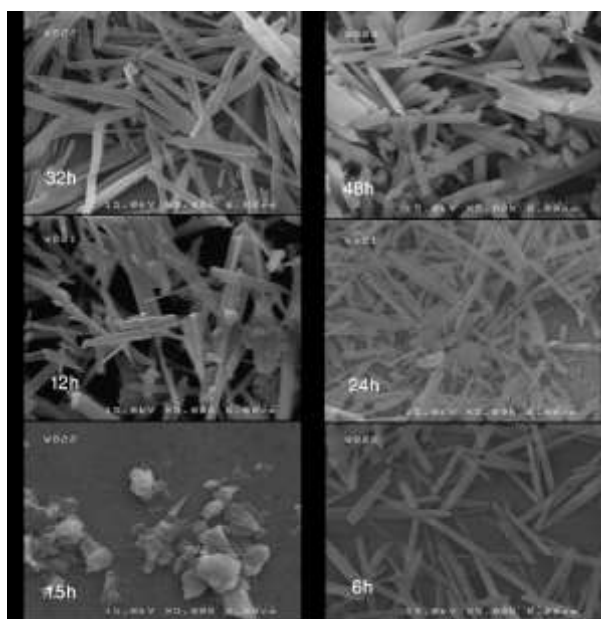


Figure 6. FESEM micrographs for nucleated samples at 668°C for 24h, and subsequently, heated at 755°C for different lengths of time (1.5, 6, 12, 24, 32, and 48h)

3.3. Leaching and Porosimetry

The prepared glass-ceramics were kept in a 1M HCl solution for one week at ambient temperature. Fig. 7 shows the porous microstructure of glass-ceramic (G) and alumina-containing glass-ceramic (Al4) after acid washing. The results of porosity analysis are presented in Table 2 through the BET method. Furthermore, Fig. 8 shows the XRD results of the Al4 sample before and after the acid washing.

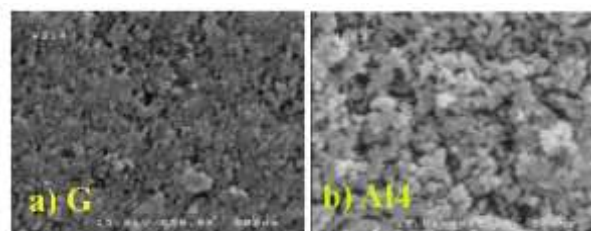


Figure 7. FESEM micrograph of crystallized samples after holding in HCl for one week: a) G and b) Al4

TABLE 2. BET results for porous glass-ceramics

Sample	G	Al4
Average pore size (nm)	12.3±2	16.1± 2
Specific surface area (m ² .g ⁻¹)	26± 3	14± 2

