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Studies on the synthesis and characterisation of metallic fine powders for special coatings

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Silver powders were prepared in aqueous medium, in well controlled conditions (pH, temperature, concentration, surface regulators) by mixing the metallic salts solutions with different reducing agents such as formaldehide, hydrazine, ferous sulphate, tris-ethanolamine (TEA) etc. The powders were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal analysis (TGA-SDTA), FTIR spectroscopy and thermal diffusivity.

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1. Introduction

Metallic powders are often used as pigments for coatings with improved properties related to the light reflection, electro- and thermoconduction, permeability to moisture and gases, and anticorrosive protection [1, 2]. Coatings are polymeric composites whose properties and applications are determined by loading degree, matrix characteristics and morpho-structural properties of the metallic powders used as pigments [3-9].

The goal of this study is to prepare powders of silver with different particle shapes and sizes utilisable for anticorrosive thermoconductive coatings.

Metallic powders were prepared in aqueous medium, in well controlled conditions (pH, temperature, concentration, surface regulators) by mixing the metallic salts solutions with different reducing agents such as iron (II) sulfate, hydrazinium hydrate, and tris-ethanolamine (TEA) etc. The powders were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal analysis (TGA-SDTA), FTIR spectroscopy etc.

Nano- and microstructurate silver powders with flakes or spherical particle shapes were prepared and tested for special coating compositions.

2 Experimental

Four samples of silver powders have been prepared using different reducing agents and/or processing procedures. The sample Ag-1 was obtained at 60÷80ºC by mixing acidic solution of silver nitrate with iron (II) sulfate. The precipitate was washed with distilled water and dried to give the powder Ag-1 that, after grinding, leads to Ag-1.1.

The sample Ag-2 was obtained by reducing a hot silver chloride suspension with hydrazinium hydrate, in presence of ammonia. Ag-4 powder was obtained by treating a warm solution of silver nitrate with tris-ethanolamine (TEA), in presence of ammonia. Precipitates were carefully washed with distiled water and dried.

XRD patterns were recorded on a DRON 3M diffractometer with Ni filtered Cu Kα radiation. The size of the particles was evaluated using Scherrer equation: $t = 0.9\lambda / (B_{1/2} \cos\Theta)$, where λ=1.54182Å is the wavelength of the Cu Kα radiation, $B_{1/2}$ is the bandwidth at the half of its intensity and Θ is the diffraction angle for the [hkl] band. The SEM images were obtained with a JEOL–JSM 5510LV electron microscope. The accelerating voltage was 10 kV. A JASCO 610 FTIR Spectrophotometer was used to record the FTIR absorption spectra (KBr pellets). A METTLER-TOLEDO TG/SDTA 851 thermogravimeter was used for the differential thermal analysis (DTA) and the thermal gravimetric (TG) measurements (alumina crucible, 20 mL/min nitrogen flow, 5ºC/min heating rate). The thermal diffusivity measurements were performed using a Flash-Line 3000 instrument from Anter Corporation.

3 Results and discussion

Three samples of silver powders (Ag-1, Ag-2 and Ag-4) have been prepared using iron (II) sulfate, hydrazinium hydrate and tris-ethanolamine as reducing agents, respectively. The chemical processes can be described by the following chemical equations:

$$3AgNO_3 + 3FeSO_4 \xrightarrow{H_3O^+} 3Ag + Fe_2(SO_4)_3 + Fe(NO_3)_3 \quad (1)$$

$$4AgCl + N_2H_4 + 4NH_4OH \longrightarrow 4Ag + 4NH_4Cl + 4H_2O + N_2 \quad (2)$$

$$3AgNO_3 + 2N(C_2H_4OH)_3 + 3NH_4OH \longrightarrow 3Ag + 3NH_4NO_3 + 3C_2H_4(OH)_2 + 3H_2O + N_2 \quad (3)$$

Depending on the reducing conditions, silver powders with different appearance and morpho-structural properties are obtained. Ag-1 is a beige mat powder with bright spots that consists of 2-10 μm platelets mixed with smaller polyhedral particles of 0.5-1.5 μm size. Grinding the Ag-1 powder results in the formation of loaf-flakes of silver powder (Ag-1.1). Sample Ag-2 with hydrazinium hydrate, is a mat -beige, fluid powder consisting of spherical clusters (20-100 μm) of much smaller spherical particles (0.5-5.0 μm). Ag-4 obtained by reducing silver nitrate with tris-ethanolamine, is a brown fluid powder consisting of sperical clusters (5-50 μm) of much smaller spherical particles (100-200 nm).

