



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

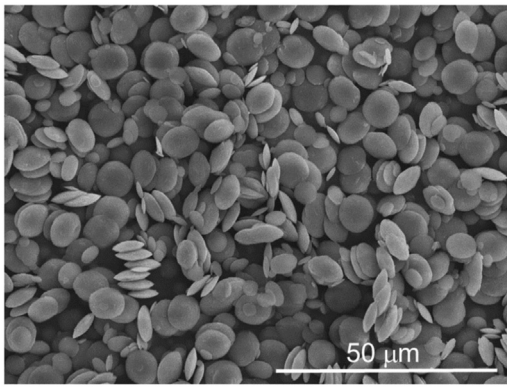


Fig. 1. Copper oxalate powder used for selective laser decomposition experiments.

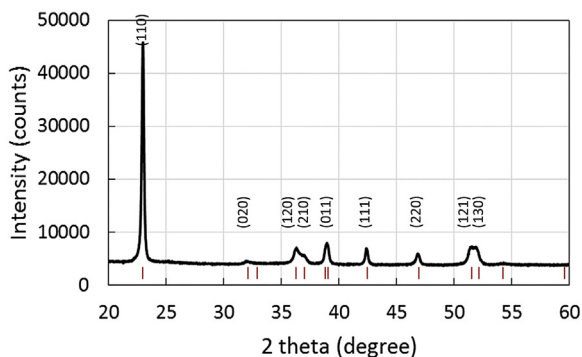


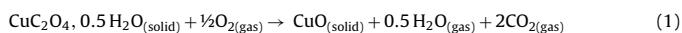
Fig. 2. X-ray diffraction pattern of copper oxalate randomly oriented powder (JCPDS 00-021-0297).

removed with ammonia (4 M). The ammonia complexes of copper are indeed very stable and allow the dissolution of the oxalate.

3. Results

3.1. Selective laser decomposition of copper oxalate

The powder precipitated is made of homogeneous lenticular micronic particles (Fig. 1) of pure copper oxalate, as revealed by X-ray diffraction pattern (Fig. 2) which is the same as those referenced in the JCPDS 00-021-0297 file. Thermogravimetry analysis shows that the mass loss in air reaches about 50% at 260 °C. This loss corresponds to dehydration and decomposition into CuO oxide according to an overall reaction, which can be described by:



The films made from a suspension of the copper oxalate powder, are homogeneous and display a low arithmetic roughness of about 5 micrometers (Fig. 3) when the oxalate thickness is close to 30 micrometers. Such films were used to start the first experiments in which the scan speed and the power of the laser were incremented to determine proper insolation conditions, ie, conditions for fully decomposing the oxalate and obtaining homogeneous, continuous and small lateral size patterns.

The values of scanning speed and power, considerably modify the definition and the quality of the patterns that can be traced. The Fig. 4 illustrates, for example, the influence of the laser spot power. From such tests, a scanning speed of 1–5 mm/sec and a power of 20–75 mW were selected, to try to form varied patterns and evaluate the possibility of the method for copper oxalate films.

First, solid millimeter squares were drawn in the oxalic layers. The laser insolation causes a strong change of color that goes from a very light blue to a very dark brown. The dark squares, character-

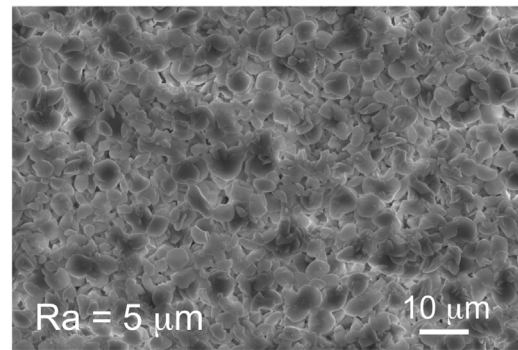


Fig. 3. Scanning electron microscopy image of a film of copper oxalate after drying (glass substrate).