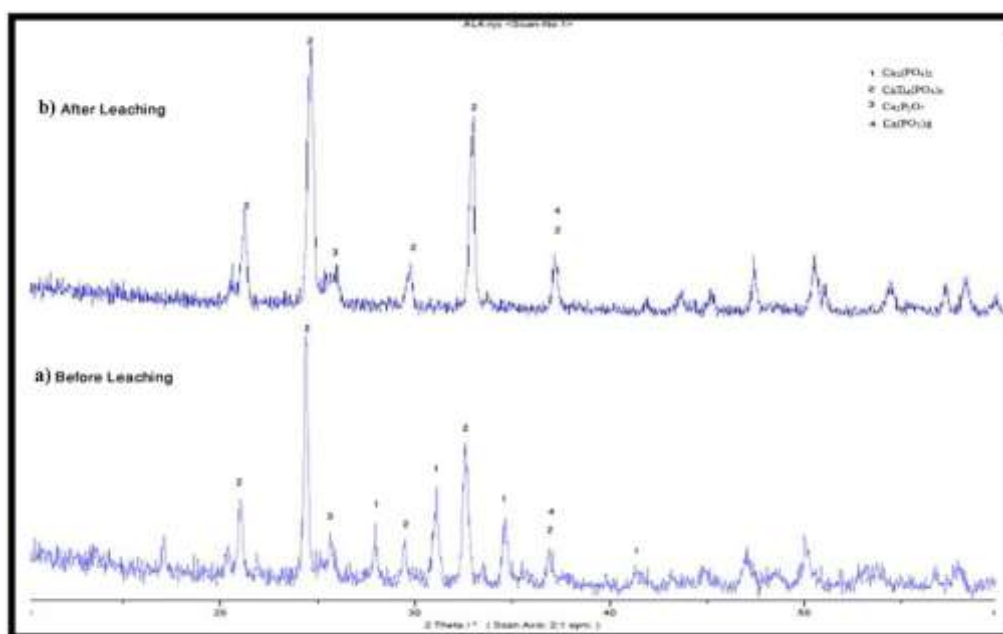


Figure 8. XRD patterns of Al4 nanoporous glass-ceramic before and after soaking in HCl for one week

4. DISCUSSION

All glasses have a violet color. This color was attributed to the existence of Ti^{4+} in the glasses [6]. There was not any change of color with adding Alumina. The glass containing 6% alumina had a more viscosity that was poured from the crucible harder than others.

The T_g increased with the addition of alumina to the base glass, which indicates the improvement of glass making. Better glass making resulted in harder crystallization and creation of larger crystals rather than finer crystals, which ultimately increased the size of the pores. This is also confirmed by the BET results (Table 2). On the other hand, the improved glass formation in this system avoided unwanted initial crystallization. Thus, the crystallization can be done arbitrarily and with greater precision.

There are a few papers that investigated the structure of the base glass-ceramic [2], which often consist of Nasicon-type $CaTi_4(PO_4)_6$ crystals and some crystalline titanium phosphates with calcium phosphate phases. T_g decreases by adding Al_2O_3 (Fig. 1). Researchers reported that T_g should increase by the addition of Al_2O_3 in phosphate glasses [13], but it seems this is not a general result. The nature of aluminophosphate glasses structures is highly dependent on the glasses composition [14]. So, it seems that a structural study is necessary to understand the main reason for the increase of T_g by adding Alumina. That study was not in the scope of this research, but further studies are under progress by the researchers of this paper. Nucleation is very important in the phosphate glass-ceramics. Fig. 3 showed that phase separation was intensified by nucleation heat treatment after a relatively long time (32 hours), but the glass may start to crystallize after a very long period of nucleation heat treatment (48 hours). Thus, it seems that 32 hours of nucleation time was quite enough. It seems that the Al_2O_3 addition keeps the interconnected spinodal microstructure by comparing the base glass with the Al4 sample in Fig. 3.

Fig. 5 shows that the formation and the growth of the major phases, $CaTi_4(PO_4)_6$, and $Ca(PO_3)_2$ are simultaneous, and Fig. 6 confirmed this observation. The comparison of Fig. 6 (1.5 hours vs. 24 hours) shows the crystallization of the samples after 1.5 and 24 hours heat treatment, respectively. The results show that the equiaxed particles eventually adopted to plate-like shapes, whereas the fibrous particles preserved their fibrous or rod-shaped morphology. There is no evidence of other phases like anatase. Also, the $\beta-Ca_2P_2O_7$ phase is very small. This is an appropriate result because $Ca_2P_2O_7$ is soluble in acid. Therefore, it can increase the pore size after leaching [15].

In the previous methods used by researchers to increase the porosity, the subsequent heat treatment process resulted in the formation of unwanted phases such as the anatase and $Ca_2P_2O_7$ phases. These phases changed the

surface chemistry and made the product inappropriate for some applications [8].

According to Fig. 7 (a), it can be seen that most pores are smaller than 100 nm. In Fig. 8, it can be seen that $CaTi_4(PO_4)_6$ and $Ca(PO_3)_2$ are the major and minor phases remaining after the soaking process and there is no evidence of the presence of the $\beta-Ca_3(PO_4)_2$ phase.

