TEM, EDX AND RAMAN STUDY OF NICKEL OXIDE MICRO- AND NANOPHASES OBTAINED BY THERMAL DECOMPOSITION OF AN ORGANOMETALLIC PRECURSOR

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Abstract
Nickel(II) polyoxalate was thermally decomposed to nickel oxide in both oxidative and inert atmospheres and the products were investigated using TEM-EDX and Raman spectroscopy. The resulting micro- and nanoparticles were compared regarding their size, morphology and composition. In dynamic aerobic conditions, the product obtained at 1000 °C shows better crystallinity and presents more well defined shapes than the one obtained at 400 °C. The 1000 °C product obtained in argon is a mixture of NiO and metallic Ni.

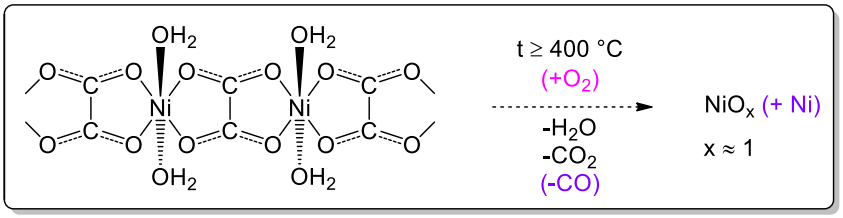
Introduction
The thermal conversion of coordination compounds to metal oxides is a convenient way to produce micro- and nanoparticles with defined properties (degree of crystallinity, size, morphology and surface area), which make them useful for a variety of applications. For example, nanosized nickel oxide exhibits anomalous electronic and magnetic properties and can be used for catalysis, electrochromic windows and sensors. In this paper we have investigated the nickel oxide obtained through the thermal conversion of a complex compound, namely nickel(II) polyoxalate hydrate [1], in both aerobic (at 400 and 1000 °C) and inert (at 1000 °C) atmospheres.

Experimental
The nickel(II) polyoxalate hydrate was prepared starting from nickel(II) nitrate and ethylene glycol by using an original method, as described in a previous paper [1].
The Raman spectrum was measured at room temperature using a MultiView 1000 system (Nanonics Imaging, Israel), which incorporates the Shamrock 500i Spectrograph (Andor, UK). A laser wavelength of 514.5 nm was used as the excitation source, with a 20 s exposure time and a 300 l mm^{-1} grating.
For the TEM analyses, the material was deposited from ethanol on a 200 mesh TEM copper grid covered with lacey carbon film. We used a Titan G2 80-200 TEM/STEM (FEI Company, the Netherlands) instrument with image correction. The images were registered at 200 kV accelerating voltage. A Digital Micrograph v.2.12.1579.0 software was used for images recorded in TEM mode, while a TEM Imaging & Analysis v.4.7 software was used for recording the EDX

spectrum. The STEM-EDX elemental distribution maps were recorded with the Esprit v.1.9 software.

Results and discussion

The global decomposition process, which takes place during both aerobic (+ O_2) and inert (- CO) heating of the homopolynuclear coordination compound, can be illustrated as shown below:



The particles obtained in aerobic conditions at 400 °C (**Fig. 1**) exhibit irregular shapes with microporous structure and with dimensions dispersed between 15 nm and 2.1 μm; the monocrystalline areas are rather small (14 nm at most) and have the crystalline planes distanced at about 2.27 Å, as seen using HRTEM. On the other hand, the aerobic samples produced at 1000 °C (**Fig. 2**) are composed of 50-750 nm polyhedrons, with extended monocrystalline areas composed of crystal planes distanced at about 2.15 Å. Lastly, the particles obtained at 1000 °C in argon (**Fig. 3**) consist of 60-220 nm parallelepipeds which present wide monocrystalline areas (2.47 Å between the crystalline planes) that are composed mostly of NiO, but also seem to contain metallic Ni particles as large as 2.6 μm in diameter (**Fig. 4**), as shown by EDX.

