

## **PREPARATION OF REACTIVE METAL POWDERS BY THERMAL DECOMPOSITION OF HYDRAZIDOCARBONATES**

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This procedure for metal powder preparation involves a combination of decomposition and reduction processes. The large mass loss through evolution of gaseous products leaves agglomerates of a fine-grained three-dimensional network of metal particle 0.2 to 1  $\mu\text{m}$  in size.

**Keywords:** hydrazidocarbonates, reactive metal powders

### **Introduction**

The processes for metal powder preparation and the fundamentals and principles that are their basis are gaining in interest due to a number of applications arising for these materials. The use of metals in the form of powders, films and coatings is gaining in momentum for catalyst production, battery and fuel cells or electrode production.

Different routes and processes for metal powder preparation are known: the preparation procedure has a great effect on the characteristics of the products such as particle size and distribution, shape, microstructure, porosity, purity and reactivity. Besides so-called mechanical processes that are already widely used for metal powder production on an industrial scale, (e.g. grinding and milling of crushable metals, granulation and atomisation), various other processes are becoming increasingly important, such as the reduction of metal oxides, electrochemical methods, precipitation from solution and gaseous phase, and thermal decomposition of various metal compounds. The last-named method is frequently used for preparation of high-purity metal powders by the decomposition of metal carbonyls,  $\text{M}(\text{CO})_n$ .

## Experimental

Starting materials for this investigation were prepared as described previously [1, 2]; chemical analyses are given in Table 1.

**Table 1** Chemical analysis of starting compounds (%)

Compound	M c.	M f.	N <sub>2</sub> H <sub>4</sub> c.	N <sub>2</sub> H <sub>4</sub> f
N <sub>2</sub> H <sub>5</sub> [Fe(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub> ]-H <sub>2</sub> O	16.83	16.1	38.57	38.9
Co(N <sub>2</sub> H <sub>3</sub> COO) <sub>2</sub>	28.20	28.5	30.63	30.2
N <sub>2</sub> H <sub>5</sub> [Co(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub> ]-H <sub>2</sub> O	17.59	17.4	38.21	38.9
N <sub>2</sub> H <sub>5</sub> [Ni(N <sub>2</sub> H <sub>3</sub> COO) <sub>3</sub> ]-H <sub>2</sub> O	17.53	17.6	38.24	38.4
Cu(N <sub>2</sub> H <sub>3</sub> COO) <sub>2</sub> · 0.5H <sub>2</sub> O	28.55	28.1	28.75	28.2

Thermal properties of the samples were investigated on Mettler TA 3000 and Netzsch STA 409 Systems. In the later case the apparatus was coupled to an Inficon Leybold Heraeus mass spectrometer for analysis of evolved gases (EGA). Sample weights ranging from 50 to 1000 (EGA) mg were used. A variety of atmospheres, e.g. air, argon, argon/hydrogen (4%) and vacuum, were applied. Experiments in air were carried out only for comparison of results in inert and reducing atmospheres. Larger amounts of samples (up to 5 g) were heated in a separate furnace with temperature programming.

The amount of iron in the samples was determined gravimetrically [3], cobalt, nickel and copper by complexometric titration [4], and hydrazine by potentiometric titration with potassium iodate(V) in hydrochloric acid solutions [5].

A LEITZ-AMR 1600T system was used for scanning electron microscopy of the metal powders, specific surface area determinations were made by the BET method, X-ray powder diffraction was carried out on a Philips PW-1710 diffractometer (30 mA, 40 kV and CuK<sub>α</sub> radiation), and infrared spectra were recorded in the range 4000 to 220 cm<sup>-1</sup> on a Perkin Elmer 1720X spectrometer.

## Results and discussion

The thermal decomposition processes discussed involve a combination of decomposition and reduction processes [6]. The various metal hydrazidocarbonate starting materials were selected on the basis that, apart from the metal present, they are easily degradable to gaseous products and have strong reducing groups built into the molecule.

All compounds examined decompose in inert or reducing atmospheres and in a vacuum to the element (Figs 1 and 2). Only the metal remains in the crucible, all other constituents gasify during heating but nevertheless have an important in-

fluence on the course of decomposition and appearance of end products. Metal powders form at relatively low temperatures (400°–550°C) except for the copper compound where the metal is obtained at 200°C.