According to BET results, the average pore size is 16.1 ± 2 nm in the Al4 sample, which means the porous glass-ceramic was in the nano range. The specific surface area for this specimen was 14 ± 3 $m^2.g^{-1}$. The average pore size and the specific surface area are 12.3 ± 2 and 26 ± 3 $m^2.g^{-1}$, respectively in the base glass-ceramic (G). The pore size moderately increased by adding Al_2O_3 to the base glass. This is due to the harder crystallization, and consequently, the creation of larger crystals. These larger crystals dissolve in the acid and leave larger pores. Since there were no new additional phases in the method described in this study, the surface chemistry of the pores was similar to the base glass-ceramic, and did not change.

5. CONCLUSION

In this research, the effect of adding alumina to the base glass was investigated on the ceramic glass system. According to the studies, the glass transition temperature and the crystallization temperature of the glass samples were decreased by adding alumina to the glass. The sample containing 4% mol alumina had good crystallization behavior, which was selected for the studies. The appropriate nucleation temperature for the sample was $667^\circ C$. The time required for nucleation was 24h, while the base glass had a glass transition temperature of $675^\circ C$ and the optimum nucleation time of 32h. The most important phases created in the glass-ceramics after being washed with hydrochloric acid were the $CaTi_4(PO_4)_6$ and $Ca(PO_3)_2$ phases. It was shown that the porosity size increased from 12.3 to 16.1 and the specific surface area was also reduced from 26 to $14 m^2.g^{-1}$ by adding 4% alumina molar to the porous glass-ceramic.

6. ACKNOWLEDGEMENTS

This work was supported financially in part by the University of Tabriz. The authors also thank Mr. Rezaei, Mr. Mohamad Reza Parsa, Mr. Naser Hosseini, Mr. Yusef Karimi, and Mr. Ahad Saeedi for helping in the laboratory.

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Crystal Structure and Lattice Parameter Investigation of La^{3+} Substituted CeO_2 in $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ Synthesized by Solid-State Method

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PAPER INFO

Paper history:

Received 16 December 2019
Accepted in revised form 3 February 2020

Keywords:

$\text{La}_2\text{Ce}_2\text{O}_7$
Solid State
Synthesis
Crystal Structure
Lattice Parameters

ABSTRACT

Lanthanum (La) doped Ceria (CeO_2) has attracted considerable interest as a candidate material for thermal barrier coating (TBC) because of its low thermal conductivity and potential capability to be operated above 1250°C. In this study, $\text{La}_2\text{Ce}_2\text{O}_7$ powder was synthesized through the ball mill method. The crystal structure of La^{3+} substituted CeO_2 solid solution was investigated by X-ray diffraction in $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ ($0 < x < 0.5$). The fluorite structure of CeO_2 did not change although La^{3+} was the largest trivalent rare-earth ion. The lattice parameter changed from 5.41 to 5.59 Å by increasing La content. Changes in the lattice parameters of $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ that were compared with the theoretical values measured by XRD were obtained based on the oxygen vacancy model. The theoretical lattice parameters were larger than the lattice parameters calculated from the X-ray diffraction pattern. Moreover, the Williamson–Hall equation was used to measure the crystallite size and strain in the $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ lattice as a function of the lanthanum content. The results showed that the presence of lanthanum in the structure reduced the crystallite size.

1. INTRODUCTION

Rare-earth metals (RE)-doped ceria with fluorite structures have recently been at the center of attention, particularly due to their unique combination of electrical, catalytic, and mechanical properties [1,2]. Increased chemical stability and ion conductivity of RE-doped ceria-based materials are mainly attributed to the replacement of Ce^{4+} ions with La^{3+} , Sm^{3+} , and Gd^{3+} ions. Such a unique combination of properties cause RE-doped ceria ceramics proposed as promising candidates for much application including solid oxide fuel cells (SOFC), oxygen sensors, and catalysts [3-7]. Additionally, due to properties such as high melting point, low thermal conductivity, high coefficient of thermal expansion (CTE), favorable chemical and thermal stability, strong adhesion to metallic substrates, and low sinterability, RE-doped ceria-based ceramics are widely used as thermal barrier coatings (TBC) [8-10].