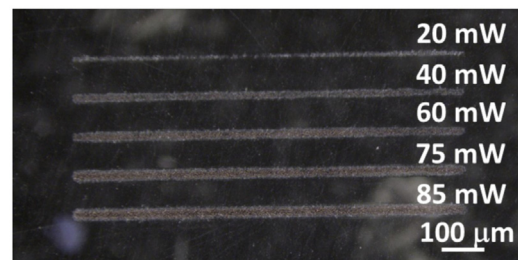


Fig. 4. Optical image of copper oxides patterns after removal of the oxalate layer (laser spot scan speed = 5 mm/sec, glass substrate).

ized by X-ray diffraction, no longer contain oxalate but are made of CuO and Cu₂O oxides. Due to the loss of matter according to Eq. (1) and a partial sintering of the oxides formed, the thicknesses in the squares are smaller than the initial thickness. This can be illustrated by Fig. 5 showing the difference in level, between an insolated surface (oxides) and the initial surface (oxalate). The difference in level is quite difficult to measure because the roughness of the oxide layer is relatively high. For the oxalate film of Fig. 5, however, the thickness decrease after laser irradiation, is of the order of 5–10 micrometers. The oxide grains appear also larger and more sintered when they are located close to the substrates than those, which are near the free surfaces of the films.

By the simple selective laser decomposition of copper oxalate, it is then possible to make well-defined two-dimensional oxide structures as illustrated by Fig. 6. These structures on a polycarbonate substrate are made within a copper oxalate film, but the latter can be removed by selective dissolution (see section 2.3.). The Fig. 7 represents a part of the pattern of the previous figure, after removing the oxalate. It can be seen that fine details, of less than ten micrometers, can be reproduced and preserved in spite of the chemical dissolution of the oxalate. Due to the strong bonding of the oxide on the polycarbonate substrate, the oxalate removing is easier than when this latter is deposited on glass.

3.2. Selective laser decomposition of mixed cobalt iron oxalate

The precipitate obtained according to the procedure described in Section 2.1.2. is a mixed cobalt-iron di-hydrated oxalate made of acicular submicronic particles (Fig. 8). Its X-ray diffraction pattern reveals a single phase having the same pattern of that of β-FeC₂O₄ · 2H₂O described by Deyrieux and Peneloux [20]. Diffraction peaks are however a little bit shifted due to the partial substitution of cobalt for iron. Thermogravimetric analysis confirms also that two water molecules are constitutive of the oxalate structure. After decomposition in air at 800 °C and quenching, the resulting

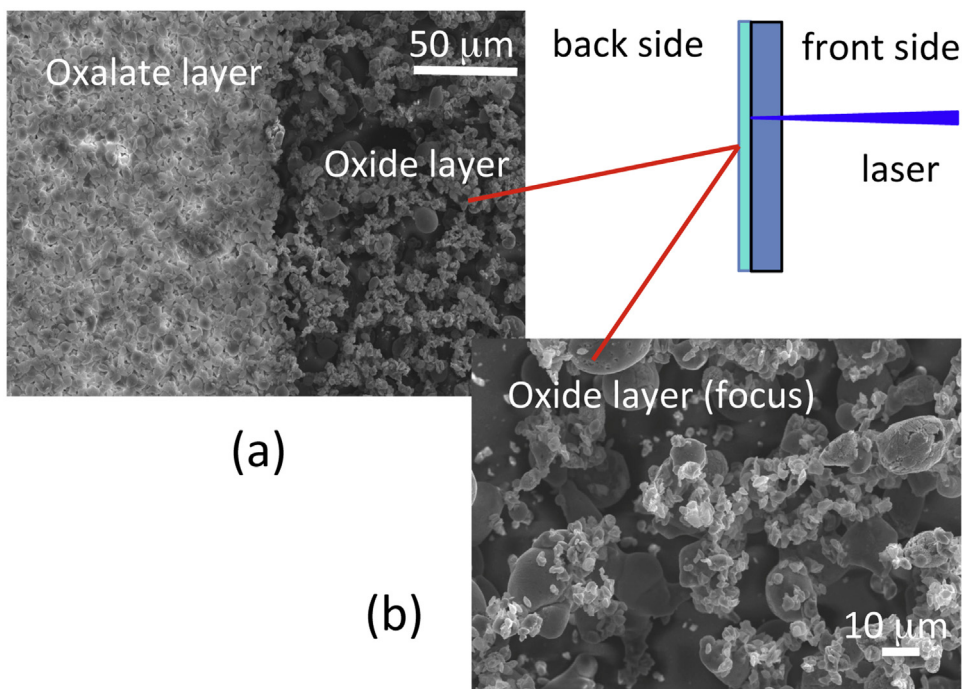


Fig. 5. Selective laser decomposition of copper oxalate, deposited on glass substrate, into copper oxides: (a) Image of the border between the virgin and the insulated zone. (b) Focus of part of the insulated zone.