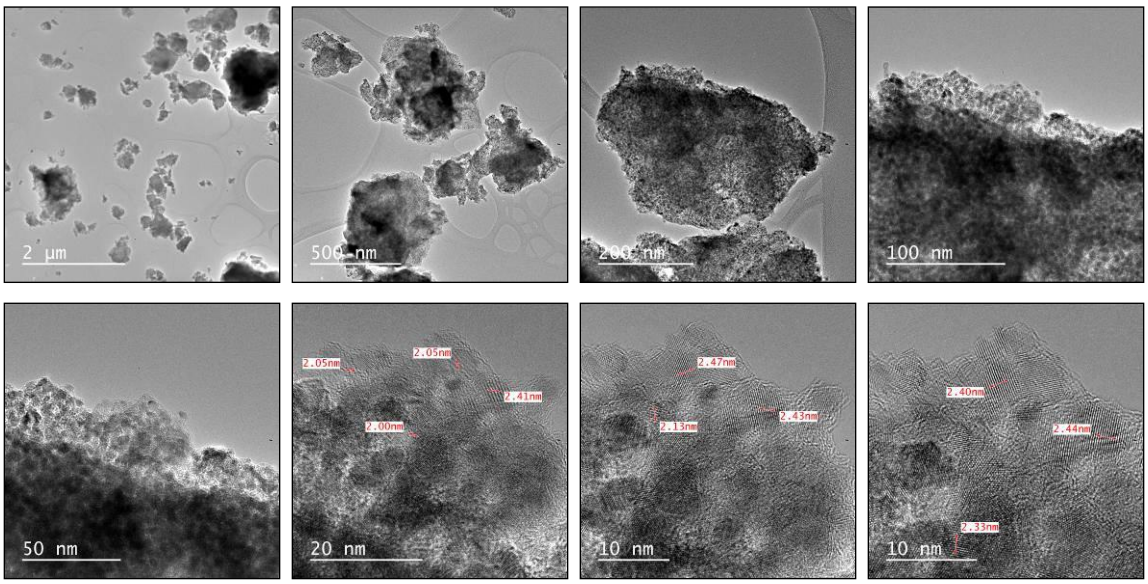


Figure 1. TEM images of the 400 °C aerobic decomposition product (mostly NiO)

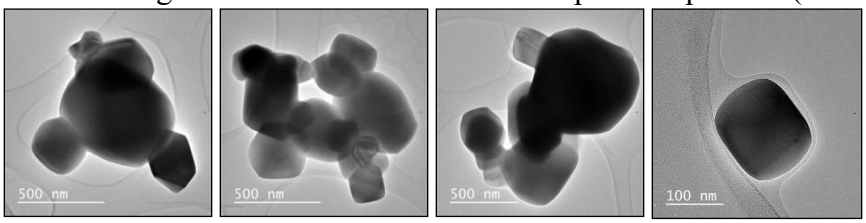


Figure 2. TEM images of the 1000 °C aerobic decomposition product (NiO)

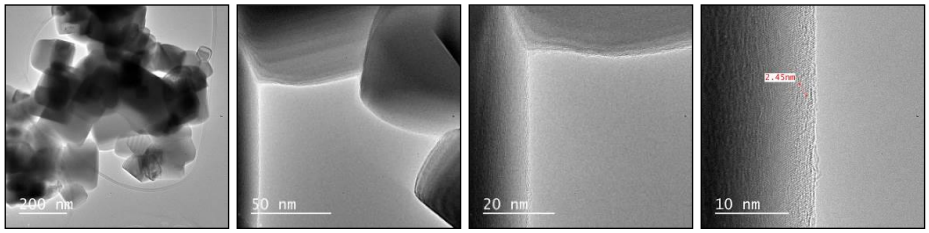


Figure 3. TEM images of the 1000 °C argon decomposition product, which show NiO nanocrystals

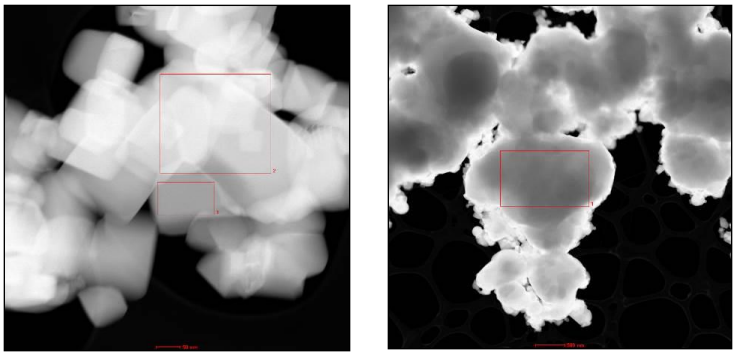


Figure 4. STEM images of the 1000 °C argon decomposition product; EDX analysis revealed mostly NiO in the two areas from the left image and mostly metallic Ni in the area from the right image

The EDX profile obtained for the aerobic 400 °C product is shown in **Fig. 5**, and is similar in shape to the one obtained in aerobic conditions at 1000 °C. The determined atomic ratios suggest a $NiO_{1.37}$ formula in the former case, and a $NiO_{0.82}$ formula in the latter.