Several methods have been proposed for $\text{La}_2\text{Ce}_2\text{O}_7$ synthesis, including sol-gel, solid-State reactions, hydrothermal treatments (for 24 hours in 180°C), pressure-less sintering sol-gel (PSSG) in 1600°C for

10h, atmospheric plasma spray, electron beam physical vapor deposition (EBPVD), and high-temperature solid-state method [11,12].

High-purity (>99.99%) lanthanum oxide and cerium oxide powders were used as raw materials for the synthesis of $\text{La}_2\text{Ce}_2\text{O}_7$ bulk ceramics by Wen Ma et. al [13]. The material was sintered at 1600°C for 6 hours and the corresponded CTE was measured through the thermal cycle of 180°C.h⁻¹.

The solid-state reaction method was used by Jong Sung Bae et al. to synthesis the $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ ceramics from La_2O_3 and CeO_2 precursors, at 1400°C for 7 hours. They achieved an XRD pattern at room temperature implying a high symmetry that confirms the formation of single-phase by calcining the mixture of constituent oxide from $x=0-0.4$ [7].

The structural study of La^{3+} substituted CeO_2 , $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ solid solution has been investigated. La^{3+} has the largest size among the trivalent rare-earth ions such that the size difference between Ce^{4+} and La^{3+} is large [7,11,14]. In the case of +3/+4 oxides, the pyrochlore structure is favored, where a cation radii ratio r_A/r_B is greater than 1.42. It is also observed that the disordered fluorite structure is favorable at lower r_A/r_B value. Since

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the ionic radii of eight-coordinated La^{3+} is $1.30\text{\AA}$, and eight -coordinated Ce^{4+} is $0.97\text{\AA}$, so $r_A/r_B=1.36$. Therefore, it is expected that the fluorite structure should be observed for the mixed oxide made out of Ce^{4+} and La^{3+} . Moreover, recent studies suggest that the rare-earth doped ceria ($\text{La}_2\text{Ce}_2\text{O}_7$) has disordered defect fluorite structure [1,11,15,16]. This paper initially concerned the process of synthesizing $\text{La}_2\text{Ce}_2\text{O}_7$ powder by the ball mill method and examined the effect of milling time and heat treatment on the synthesize process. Then, the effect of changing the amount of lanthanum is investigated in the oxide mixture of $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ for $0 < x < 0.5$ on the crystal structure, crystal size, and lattice parameter. The X-ray diffraction analysis (XRD) is used to examine the microstructure of the present phases and Energy Dispersive X-ray spectroscopy (EDS) is used to verify the stoichiometric composition.

2. MATERIALS and METHOD

CeO_2 and La_2O_3 (99.5%) powders, products of Strategic Elements Co. were used as raw materials for the solid-state synthesis of LC. The powder mix—48% lanthanum oxide and 52% cerium oxide—was milled for 20 hours at 300rpm in a zirconia cup with 10:1 zirconia ball to powder ratio, and then heat-treated at 1300°C for 3 hours. The $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ ($x = 0.1, 0.2, 0.3, 0.4$, and 0.5) solid solution with different ratios of La_2O_3 and CeO_2 were synthesized to investigate the crystal structure and to study the effect of changing the Lanthanum content on the lattice parameter and crystallite size.

The crystal structures and lattice parameters of the synthesized solid solutions were studied using a Philips pw3710 diffractometer, and the chemical composition of the LC was investigated by EDS analysis. The crystallite size and strain in the $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ lattice were calculated using the Williamson–Hall equation because the broadening of the peak can be partially attributed to the finer crystallite and partially to the increased lattice strain. The crystallite size was also obtained from the Scherrer equation:

$$\beta = \lambda.K/D \cos \theta \quad (1)$$

Where, λ represents the wavelength of the X-ray, θ is the diffraction angle, K is a constant (0.9), β shows the Full Width at Half Maximum (FWHM) for the highest peak.

$$\beta_D^2 = B^2 - b^2 \quad (2)$$

The FWHM of the specimen is denoted by B , whereas b represents the FWHM for a standard silicon reference specimen [17].

