

The formation of silver particles during the decomposition of long chain silver carboxylates

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Abstract

The change of the morphology and structure of silver particles formed from silver carboxylates, $[Ag(O_2C_nH_{2n-1})]_2$, (SC) during the photothermographic process (1) and during thermal and photochemical decomposition (2) were investigated using TEM, X-ray diffraction and DTA. The major results of this investigation show that the shape and size of the silver crystals depend on several factors, including:

a) The method of preparation of the silver halide/silver carboxylates (AgX prepared *in situ* or *ex situ*). For example, in the case of the *in situ* materials, silver filaments are formed during the photothermographic process while *ex situ* AgX prepared materials yield dendritic silver particles.
b) The number of carbon atoms in the carboxylic acid (n). For example, silver particles on the order of 30-50 nm are formed from decomposition of SC with n = 1-5. For n > 10, the formation of nano-sized silver particles (3-5 nm) was observed. The morphology of metallic silver is determined by the layered structure of the solid SC crystals as well as by the organic by-products formed, which can prevent the addition of new silver atoms to the growing crystallite.

Introduction

Silver carboxylates $[Ag(O_2C_nH_{2n-1})]_2$ where n = 10-22 are one of the major components in thermographic and photothermographic imaging materials [1,2]. However, in spite of the reports of the morphological properties of silver particles formed during the thermal development of photothermographic materials, literature is lacking on the investigation of the morphology and structure of silver particles formed during thermal and photochemical decomposition of pure silver carboxylate crystals.

Results and Discussion

We now report the results of an investigation of the changes in the composition of silver carboxylates during decomposition by X-ray diffraction, electron microscopy, and DTA of the decomposed silver carboxylates.

X-ray studies of thermal decomposition of silver carboxylates $[Ag(O_2C_nH_{2n-1})]_2$ revealed similar changes occurring both in the silver carboxylate structure and in the formation of the silver phase, independent of the number of carbon atoms in the methylene chain. Heating to 140°-160°C for 30 min leads to substantial decreases of the layer reflections d(001) intensities. The intensity of reflections with hkl indices (where h and k are not zero) also decreases substantially and the reflections are broadened. For this heating time, X-ray patterns do not exhibit the formation of a silver phase or any other phases.

Electron microscope investigation of the thermal decomposition of silver carboxylates directly in the electron microscope column showed that heating the silver carboxylates is accompanied by changes in the appearance of the crystals, namely, the faces become rounded. The formation of large number of particles, 1-2 nm, is observed within the silver carboxylate crystals. Small angle XRD of this sample shows a set of diffraction rings characteristic of an amorphous material. Increasing the heating time is accompanied by particle coalescence. Electron diffraction patterns exhibit, along with the amorphous phase halo, reflections characteristic of metallic silver. Prolonged heating leads to a further increase of the metallic silver crystal size. After heating $[Ag(O_2C_{18}H_{35})]_2$ crystals for 1 h at 170° C the silver crystallites vary within a rather wide range, from 5 to 10 nm. The amorphous phase halo, which is characteristic of the initial stages of thermal decomposition, now disappears nearly completely and the silver crystal phase diffraction lines appear. It should also be noted that the decomposing silver carboxylate crystal exhibits an increase of the amorphous layer thickness at the edges of the crystal with increasing the heating time. It is reasonable to propose that hydrocarbon compounds form during the thermal decomposition of silver carboxylates along with the metal phase. The destruction of these hydrocarbons under the electron beam leads to the deposition of carbon on lateral faces of the decomposing $Ag(O_2C_{18}H_{35})]_2$ crystal.

The studies of the silver particle morphology during photochemical decomposition of silver carboxylates

revealed that the sequence of stages leading to the formation of the silver phase during the photolysis of $[Ag(O_2C_{18}H_{35})]_2$ is generally similar to thermal decomposition. First, at low levels of irradiation the formation of very small particles is observed (1-3 nm). Electron diffraction from these particles is characterized by the presence of an amorphous halo. Then, increasing the irradiation intensity causes a slight increase of the size of particles formed (up to 3-5 nm). Electron diffraction patterns exhibit reflections characteristic of the silver phase. Similar to the thermal decomposition of silver carboxylates, silver particles are observed to form on the lateral faces of the crystal. The size of these particles is somewhat larger than those formed inside the decomposing silver carboxylate crystal. Similar to thermal decomposition, a decrease in the number of small silver particles is observed in the regions adjacent to a large silver particle growing at the lateral face.

We believe that the morphology of the silver particles formed during thermal and photochemical decomposition of silver carboxylates is also affected by the formation of the organic reaction by-products. The new organic material may be adsorbed on the surface of the silver particle hindering the addition of new silver atoms and thus preventing the growth of silver particles.

The major results of this investigation can be highlighted as follows:

The shape and size of the silver crystals change during thermal and photochemical decomposition of pure silver carboxylates depending on the number of carbon atoms in the carboxylic acid chain of the $[Ag(O_2C_nH_{2n-1})]_2$ crystals. Silver particles on the order of size 30-50 nm are formed from decomposition of silver carboxylates with n = 1-5. Thermal and photochemical decomposition of silver carboxylates with n > 10 leads to the formation of nano-sized silver particles (3-5 nm).

This type of metallic silver formation can be directly attributed to the layered structure of the solid state structure of the $[Ag(O_2C_nH_{2n-1})]_2$ crystals as well as to the formation of the organic by-products which can prevent the addition of new silver atoms to the growing crystallite.

References

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