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Microstructure and structure of $NiO–SnO_2$ and $Fe_2O_3–SnO_2$ systems

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Abstract

The microstructure and the structure of $NiO–SnO_2$ and $Fe_2O_3–SnO_2$ were studied by X-ray diffraction (XRD) and adsorption analysis (BET). The segregation of Ni or Fe on the surface of SnO_2 was observed even in specimens with 30 mol% addition. The segregation caused a decrease in the surface energy of the powders and, therefore, an increase in the surface area as expected by the Ostwald ripening model. After the saturation of the tin oxide surface, there is no increase in the surface area, but a decrease due to second phase nucleation. Adding more Ni to the system, similar segregation of Sn on the surface of NiO as well as the effect on the surface area were observed. In $Fe_2O_3–SnO_2$, an iron phase other than hematite was detected at high concentrations of Fe (Fe_2O_3–20% SnO_2), suggesting the formation of magnetite or a ferrite spinel. Gibbs energy diagrams that could be used to predict stable phases of certain compositions were drawn for both systems based on the observed data.

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Keywords: Tin oxide; Microstructure; Additives; Surface

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1. Introduction

Many studies have shown that several additives (cations: Fe, Cu, Co, Cr, Al, Mn, Mg; and anions: P, S) lead to an increase of the surface area of SnO_2-based powders [1,2]. Since the studied additives were chemically different, it was firstly suggested that the active elements that stabilize the SnO_2 surface, and promote a decrease in grain size, are not the additives themselves, but some induced defects related to either tin or oxygen, influencing diffusion parameters [3–6].

Actually, the influence of additives in the microstructure of ceramic powders is usually related to such diffusion parameters during thermal treatments [7]. However, the diffusion may be regarded as just the path by which the system reaches the most stable energetic state and some additives should also be acting on driving forces for the microstructure modifications. The use of the Ostwald ripening model for studying the influence of additives on the microstructure of oxides has already been proposed [8]. The model describes the particle size evolution during

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crystallization at a constant temperature. The influence of additives on the surface energy, an intrinsic variable of Ostwald equation [7], is proposed to explain the morphologic data. The surface energy decrease is related to the segregation of the additives onto the surface powder.

Usually, for many multicomponent systems, the surface will be enriched by the constituent that has the lowest surface free energy in order to minimize the positive surface energy [9]. This enrichment should, therefore, change the energy balances related to the morphology of the powder, e.g. grain sizes and dihedral angles, since interface energies are modified.

Reports have shown that several additives that influence particle growth are prone to segregate onto the surface of SnO_2-based powders, and a significant modification of the surface properties related to surface composition was noted [3,4,8,10]. The aim of this paper is to study the morphology of the Fe_2O_3–SnO_2 and NiO–SnO_2 systems prepared by the Pechini's method [4,11] and to observe the relationship between the segregation of the components and the observed morphology. The effect of NiO or Fe_2O_3 as additives on SnO_2 as well as SnO_2 as additive in both NiO and Fe_2O_3 were carefully studied by X-ray diffraction (XRD) and specific surface area measurements.

2. Experimental procedure

Tin oxide-based powders, containing Fe and Ni ions as additives, were synthesized by the polymeric precursor method [12], derived from the Pechini's method [11], without and with 0.5, 1, 2, 3, 4, 5, 10 and 30 mol% additive concentrations. Iron and nickel oxide-based powders without and with 20 mol% Sn were also prepared by the same method.

The synthesis process for the SnO_2-based powders can be described as follows: (a) addition of a cationic precursor, $Sn_2(C_6O_7H_4)\cdot H_2O$ (tin citrate prepared from $SnCl_2\cdot 2H_2O$—Synth [13]), into a solution of 20.6 wt.% ethylene glycol (Synth) and 47.7 wt.% citric acid; (b) polysterification of the solution at a temperature between 110 and 120 °C; and (c) thermal decomposition [11,12,14]. In the thermal decomposition, the liquid precursor was first treated at 450 °C for 4 h and, after grinding in an agate mortar; treated for 15 h at 500 °C. Fifteen hours was considered adequate time for the system to reach the particle size equilibrium. $Fe(NO_3)_3\cdot 9H_2O$ (Reagen—99.9%) and $Ni(NO_3)_2\cdot 6H_2O$ (Merk—99.9%) were added directly into the liquid precursor.