According to the Scherrer equation, the broadening of the peak is a result of the crystallite size. However, the strain developing in the lattice is also a culprit of the broadening of the peak. The lattice-strain-induced change in the width of the peak can be calculated from Eq. 3:

$$\beta_s = 2A\varepsilon \tan \theta \quad (3)$$

According to these equations, the total peak broadening is:

$$B = \beta_D + \beta_s \quad (4)$$

$$\beta = \lambda.K/D \cos \theta + 2A\varepsilon \tan \theta \quad (5)$$

By multiplying both sides in $\cos \theta$, it would be:

$$\beta \cos \theta = \lambda.K/D + 2A\varepsilon \sin \theta \quad (6)$$

Equation 6 is the Williamson–Hall (W–H) equation where ε represents the lattice strain and A is a constant (often 1). In the general form of the equation, the slope shows the lattice strain, whereas the vertical intercept is used to estimate the crystallite size [18].

3. RESULTS and DISCUSSION

3.1. X-Ray diffraction

Figure 1 shows the X-ray diffraction (XRD) patterns of the synthesized LC powder. The resulting diffraction pattern resembles the cubic fluorite CeO_2 , but shifted to smaller angles with no peak corresponding to La_2O_3 , indicating the formation of the $\text{La}_2\text{Ce}_2\text{O}_7$ solid solution. The resulting pattern is a basic reflection with no additional peaks, showing only one phase after the synthesis. Therefore, the CeO_2 can fully incorporate the larger La^{3+} ions, while preserving its fluorite structure.

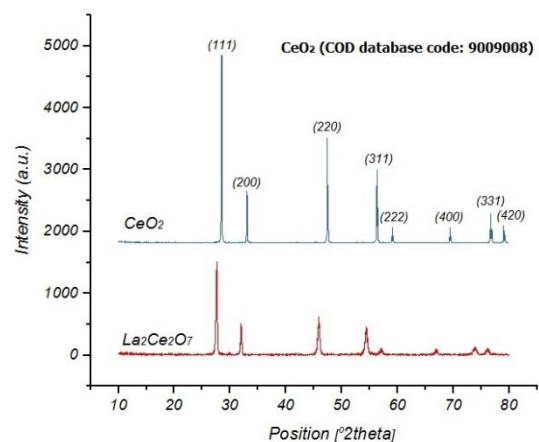


Figure 1. The X-ray diffraction patterns of CeO_2 and synthesized $\text{La}_2\text{Ce}_2\text{O}_7$ powder

The EDS analysis of the LC powder (Fig. 2) also indicates 64.35 at.% oxygen, 17.46 at.% lanthanum, and 17.79 at.% cerium in the chemical composition, which is similar to the stoichiometric ratio of the $\text{La}_2\text{Ce}_2\text{O}_7$.

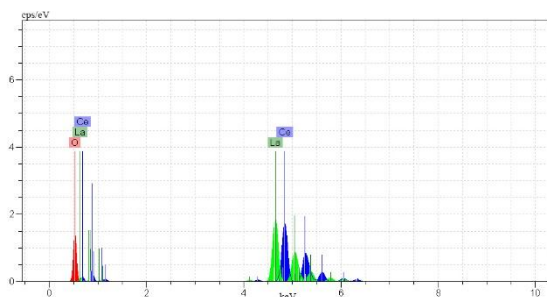


Figure 2. The EDS analysis of the synthesized LC powder

Fig. 3 shows the XRD patterns for $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ ($x = 0.1, 0.2, 0.3, 0.4$, and 0.5) and pure cerium oxide ($x = 0$).