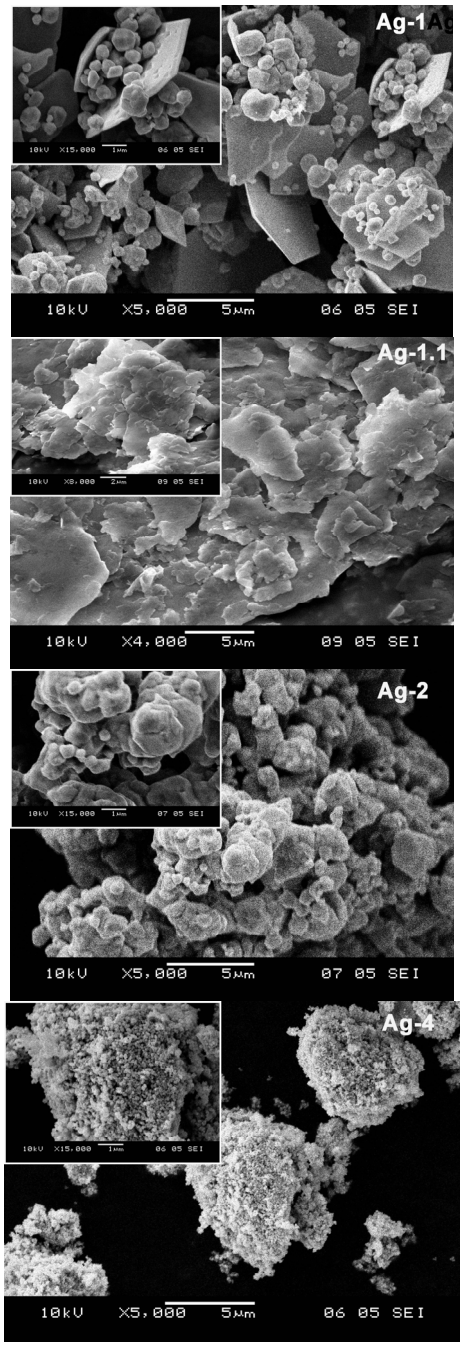

Fig.1. SEM Images of different silver powder samples

The crystalline structure of the silver samples was determined on the basis of XRD patterns.The XRD diagrams are similar and corespond to face centered cubic structure according to the theoretical data (PDF 040783).

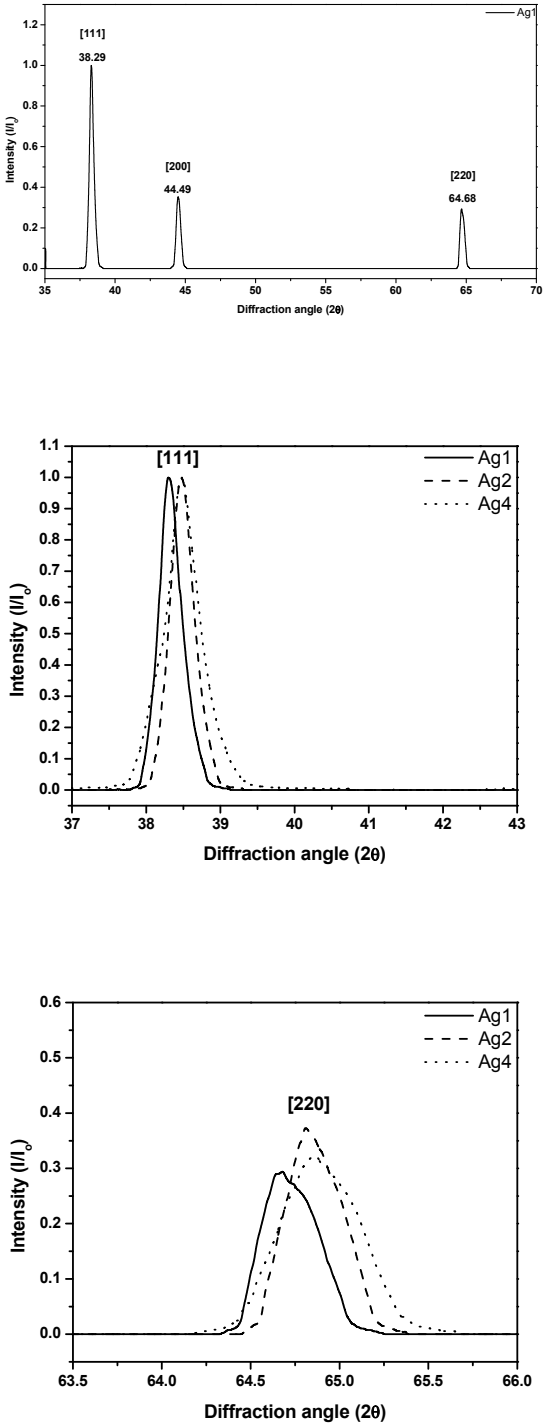

Fig. 2. The XRD patterns of Ag-1, Ag-2 and Ag-4 powder samples.

