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Feature article

Direct shaping of oxides by laser insolation of transition metal oxalates

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ABSTRACT

Films of copper and cobalt-iron oxalates were prepared from suspensions of powders in ethane-1,2-diol deposited on glass or polycarbonate substrates. Two-dimensional structures of oxides, resolved on the scale of less than ten micrometers, were formed by laser insolation of these films, using a photolithography machine. The nature of the constitutive phases of the oxides formed tends to show that the laser heating makes it possible to reach locally, temperatures higher than 1000 °C. The oxides formed are thus sintered. The residual oxalate can be removed by washing or dissolving, leaving the oxide structure on its substrate. In spite of a perfectible sintering, the formed structures could interest different technological applications (electronic or magnetic devices, gas sensors, photovoltaic systems. . .) requiring the shaping of simple or mixed oxides on a scale close to the micrometer. The process of selective laser decomposition of oxalates, could subsequently be suitable for additive manufacturing of 3D parts.

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1. Introduction

Oxalates, described by the general chemical formula: $M^{n+}_{2/n}C_2O_4^{2-} \cdot mH_2O$ ($n \geq 1$ and $m \geq 0$), can be easily prepared by chemical precipitation, with controlled particles size and shape. Moreover, because a lot of oxalates are isomorphous or have a similar crystalline structure, solid solutions in a wide range of composition can be obtained. The decomposition of such oxalates is generally possible at moderate temperature (<250 °C) in different atmospheres, making them interesting chemical precursors to get metals, alloys and simple or mixed oxides. The temperatures required for the decomposition, are generally enough low to retain, in a certain extend, the size and the shape of the starting oxalate particles. Such pseudomorphous decompositions were then used to get calibrated powders for powder metallurgy [1,2] and ceramics processing [3]. Powders made from oxalate, were used or proposed for a lot of technological applications such as

catalysis [4,5], sorption of pollutants [6], support of solid oxide fuel cells [7], energy storage [8–10], magnetic recording [11,12], inert anode for aluminium electrolysis [13] and low temperature solders [14].

It is well-known that focused laser diode beam with a power of few 10^{-3} W applied for few nanoseconds, can oxidize or transform various materials in the form of films. This type of rapid chemical or crystalline change is widely used to record information in optical discs, mainly in the so-called “Write Once Read Many” discs. Polymer or metallic materials were the most used materials for optical recording applications, but ceramic materials such as spinel oxides have also been implemented in these media. In spite of the quite good stability of these oxides, their oxidation state, crystalline structure, crystallization state and topography, can be modified by a very short and low power laser insolation [15]. Due to their moderate decomposition temperature and their optical absorption in the infrared, ultra-violet or visible range, the decomposition of oxalate by a focused laser beam, seemed then feasible. In this way, films or thick layers made of oxalates particles, could be locally transformed to get different micronic patterns of oxides. The oxides thus formed could be integrated very advantageously in various systems, taking

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benefit of their catalytic, semiconducting or magnetic properties, for instance.

Such a process is different from other methods, which were mainly proposed to obtain pure metallic copper, even if some of them proceeded on copper oxide nanoparticles [16,17]. Similarly, it differs from inkjet printing and stereolithography, which are also methods capable of forming 2D ceramic patterns [18,19]. The proposed method is in fact free from the addition of polymers or the highly complex formulation required, in particular for inkjet printing processes. It reaches also resolutions of the order of ten microns or even better. Finally, it simply requires a conventional photolithographic machine identical to those that are frequently installed in laboratories or production centers for microelectronics.

In this paper, selective laser decomposition of some oxalates is then used to draw different oxide patterns and show the value of the method and the associated materials, for the construction of two-dimensional structures. The potentialities of selective laser decomposition of oxalates to build three-dimensional parts by additive manufacture are also discussed. The preparation of the oxalates studied, is briefly described and their chemical, granulometric and morphological characteristics are given. The oxides formed after laser decomposition are also characterized by electronic microscopy, X-ray diffraction and magnetic measurements. The local temperatures reached during the heating by the laser, are estimated from the phase diagrams and the nature of the oxides formed during the decompositions.

2. Materials and methods

2.1. Oxalates preparation

2.1.1. Copper oxalate

The copper oxalate was prepared by reacting a 1 M aqueous solution of copper nitrate with a 0.3 M aqueous solution of ammonium oxalate in a reactor containing deionized water. The precipitate in suspension in the liquid medium, was aged for 1 h, filtered and then dried at 80 °C.