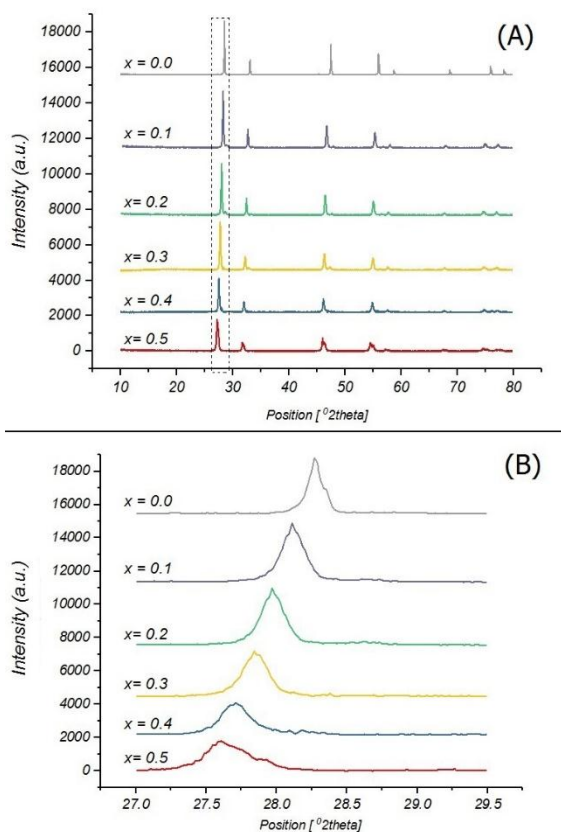


Figure 3. The X-ray diffraction patterns for $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ as a function of x

As evident from the Fig. 3 (A), all oxide mixes exhibit shifted fluorite ceria patterns (Fig. 3(B)).

No secondary phase or additional peaks is found in the powder mixes, indicating the formation of a homogeneous oxide phase. This implies that the CeO_2 structure can completely incorporate the larger La^{3+} ions in its lattice and still maintains its fluorite structure despite the La^{3+} substitution. The diffraction patterns further shift to smaller angles as a result of the change in the lattice parameter by increasing the La content [11,14,19,20].

3.2. Crystallite size

One thing to note in Fig. 3 is the broadening of the peaks by adding La, which is suggestive of a reduction in crystallite size at higher La contents. Therefore, adding La impedes the growth of ceria crystals [11,14].

Considering the growth mechanism of ceria is required to rationalize the observed decline of the crystallite size with La content.

The synthesis process includes two major steps; the formation of stable nucleus and crystal growth through the Oswald Ripening (OR) or oriented attachment (OA) mechanism [21,22].

It is expected that the replacement of host cations with dopant ions in ceria influences the thermodynamic and kinetic of the growth process. The growth mechanism of the ceria particles should also be illustrated to indicate the effect of increased La content on decreasing the crystallite size. Considering OA as the dominant growth mechanism and removing the high energy surfaces (the driving force of OA mechanism) can cause a significant decrease in the surface free energy. Consequently, Van der Waals (VW) forces can cause sufficiently close crystals to absorb each other [23,24]. Ivanov et al. reported that the decreased crystallite size of ceria with an increasing fraction of dopant can be well described through the delayed ceria crystallite growth, which is promoted by the segregation of dopant ions at the surface. Such surface segregation causes decreased surface energy of the particles and consequently, restricts the OA mechanism (derived by high-energy surfaces) [24].

However, the mentioned surface segregation mechanism cannot be used in this case due to the homogenous distribution of La in CeO_2 particles. Therefore, a simplified model has been used to illustrate the effects of the replacement of La^{3+} ions with Ce^{4+} ions through the OA growth mechanism. The model includes two $N \times N$ arrays of nodes as the rectangular crystalline planes. Each node consists of x mole A (dopant) atoms and $1-x$ mole B (host) atoms. The average distance between the nodes is defined as the lattice parameter, which may be different for different planes, as the number of A and B atoms are different in each crystalline plane [24].