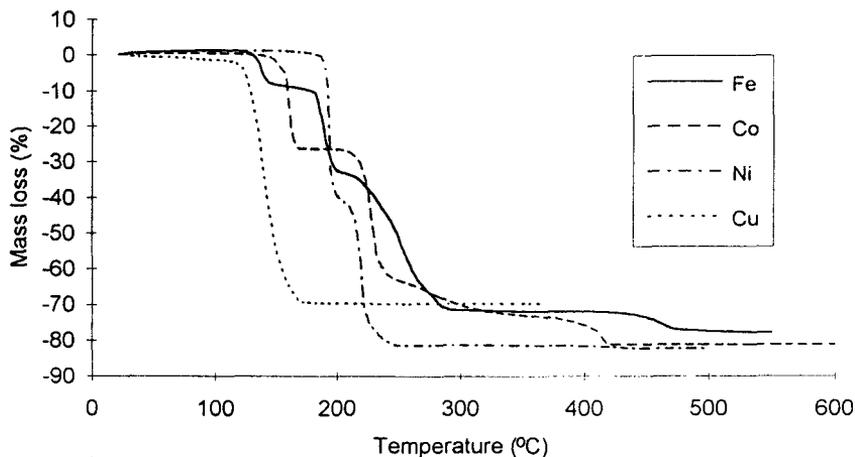


Fig. 1 TG curves for hydrazido-carbonates

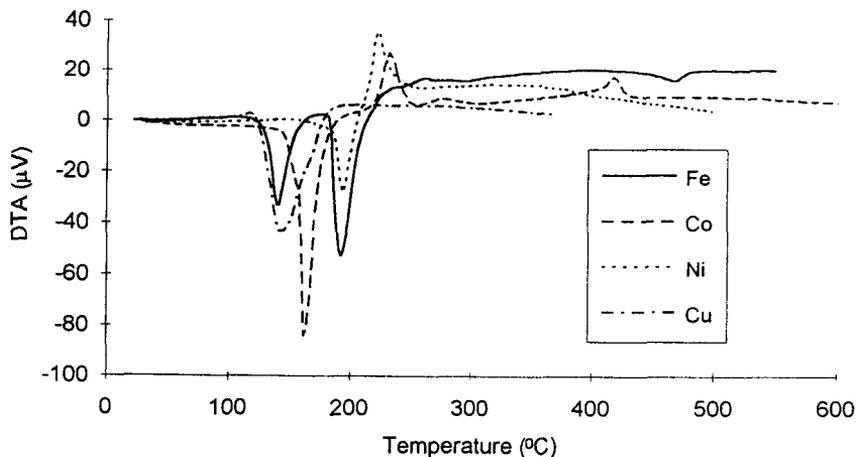


Fig. 2 DTA curves for hydrazido-carbonates

During heating the sample undergoes a volume reduction because of the large mass loss: 79.5% for iron, 81.5% for cobalt, 82.6% for nickel and 71.0% for the copper compound. This process is not uniform, leaving behind a spongy mass with a three-dimensional network of metal particles. The porosity of the material is a result of gasification.

The wide range of hydrazidocarbonates allows selection of the amount of evolved gases released per mole of starting compound and thus control of the porosity and other characteristics of the metal powder residue. For  $\text{Co}(\text{N}_2\text{H}_3\text{COO})_2$  with 28.2% of cobalt, 5 moles of gaseous products are released, compared to  $\text{N}_2\text{H}_5[\text{Co}(\text{N}_2\text{H}_3\text{COO})_3]\cdot\text{H}_2\text{O}$  with an initial metal content of 17.53% and 11 moles of gases per mole of starting compound.

