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Magnetic Study of $\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$ Nanocomposites Prepared by the SOL-GEL Method

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Abstract. Nanocomposites of $\gamma\text{-Fe}_2\text{O}_3$ in a silica matrix were prepared by the sol-gel method using tetramethylorthosilicate (TMOS) as a precursor of silica and introducing iron as $\text{Fe}(\text{NO}_3)_3$ with Fe/Si ratios of 2, 5, 10 and 20%. The obtained gels were calcinated at temperatures between 600°C and 1000°C. Magnetic measurements performed with a vibrating magnetometer showed that superparamagnetic $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles began to form at 700°C, as confirmed by X-rays and Mössbauer spectroscopy. Superparamagnetic magnetization curves were fitted by a Langevin function considering a log-normal particle size distribution. This allowed to determine the saturation magnetization and the particle size distribution of the samples. The latter results were in good agreement with observations made by Transmission Electronic Microscope. For all studied concentrations, the $\gamma\text{-Fe}_2\text{O}_3$ particles size increased with the calcination temperature up to a maximal average diameter of 40 Å. This maximum was reached at 900°C for the highest concentrations and 1000°C for the lowest. Calcinations at higher temperatures led to the degradation of the $\gamma\text{-Fe}_2\text{O}_3$ phase with creation of defects in the particles and formation of $\alpha\text{-Fe}_2\text{O}_3$. This phenomenon was accompanied by a decrease in the saturation magnetization and the presence of an hysteresis in the magnetization curve.

1. EXPERIMENTAL

Xerogel strips were obtained from $\text{TMOS}^1/\text{H}_2\text{O}$ / formamide / methanol sols containing 2, 5, 10 and 20 molar % of Fe added in the form of nitrates. These strips were calcinated at temperatures between 600 and 1000°C. They were then finely ground and studied by vibrating magnetometer and high resolution transmission electronic microscopy.

2. MAGNETIZATION MEASUREMENTS

The magnetization measurements were performed with a Varian Foner at room temperature (Figure 1). The samples were paramagnetic until a calcination temperature of about 700°C and became superparamagnetic for higher calcination temperatures. This superparamagnetic behaviour is due to the formation of $\gamma\text{-Fe}_2\text{O}_3$ magnetic nanoparticles whose size is below critical size. The presence of $\gamma\text{-Fe}_2\text{O}_3$ is confirmed by X-rays and Mössbauer spectroscopy. The magnetization curves corresponding to a superparamagnetic behaviour can be fitted with a Langevin curve. As the particle size distribution could not be considered as uniform we introduced a log-normal particle size distribution [1], characterized by an average particles diameter and a standard deviation. Thus fitting the magnetization curves allowed us to determine the saturation magnetization of the samples and the particle size distribution. The maximal saturation magnetization, obtained for a calcination at 900°C for the highest concentrations (10 and 20%) and 1000°C for the others (2 and 5%) is never

Figure 1: magnetization curves of the sample containing 10% iron calcinated at different temperatures

¹ tetramethylorthosilicate

higher than 50% of the $\gamma\text{-Fe}_2\text{O}_3$ bulk saturation magnetization. This can be explained by two factors. First, the surface of the particles, which is, for such small sized particles, very important compared to their volume, is magnetically less ordered. Secondly, all the introduced iron is probably not in the form of $\gamma\text{-Fe}_2\text{O}_3$. There may remain free iron III ions in the silica matrix. The width of the particle size distribution increases with the iron concentration and the calcination temperature. For all concentrations, the average particle diameter increases with the calcination temperature until it reaches a maximum of about 40Å. This value is reached at 900°C for the highest concentrations and at 1000°C for the others. These temperatures are thresholds beyond which one observes the creation of defects in the particles and the deterioration of the $\gamma\text{-Fe}_2\text{O}_3$ phase, apparently in favor of the $\alpha\text{-Fe}_2\text{O}_3$ phase. This phenomenon is accompanied with a strong decrease of the saturation magnetization and the presence of an hysteresis in the magnetization curve.

3. HIGH RESOLUTION TRANSMISSION ELECTRONIC MICROSCOPY

Observations of the samples containing 2, 5, 10 and 20% of iron, calcinated at 900°C, were done by HR TEM (Figure 2). A numerical treatment of these observations allowed us to determine the particle size distributions of the samples. A good agreement was found between these distributions and the log-normal distributions deduced from the magnetic measurements (Figure 3). The slightly lower values found from the magnetic measurements can be explained by the non-magnetic surfaces of the particles which were not taken into account by this method.

Figure 2: HR MET observation of the sample containing 10% of iron and calcinated at 900°C (the bar represents 100Å)

Figure 3: particle size distributions as seen by HR TEM (bars) and deduced from magnetic measurements (line) for the sample containing 10% of iron and calcinated at 900°C

4. CONCLUSION

Magnetic measurements and HR TEM were used to study the influence of the concentration of iron on the size of the $\gamma\text{-Fe}_2\text{O}_3$ particles formed in the silica matrix. It was found that, for all studied concentrations (2-20%), the $\gamma\text{-Fe}_2\text{O}_3$ particles appear for calcination at 700°C and their size increases with higher temperature calcinations. The particle size distribution is log-normal, with an average maximum diameter of about 40Å. This maximum value is reached for calcination at 900°C for the high concentrations and at 1000°C for the lower ones. Calcination at higher temperatures leads to the creation of defects in the particles and progressive destruction of $\gamma\text{-Fe}_2\text{O}_3$ in favor of $\alpha\text{-Fe}_2\text{O}_3$, as confirmed by X-rays and Mössbauer spectroscopy. This phenomenon is monitored by a strong decrease in the saturation magnetization of the samples and creation of an hysteresis.

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