For the nickel and iron-based powders with 0 and 20 mol% of Sn, the cationic precursors were $Fe(NO_3)_3\cdot 9H_2O$ and $Ni(NO_3)_2\cdot 6H_2O$ and the process followed the procedure detailed above. The additive was tin citrate.

The powders were analyzed by X-ray diffraction with a model D8 Advance Bruker—AXS diffractometer, with Cu Kα radiation ($\lambda = 1.5406$ Å). The specific surface area, S_{BET}, of the calcined powders was determined from N_2 adsorption–desorption experiments using the BET method. The measurements were performed with Micromeritics Gemini III 2375 equipment.

3. Results and discussions

Specific surface area measurements of SnO_2-based powders show that both iron and nickel additives drastically influence the morphology of the powders. Table 1 summarizes S_{BET} data and is an evidence that the addition of 30 mol% of either Ni or Fe increases the surface area by a factor of ~3, and that the increasing effect is independent on cation type. Considering diffusion parameters, the experimental surface area data would only be expected if the diffusion of the system decreases for increasing additives concentration. However, one may note that the valences of both additive ions are lower than that of tin (4+).

Table 1
Specific surface area (S_{BET}) of SnO_2-based powders with different additive concentration (Ni or Fe)

Additive concentration (mol%)	S_{BET} (m^2/g)	
	Ni	Fe
0	29.2	29.2
0.5	33.6	35.4
1	38.8	36.8
2	43.3	38.1
3	51.1	42.2
4	55.8	44.3
5	59.0	46.9
10	61.2	62.1
30	90.0	93.5

Hence, even if the ions disperse into the lattice, oxygen vacancies would be expected to be produced in order to maintain charge neutrality, and hence the diffusion would increase as well as the particle size.

As proposed [8], the final particle size should be mainly dependent on the ratio between surface area energy and bulk volume 1. A modification of any of these energies by changes in the system composition would generate microstructure changes. Except for the nucleation of a second phase, the introduction of an additive into the system should change the energy balances and morphology of the powder, since the additive would be positioned inside the lattice or at the interface. XRD measurements of SnO_2 with Fe or Ni presented only the SnO_2 tetragonal phase, even with 30 mol% of both additives (Figs. 1 and 2). Moreover, two important points to note are the absence of second phases nucleated by the additives for all concentrations, and no displacements of the SnO_2 reflections, indicating that there must be small or no solubility of the additives in the crystalline bulk. These results suggest that the ions must be segregated onto the surface of the powder even at high concentrations (<30%), and just an enlargement of the diffraction peaks (after addition) is noticeable because the crystallite size decreases.

Since multicomponent systems surfaces are usually enriched by the component with the lowest surface energy [9], the observed segregation indicates that both Ni and Fe oxides have lower surface energies than SnO_2. The segregation decreases the surface energy of the powder while the bulk energy is maintained constant. Hence, there is a driving force for the particle size decrease, in order to raise the ratio between surface area and bulk volume.

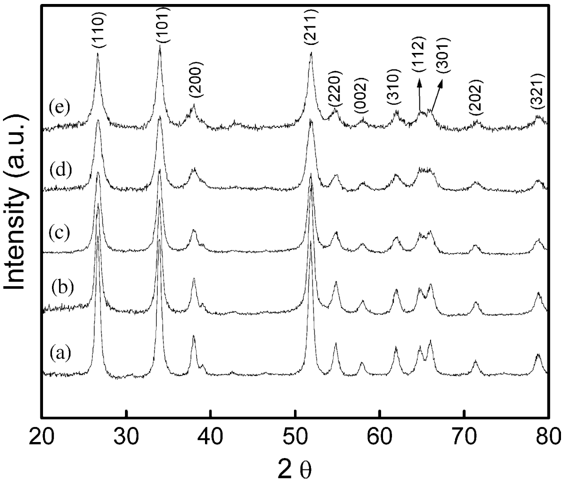

Fig. 1. XRD patterns of tin oxide powders containing Ni: (a) 0 mol%, (b) 0.5 mol%, (c) 2 mol%, (d) 10 mol% and (e) 30 mol%.