2.1.2. Mixed cobalt iron oxalate

A 2 M solution of cobalt nitrate and iron sulfate dissolved in a mixture of water (40% vol.) and ethane-1,2-diol (60% vol.) was poured drop-wise into a 0.5 M hydro-alcoholic solution of oxalic acid. The oxalate precipitate, formed almost immediately, was then aged for 30 min. After filtration of the oxalate suspension, the precipitate was washed with deionized water and then with ethyl alcohol to accelerate drying. The latter was carried out at 80 °C in a ventilated oven. The ratio iron/(cobalt + iron) in the final oxalate was close to 0.59.

2.2. Characterizations

The oxalate powders and the oxides formed were characterized by X-ray diffraction with a Siemens D 5000 diffractometer equipped with a Brucker sol-X detector. The X-ray wavelength was that of the copper K α ray (K α_1 = 0.15405 nm and K α_2 = 0.15443 nm). The starting oxalate powders, randomly oriented, were first studied in theta-2theta configuration. Using the same diffractometer configuration, the films treated by the laser spot, were directly analysed to check whether the decomposition of the oxalate was complete and to characterize the nature of the oxides formed. The chemical composition of the mixed cobalt iron oxalate was determined by Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) on oxalate decomposed under air at 600 °C in a conventional furnace. The samples were also investigated by scanning electron microscopes (SEM) with a field emission gun SEM JEOL JSM 6700F

equipped with an Energy-dispersive X-ray spectroscopy (EDS) system of Princeton Gamma Tech and by a Keyence VHX 1000 optical and profilometer microscope. Thermogravimetric measurements were carried out with a Setaram TAG 16 symmetrical weighing system.

The magnetic properties of the starting oxalate and the mixture of oxides coming from the laser decomposition, were measured with a vibrating sample magnetometer (VSM Quantum Design Versalab) from Quantum design. The oxalate and the oxide removed from their glass substrate were placed in a dedicated Quantum Design polymer sample holder. The curves of the magnetization versus magnetic field were plotted at room temperature for the two samples. After this measurement, the mixture of oxides was cooled down 50 K under a magnetic field of 30 kOe. The measurement of the magnetization as a function of the field was again made at this low temperature to try to reveal magnetic coupling effects between antiferromagnetic and ferromagnetic phases. Each measurement was corrected from the sample holder system contribution.

2.3. Oxalate patterning

The oxalate powders were dispersed by sonication in ethane-1,2-diol (C₂H₆O₂) at the rate of 1 g of oxalate for 4 g of polyol. These suspensions were spread on transparent substrates of glass or of polycarbonate, to form films. The films were dried under a freeze-drying system (condensation temperature: 193 K, residual pressure: 0.1 Pa). Their thicknesses were between 30 and 300 μ m after drying.

A conventional photolithography machine (Dilase 250 from Kloé company) was used for films patterning. This machine was equipped with a laser diode of 300 mW maximum power, emitting a blue radiation (wavelength: 405 nm). This blue laser diode was selected because of its quite high power level and because of the compatibility with most of the transition metal oxalates which have an adequate optical absorption at the 405 nm wavelength. The optical device used, made it possible to obtain a circular spot of approximately 2 micrometers in diameter. The laser passed through the transparent substrate and was focused at the interface between the substrate and the oxalate film. For the experiments, the laser power and the scanning speed of the spot, were set between 5 and 90 mW and 0.5 mm/sec and 10 mm/sec respectively, depending on the experiment carried out and the nature of the sample treated. The laser powers and the scanning speeds were selected from preliminary experiments to reach a complete oxalate decomposition and a partial sintering of the oxide formed.

After insolation with the photolithography machine, the patterned regions issued from the decomposition of the oxalate, have a very different chemical behavior than the virgin oxalate regions. It is therefore possible to selectively remove the oxalate by simple washing, with deionized water, or chemical etching, with an acid or with an ammoniac compound. The different methods proposed may therefore be suitable. Concentrated ammonia solutions (i.e. ammonia, ammonium nitrate >1 M) are well suited to the dissolution of oxalate from cations which strongly complex with ammonium ions (eg copper). Concentrated acid solutions (>1 M), for example hydrochloric acid, can be useful to dissolve iron or cobalt oxalates. In this case, care must be taken to adjust the etching times so as not to damage the oxide formed.

The compounds formed by laser insolation are well bonded to the polycarbonate substrates. On the other hand, they are only very weakly bonded to the glass substrates. A vigorous washing can thus detach them from the substrate and destroy the formed structure. The most efficient process is then to remove oxalic residues by selective chemical etching. Copper oxalate, in particular, could be

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