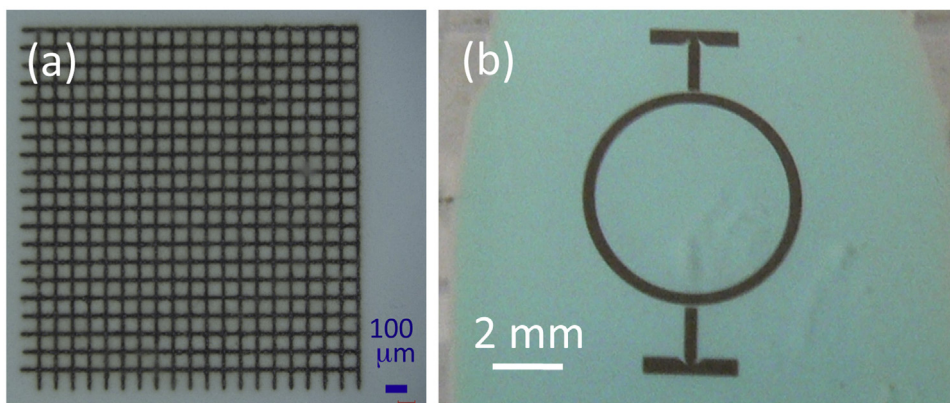


Fig. 6. Various two-dimensional structures formed in a film of copper oxalate deposited on polycarbonate substrate: (a) grid of pitch 100 micrometers (b) structure inspired by RF circuits.

oxide is a pure spinel oxide described by the chemical formula: $\text{Co}_{1.22}\text{Fe}_{1.78}\text{O}_4$, according to chemical analyses.

A film made from a suspension of this mixed oxalate, was prepared and insulated by the laser spot of the machine described in Section 2.3. A scan speed of 1 mm/sec was chosen. The laser spot was passed 4 times at successive powers of 10, 20, 30 and 40 mW to ensure decomposition throughout the thickness of the layer. The insulation leads to a strong change of color, the bright yellow of the initial oxalate becoming dark brown. X-ray diffraction analysis shows that the oxalate has been completely decomposed to give place to a mixture of mixed oxides, one of the spinel type and the other one of the wustite type (Fig. 9).

The magnetic measurements of the oxalate on the one hand, and the oxides formed on the other hand, show the very different magnetic properties of the starting and final materials. The oxalate is paramagnetic and the global behavior of the oxides is ferromagnetic. At room temperature, the hysteresis curve for the oxides shows a coercive field of about 1 000 Oe and a magnetiza-

tion at 30 kOe of about 17 emu/g. After cooling the oxides at 100 K under a magnetic field of 30 kOe the coercive field and the maximal magnetization are increased up to 6 kOe and 20 emu/g. The hysteresis curve is shifted towards the negative fields. The so-called bias magnetic field is close to 1.5 kOe (Fig. 10).

As in the case previously studied, mixed cobalt iron oxide patterns of various shapes exhibiting a resolution of the order of 10 micrometers, can be created on glass or polycarbonate substrates. However, an acid is required to remove the oxalate because iron and cobalt ions are not highly complexed by ammonia.

4. Discussion

The above results show that a focused laser beam of low power, available on a conventional photolithography machine, can decompose the oxalates of copper or cobalt-iron. If the laser spot diameter is estimated to be about 2 micrometers and the laser power lies from 20 to 75 mW, the laser power densities are in between 6 and

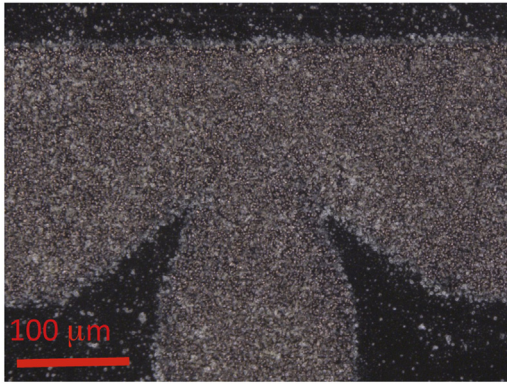


Fig. 7. Detail of Fig. 6(b) observed by optical microscopy after oxalate removing (dark regions).