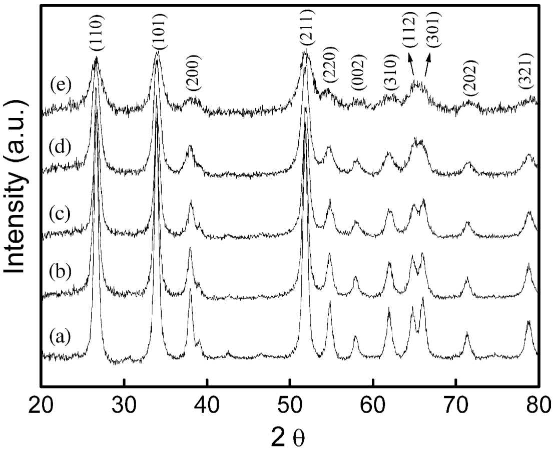

Fig. 2. XRD patterns of tin oxide powders containing Fe: (a) 0 mol%, (b) 0.5 mol%, (c) 2 mol%, (d) 10 mol% and (e) 30 mol%.

Despite even at 30 mol% total segregation of the additives is still observed, since the surface has a finite area and just a mono-atomic covering layer may be expected [9,10], at a certain critic concentration the additive will totally cover the surface. Beyond this critical concentration, the additives cannot further segregate and additional quantities will disperse inside the lattice or nucleate a second phase, depending on the total energy increment associated with each path.

Since the segregation is related to the surface energy decrease, the saturation of the surface by the additive indicates a point beyond which the surface energy cannot be further lowered. If the bulk energy is kept constant, this means that the particle size would be constant with further increase in concentration of the segregated component. This is expected when, after surface saturation, there is nucleation of a second phase. However, if the additive component disperses inside the lattice after saturation, the bulk energy would be changed and, therefore, also the particle size, which depends on the ratio.

To further evaluate the behavior of the NiO–SnO_2 and Fe_2O_3–SnO_2 systems, we analyzed the morphology of nickel and iron oxides with 0 and 20 mol% of

Table 2
Specific surface area (S_{BET}) of NiO and Fe_2O_3-based powders as a function of Sn concentration

Sn concentration (mol%)	S_{BET} (m^2/g)	
	Ni	Fe
0	17.1	11.5
20	43.4	47.8

Sn (that would correspond to SnO_2 systems with extremely high concentrations of Ni or Fe). Pure nickel and iron oxides presented low surface areas (17.1 and 11.5 m^2/g, respectively), but the areas increased with the addition of the component Sn to the system (Table 2). Influenced by Ostwald model, this could be explained considering the segregation of the Sn cations onto the powder surface. Actually, the XRD measurements of NiO–20% Sn presented SnO_2 tetragonal phase as well as NiO (Fig. 3) but, a preliminary analysis shows no displacements of the NiO or SnO_2 peaks. However, a broadening of NiO peaks with the addition of the cations is observed. This indicates a decrease of the crystallite size, possibly related to the minimization of the interface energy by the segregation of the cations.

This observation contradicts the hypothesis that components with the lowest surface tensions are expected to segregate to the surface [9]. The experimental data show that for both SnO_2–30% Ni and NiO–20% Sn systems, the lower concentration component segregates to the interface and, moreover, the surface energy and the particle size decrease in both cases. The segregation is not directly related to the surface energy of pure oxides but to the total energy entailed to the system after the segregation. Considering each crystal a closed system, and applying simple energetic arguments, it is clear that, if the segregation of the additive component is observed, the total energy of the crystal, specially of its surface, must be lower than that of the pure one; otherwise, the component would have nucleated a second phase or dispersed inside the lattice.