Strong chemical bonding can be formed between the plans if the number of similar atoms in atomic rows of two adjacent planes does not show a significant

difference. In other words, the atomic rows of each plane can fit together when the difference between the numbers of atoms in each row did not exceed the m factor. Such a parameter is defined as the difference between the lattice parameters of pure A and B can be calculated as follows [24]:

$$m \approx d/\Delta d \quad (7)$$

Whereas, d shows the lattice parameter in Eq. 7, the probability of row fitting (P_1) can be calculated via the following formula [24]:

$$P_1 \approx m[\pi x(1-x)N]^{-1/2} \quad (8)$$

Eq. 8 has been derived from the calculations of the probability theory, based on the presence probability (PP) of A and B atoms in rows accompanied with considerations such as $d \gg \Delta d$ and $N \gg 1$. Whereas the presence probability (PP) in a row is considered as x for A atoms and the PP for B should be considered as $1-x$ [24].

P_2 is defined as the fitting probability of two perpendicular rows in one plane with the other planes. This parameter can be considered as the square of P_1 and calculated as follows [24]:

$$P_2 \approx m[\pi x(1-x)N]^{-1} \quad (9)$$

If the condition $P_2 \approx 1$ is considered as the criterion for the stopped particle growth, the indexed parameter of particle size ($D=Nd$) can be calculated through the following equation [24]:

$$D \approx [\pi x(1-x)]^{-1}(d/\Delta d)^2 d \quad (10)$$

Eq. 10 clearly illustrates that the particle size is decreased by the increased fraction of dopant (x). As the OA process intrinsically includes the formation of crystalline defects such as twinning, porosities and surface disorders, other processes such as recrystallization and OR should be occurred to decrease the lattice defects.

The high cohesion energy of ceria causes a slow recrystallization process through surface diffusion mechanism. Therefore, it seems that the atomic movements majorly occur through the OR process, which confirms the important role of the OR process in addition to OA [24,25].

It must be noted that both the particle size and the lattice strain broaden the XRD peaks [11,14,19].

Lattice strain also affects the peak width considering that the W-H equation was used to calculate the crystallite size and lattice strain besides changing the crystallite size. The W-H equation is first-order, and its slope and intercept yield the lattice strain and the crystallite size. Table 1 shows the crystallite sizes and

lattice strains obtained from the W-H equation for $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ compounds as a function of x . The results show that the incorporation of La into the structure reduces the crystallite size.

TABLE 1. Crystallite sizes and lattice strains of the synthesized compounds

x in $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$	Crystallite Sizes (nm)	Lattice Strains (%)	R^2
$x=0$	115.6	0.0016	0.9531
$x=0.1$	99.1	0.0023	0.9137
$x=0.2$	86.7	0.0026	0.8068
$x=0.3$	77.0	0.0030	0.9119
$x=0.4$	69.4	0.0034	0.8972
$x=0.5$	63.0	0.0038	0.9073

Figure 4 shows the variations of crystallite size and lattice strain as a function of La content. As evident, the lattice strain increases by raising the La content. The La^{3+} forms oxygen vacancies in the CeO_2 lattice, converting the Ce^{4+} cations to Ce^{3+} . The conversion changes the local symmetry in the lattice, which in turn, changes the Ce-O bond length [18,26]. Further, the La^{3+} cation with a larger ionic radius also disturbs the local symmetry of the lattice. All the above contribute to the increase in the lattice strain when La is introduced to the structure.

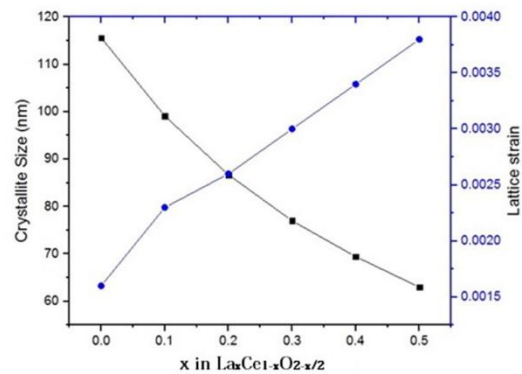


Figure 4. Lattice strain and crystallite size variations in $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ compounds as a function of x

3.3. Lattice parameter

In this study, the XRD patterns, experimental lattice constant results, and the oxygen vacancy model were used to calculate the theoretical lattice parameter for the $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ powder, and the results were compared. Equation 11 was used to calculate the lattice parameter of the cubic structure based on XRD patterns.