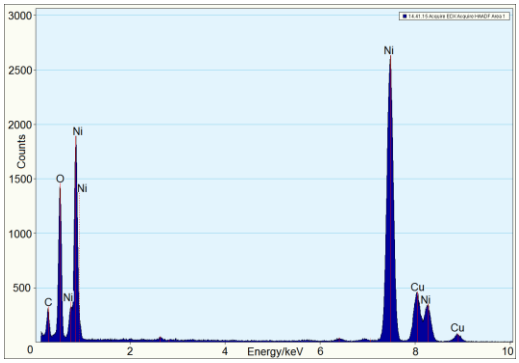


Figure 5. EDX profile in a surface area of the product obtained by aerobic thermal conversion of the complex compound at 400 °C (C and Cu peaks belong to the grid)

The EDX profiles for two distinct particles (**Fig. 4**) of the product obtained by the coordination compound's annealing in argon at1000°C are shown in **Fig. 6**. The analysis of the two selected surface areas reveals that this product is a mixture of NiO and metallic Ni.

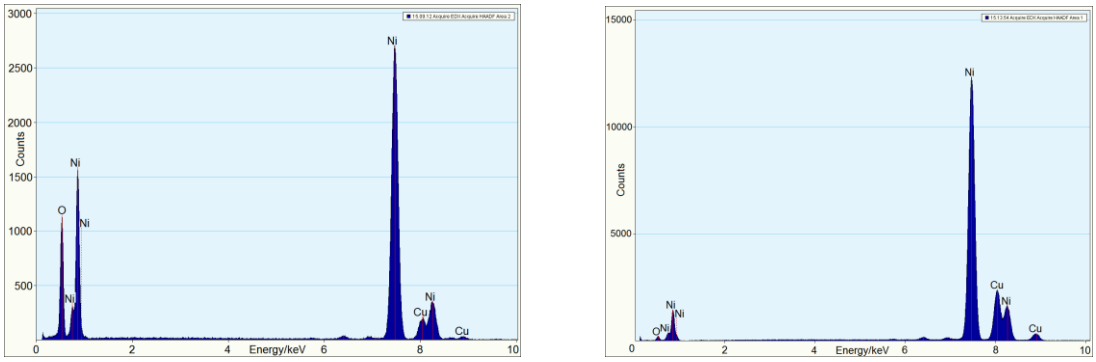


Figure 6. EDX profiles corresponding to the surface areas shown in **Fig. 4** (C and Cu peaks belong to the grid): left $NiO_{0.87}$, right metallic nickel (Ni > 97 atomic %)

The Raman spectrum of the final argon decomposition product is shown in **Fig. 7**. Peaks due to one-phonon (553 cm^{-1}), two-phonon (709, 892 and 1086 cm^{-1}) and two-magnon (1369 cm^{-1}) scattering for NiO [2] are all present.

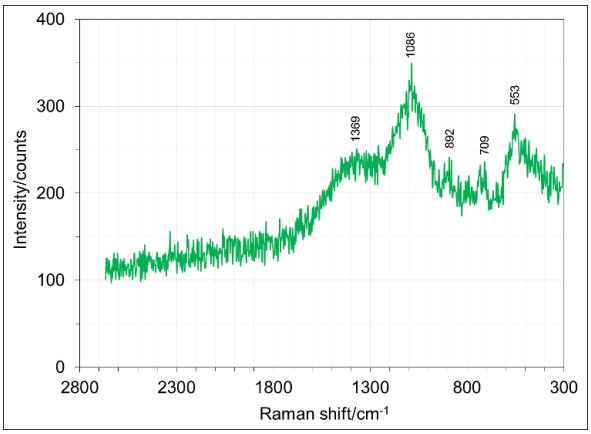


Figure 7. RAMAN spectrum of the 1000 °C argon decomposition product

Conclusions

The thermal conversion of the nickel(II) polyoxalate hydrate gave mostly NiO, which also contains some metallic Ni when inert (argon) dynamic atmosphere is used. The samples obtained at 1000 °C show more well defined edges and larger monocrystalline areas than the ones obtained at 400 °C.

Acknowledgements

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References

[1] M. Niculescu, M.C. Pascariu, C. Muntean, J. Therm. Anal. Calorim. (2016), *in press*.
[2] N. Mironova-Ulmane, A. Kuzmin, I. Steins, J. Grabis, I. Sildos, M. Pärs, J. Phys.: Conf. Ser. 93 (2007) 012039, doi:10.1088/1742-6596/93/1/012039.