A free energy diagram as a function of the composition for the bi-component system may be constructed based on the presented data. The Gibbs free energy is here a composition of bulk and surface energies contributions:

$$G = G(\mathrm{b}) + G(\mathrm{s}) \tag{1}$$

As Ni is introduced to SnO_2, the surface energy of the single phase is decreased due to segregation of the cation, and the bulk energy is kept constant. Therefore, total free energy is expected to decrease in Fig. 4 and the phase is stable. When the segregated element saturates the surface of the base material, the component is expected to nucleate a second phase or to disperse into the lattice. The X-ray diffraction pattern of SnO_2–40% NiO in Fig. 5 shows the SnO_2 tetragonal phase as well as small amplitude peaks of NiO as a second phase. Therefore, no further decrease in the surface energy may be expected and an adobe single

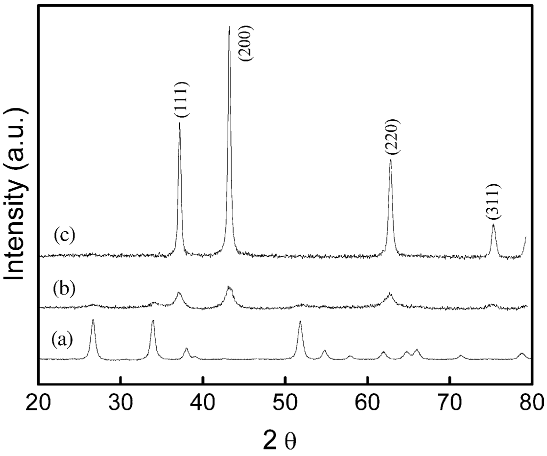

Fig. 3. XRD patterns of nickel oxide powders containing Sn and SnO_2 powder: (a) SnO_2, (b) NiO–20% SnO_2 and (c) NiO.

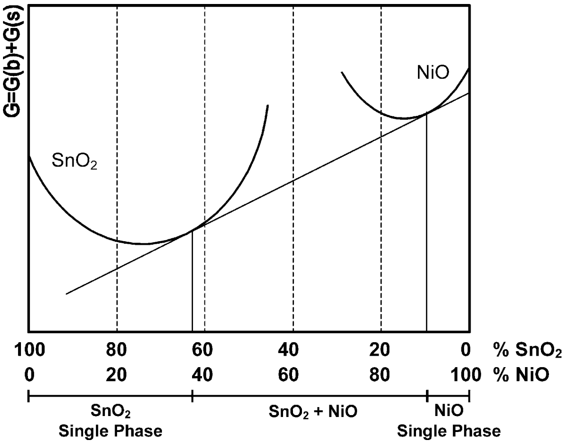

Fig. 4. Gibbs energy diagram for NiO–SnO_2.

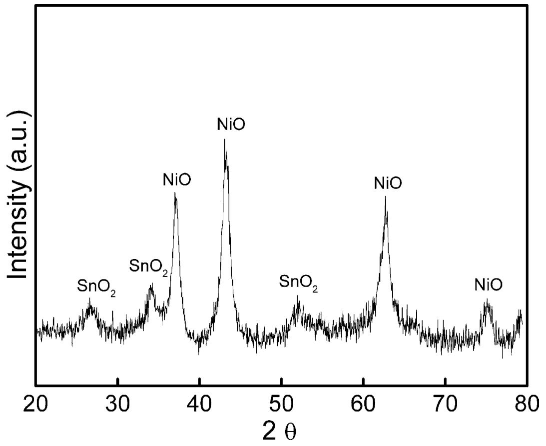

Fig. 5. XRD patterns of tin oxide powder containing 40 mol% NiO.

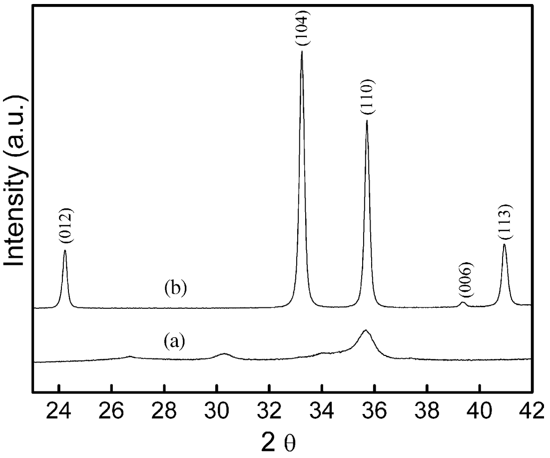

Fig. 7. XRD patterns of iron oxide powders containing Sn: (a) 0 mol% and (b) 20 mol%.