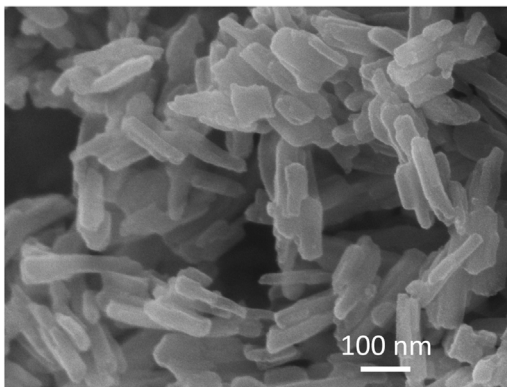


Fig. 8. Scanning electron micrograph of $\text{Co}_{0.41}\text{Fe}_{0.59}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ particles.

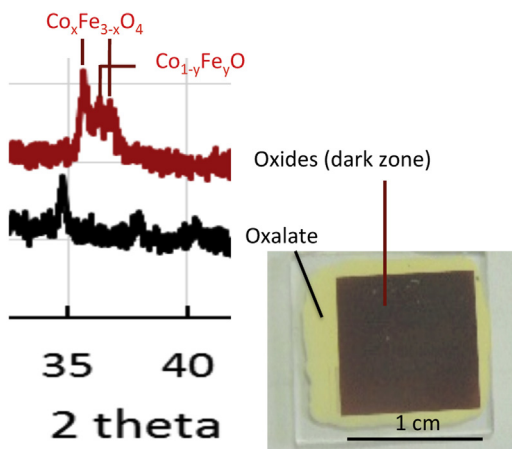


Fig. 9. Selective laser decomposition of mixed cobalt-iron oxalate deposited on glass substrate. Formation of mixed spinel and wustite oxides.

$24\text{ mW}/\mu\text{m}^2$. Since the speed of movement of the spot is between 1 and 5 mm/sec, the energy density provided by the laser can be evaluated at about 2.10^{-6} to $4.10^{-5}\text{ J}/\mu\text{m}^2$. Under these conditions, the oxalates are not only decomposed, but the oxides formed are partially sintered as it is shown by the large grains observed after copper oxalate decomposition. The films studied are not sintered in a totally homogeneous manner. The grains of oxide formed are larger and better sintered near the substrate, on the side by which the insolation takes place, than their counterparts, which are distant from it. Due to the loss of matter and the sintering, the decomposed regions have a lower thickness than that of the

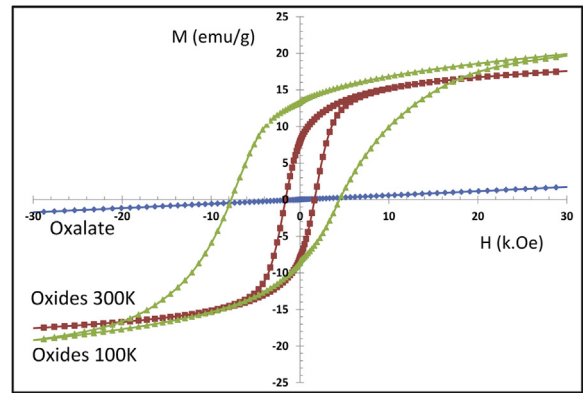


Fig. 10. Magnetization versus magnetic field for mixed cobalt-iron oxalate at room temperature (full diamonds) and for the oxides resulting from the selective laser decomposition at room temperature (full squares) and at 100 K (full triangles).

starting oxalate film. The relative density of the oxides near the substrate is difficult to measure but some porosity can be observed. Optimizing the laser insolation conditions could reduce this porosity. However, decomposition of the oxalates produces gases, which tend to generate porosity. This characteristic may limit the advantage of the method when it is important to have, for example, high electrical conductivities or strong specific magnetizations. Porosity may, however, be an asset for other applications to catalysis or gas detection, for which semiconductor oxides are good candidates [21,22].