$$1/d^2 = (h^2 + k^2 + l^2)/a^2 \quad (11)$$

d: Spacing of crystal planes

h k l: Miller indices

a: Lattice parameter

Theoretical lattice parameter results were calculated based on the oxygen vacancy model using Eq. 12 [7].

$$a = \frac{4}{\sqrt{3}} [r_M - r_{Ce} - 0.25r_o + 0.25r_{vo}]x + \frac{4}{\sqrt{3}} [r_{Ce} + r_o] \quad (12)$$

M = La³⁺

Ce = Ce⁴⁺

O = O²⁻

V_o = oxygen vacancy

Fig. 5 plots the changes in the lattice parameter calculated from diffraction patterns and the theoretical lattice parameter calculated based on the oxygen vacancy model as a function of the La dopant content.

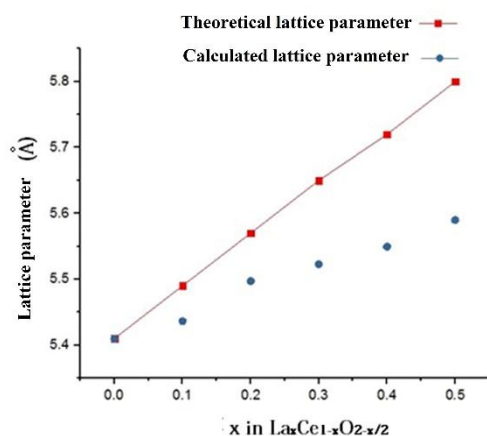


Figure 5. Changes in the lattice parameter as a function of the La dopant concentration

As evident, the lattice parameter increases by further adding of La. The substitution of Ce⁴⁺ with La³⁺ in the lattice enlarges the octahedral face in the lattice of the cubic fluorite CeO₂, which also increases the lattice parameter in La₂Ce₂O₇. The shift of CeO₂ peaks to smaller angles in Fig. 3 also verifies this phenomenon [11,12].

As evident from Fig. 5, the theoretical lattice parameters were larger than the lattice parameters calculated based on XRD patterns. Further, the discrepancy between the experimental and theoretical results increases by adding La. The discrepancy shows that the volume of the fluorite unit cell can shrink as a result of the joining the vacancies. Further, given that the number of vacancies increased by the addition of La and the contraction is also exacerbated by increasing the

difference between the theoretical and experimental lattice parameters [7].

In conclusion, two factors control fluorite lattice parameters. The first is the size difference between La³⁺ and Ce⁴⁺ ions. Note that La³⁺ has a larger ionic radius than the Ce⁴⁺, thus increasing the lattice parameter (a). The second less significant factor is the defects in the crystal lattice that contract the unit cell.

4. CONCLUSIONS

1. In La₂Ce₂O₇ compounds, where x is between 0.1 and 0.5, the CeO₂ structure can embed the larger La³⁺ ions in its lattice, while preserving its fluorite structure. Changing the La content of the compound resulted in a shift in diffraction patterns due to the different lattice parameters and the broadening of the peaks as a result of the reduced particle size.
2. The La³⁺ formed oxygen vacancies in the CeO₂ lattice, converting the Ce⁴⁺ cations to Ce³⁺. The conversion changed the local symmetry in the lattice, which in turn, changed the Ce–O bond length. Further, the La³⁺ cation with a larger ionic radius also disturbed the local symmetry of the lattice. All the above contributed to the increase in the lattice strain when La is introduced to the structure.
3. The theoretical lattice parameters were larger than the lattice parameters calculated based on XRD patterns. Further, the discrepancy between the experimental and theoretical results increased by adding La. Given that increasing the La content increases the number of vacancies, the contraction induced by the joining of vacancies and the difference between the theoretical and experimental lattice parameter results also increased.

5. ACKNOWLEDGEMENTS

Authors would like to thank the Materials and Energy Research Center for financial support of this research.

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