SnO_2 phase would become unstable (SnO_2 Gibbs energy increases). At least up to NiO–20% Sn, the bi-component system is composed by two phases. At certain point between NiO–20% SnO_2 and NiO–0% SnO_2, no SnO_2 second phase would be observed, but just small particles of NiO with Sn on the surface. Therefore, a Gibbs energy curve for NiO may be constructed in Fig. 4. This is the energy diagram for the system at 500 °C. A phase diagram could be constructed joining energy curves for other temperatures but this is not in the scope of this work. A schematic representation of the morphology of the system is presented for clearness in Fig. 6. Note the decrease in grain size with increasing coverage of the SnO_2 (NiO) surface by Ni (Sn). Surface saturation is followed by the nucleation of second phases.

A similar diagram can be constructed for the bi-component system Fe_2O_3–SnO_2. However, for such system the diagram should be more complicated. In Fig. 7, very small quantities of hematite (Fe_2O_3) are identified in the X-ray diffraction pattern of Fe_2O_3–20% SnO_2, but SnO_2 tetragonal phase and some foreign peaks ($2\theta = 30.30$ and 35.68°) are clearly observed. These foreign peaks could be attributed to (2 2 0) and (3 1 1) magnetite planes, respectively; however, the angles would be slightly displaced to higher values indicating a decrease in the lattice parameters. The peaks could also be related to ferrite spinels as $Fe_{2.95}Sn_{0.05}O_4$ [15]; however, this should be discussed in more details.

Despite the non-evidence of the nature of the foreign diffraction peaks, an energy diagram may be drawn. Up to the saturation of the surface of SnO_2 by Fe cations,

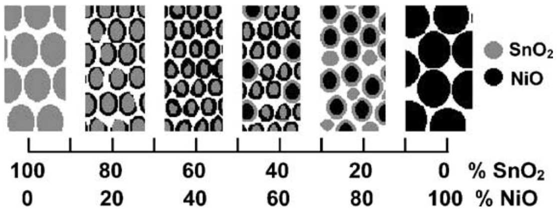

Fig. 6. Schematic representation of the powder morphology evolution with the composition of the NiO–SnO2 system.

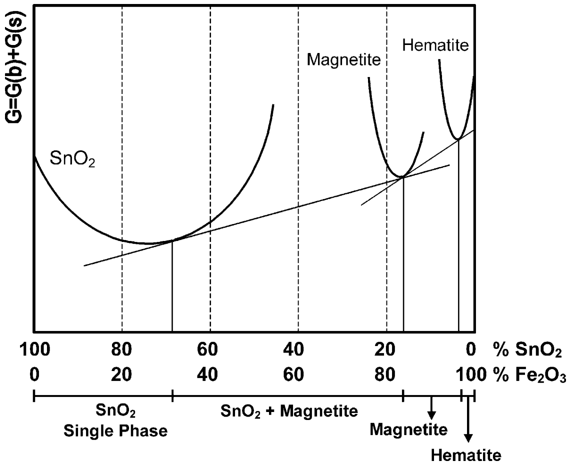

Fig. 8. Gibbs energy diagram of Fe_2O_3–SnO_2.

the energy curve should be similar to that of NiO–SnO_2. With increasing iron content, "magnetite" is nucleated up to a certain point. With further increase, hematite is expected to occur as shown in Fig. 8. Due to the formation of the unexpected phase, there are insufficient data to construct a schematic representation of the morphology of the system, as constructed for NiO–SnO_2.

4. Conclusions

Microstructure and structure of NiO–SnO_2 and Fe_2O_3–SnO_2 systems were studied and the segregation of the lower concentration component to the surface of the powder matrix was observed in both cases. The segregation caused a decrease of the surface energy of the powders and hence an increase of the surface area. After surface saturation by the component, there is no further increase of the surface area, but instead a decrease due to second phase nucleation. For Fe_2O_3–20% SnO_2, an iron phase other than hematite was detected and supposed to be either magnetite or a ferrite spinel. Gibbs energy diagrams that could be used to predict phases at certain composition were proposed for both systems based on the observed data.

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