The selective laser decomposition of oxalate, allows drawing well-defined two-dimensional structures with a resolution less than 10 micrometers. This can be done without the addition of additives such as reducing compounds, dispersants or wetting agents, sometimes used to achieve the formation of metal or ceramic units [23,24]. The most critical step is not laser insolation. At this stage the resolution is mainly fixed by the size of the laser spot and the lateral thermal propagation in the oxalate layer. The wavelength and the numerical aperture of the optical system fix the size of the laser spot. The diffusion of heat can be partly controlled by the insolation conditions. If the adjustment of these parameters does not allow reaching submicron resolution, it does however make it possible to have repeatable experiments. This reproducibility is more difficult to control, during the step of removing residual oxalate, which is the most critical step. Indeed, the bond between the oxalate and the substrate is not always strong, especially when the substrates are made of glass. The patterns drawn by the laser can therefore be deteriorated, displaced or eliminated by washing or chemical dissolution. From this point of view, the polycarbonate substrates are more favorable. The laser insolation seems indeed to cause a very superficial melting of the polycarbonate, which then binds strongly with the oxides formed.

During and after insolation, it would be interesting to know the temperature of the area treated by the laser, as well as the temperature profile and its evolution over time, in neighboring regions. This information is not currently available for our group, either experimentally or at the simulation level. It is, however, interesting to read, on the phase diagrams, the minimum temperatures at which the phases identified after the laser treatment coexist. It is found that copper monoxide CuO is partially reduced in air to Cu_2O at about 1040°C . On the phase diagram given by Hirano et al. [25], the mixed cobalt-iron oxide of the spinel type coexists in air with a mixed monoxide, above 1100°C for an iron/(cobalt+iron) ratio close to 0.59. These observations seem to indicate that the temperature reached locally is very high and of the order of 1100°C or more.

The fine study of the oxide grains formed was not carried out for this article. It is, however, interesting to note that the mixed oxides of cobalt and iron formed exhibit a cycle of hysteresis displaced along the abscissa axis, when the measurement is made at 100 K after cooling under a high magnetic field. This behavior is indicative of a magnetic coupling between the ferrimagnetic spinel phase and the antiferromagnetic $\text{Co}_{1-x}\text{Fe}_x\text{O}$ mixed monoxide whose, Néel temperature is in between 100 and 300 K (T_N FeO = 198 K [26], T_N CoO = 290 K [27]). These magnetic coupling occurring only when at least one phase consists of crystallites of a few hundred nanometers at the most and is closely related to the second one, it can therefore be supposed that the various oxides formed must be small and intimately related, for the most part.

In this work, only two-dimensional structures were formed. However, the superimposition of layers treated one after the other, by a laser beam, could make it possible, according to an additive manufacturing method, to construct small-sized three-dimensional parts. Due to the high temperature rise, which seems to be reached by the process studied, it would be possible to form 3D structures. It remains to be verified, however, that the links between the superimposed layers during the decomposition of the oxalates, may be sufficiently strong to finally obtain coherent parts.

5. Conclusion

The selective laser decomposition of pure or mixed oxalates allows to form two-dimensional oxide structures. These structures can be well defined with a resolution of less than 10 micrometers.

Glass or polycarbonate, were used as substrates for this study. Due to the superficial melting of the polycarbonate during oxalate decomposition, the oxides formed are strongly bonded to this type of substrate. The removal of the residual oxalates by washing or chemical dissolution, is therefore easier than for the glass substrates on which the patterns formed, can be deteriorated during this operation.

Considering the phases obtained after laser decomposition, it seems that the temperatures reached exceed 1000 °C. These temperatures allow a partial sintering of the oxides formed even if the latter are not perfectly dense and a sintering gradient is observed in the thickness of the layers. These characteristics can be an advantage or a drawback, depending on the technological applications concerned. It seems, however, that selective laser decomposition of oxalates could be an interesting method to make some small devices with pure or mixed oxides, deposited in particular on flexible substrates.

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