There are only small differences between samples, regarding the position and the relative intensity of the diffraction lines suggesting a different crystalline order degree. More important differences are observed when XRD band profiles are compared indicating the presence of crystallite with different sizes and packing defaults, depending on the preparation method.

The relative size of the crystallites (t) was evaluated using the Scherrer equation (without correction) leading to the following results: t_{Ag-1}=24.8 nm; t_{Ag-2} = 23.6 nm and t_{Ag-4} =16.8 nm. The finest silver powder seems to be Ag-4, prepared with TEA as reducing agent. Thermal analysis was used to compare the silver powders prepared with different reducing agents. As expected, there is no significant weight loss on heating the silver powders Ag-1 and Ag-2. The higher dispersed silver powder, namely Ag-4, shows a 2.54% weight loss (at 1200C) due to some adsorbed water and other contaminants.

The endothermal peak observed on DTA curve corresponds to silver melting. The melting point is different for samples prepared with different reducing agents: 958.4 (Ag-1), 957.2 (Ag-2) and 975.3 (Ag-4) respectively. The smaller dimensions of powder particles leading to high surface area and favorizing the adsorption of other species could explain the relative higher melting point of sample Ag-4

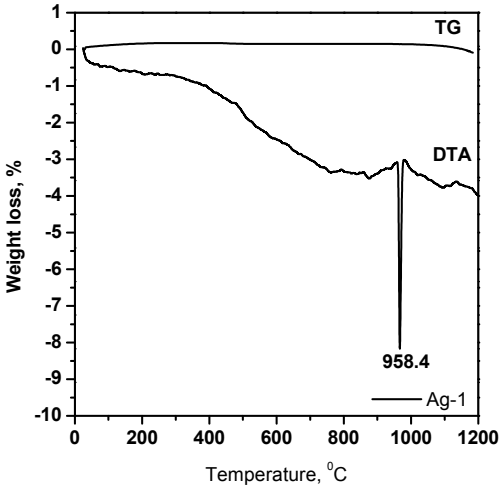

Fig. 3. TG and DTA curves obtained for the sample Ag-1.

The FT-IR spectra of the silver powder samples show only very week bands, characteristic for water and other contaminants from the reducing medium.

The thermal conductivity of each sample was calculated from the thermal diffusivity in the 20-160ºC ranges. The obtained values of 400-450 W/mK are in good agreement with the literature [10]. There is a small difference between the powders obtained in different conditions. Thermal diffusivity is relatively better for Ag-2 powder sample containing smaller crystalites and characterised by relative lower melting temperature, as compared with Ag-1. From this point of view, Ag-4 powder seems inhomogeneous as thermal behaviour.

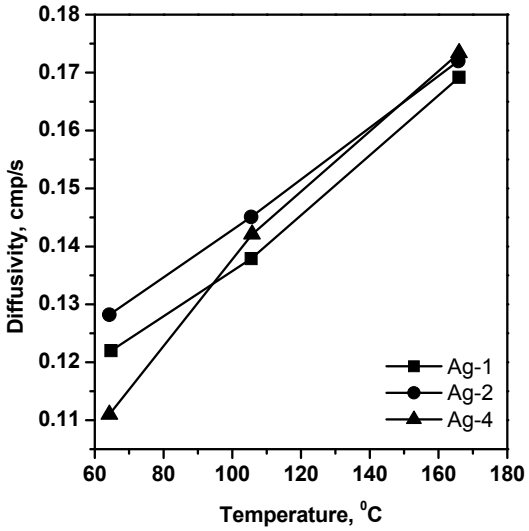

Fig. 4. The variation of thermal diffusivity versus temperature for silver powders obtained with different reducing agents.

4. Conclusions

The morpho-structural properties of silver samples depend on the preparation conditions: (reducing agent, pH, temperature, surface regulators). The powder prepared with $FeSO_4$ (Ag-1) shows flakes-like, adherent particles, while the one prepared with hydrazinium hydrate (Ag-2) is particulated and easy to disperse. The other sample, prepared with tris-ethanolamine (Ag-4) consists of the smallest particles (100-200 nm). All the prepared powders can be easily incorporated into polymer matrices in order to develop anticorrosive thermoconductive coatings.

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