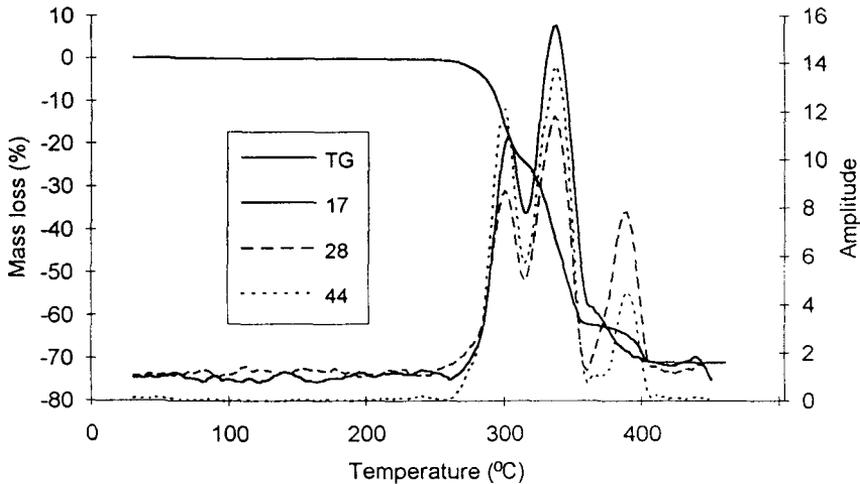


Fig. 3 EGA of  $\text{Co}(\text{N}_2\text{H}_3\text{COO})_2$

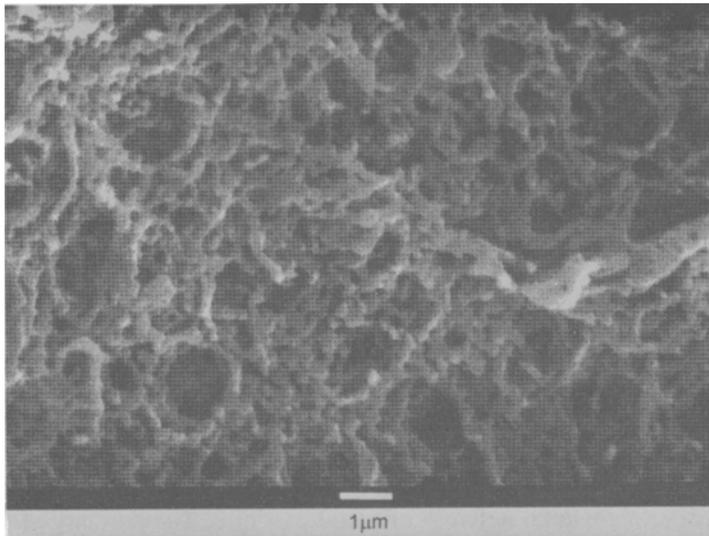


Fig. 4 Scanning electron micrograph of nickel powder obtained in inert atmosphere

During thermal decomposition these constituents provide a reducing environment in the solid as well as in the gaseous phase. The exact reaction scheme for the thermal decomposition of hydrazidocarbonates cannot be deduced from thermogravimetric data. It is known [6] that cobalt and nickel tris-hydrazidocarbonates metalates monohydrates decompose through intermediates of the type  $M(N_2H_3COO)_2 \cdot N_2H_4$ . Since the majority of the molecules decompose to gaseous products, evolved gas analysis was included in the experimental program. Results are shown in Fig. 3.

Common to all the end products is their very high reactivity, as shown during exposure to air when all of them except copper immediately displayed pyrophoric properties and rapidly oxidised to the corresponding metal oxides. The reactivity of the products of thermal decomposition was also followed by controlled oxidation/reduction on a thermobalance by switching atmospheres consecutively.

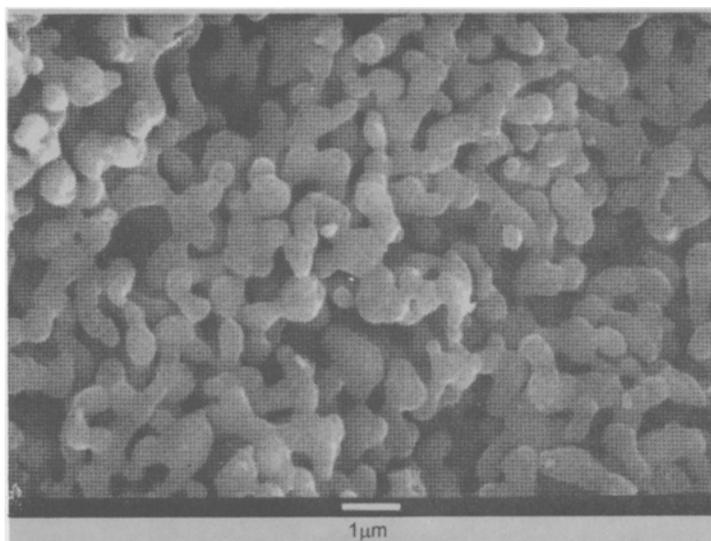


Fig. 5 Scanning electron micrograph of nickel powder obtained in vacuum

Cobalt and nickel metal powders in general retained their original particle or crystal shape. Scanning electron microscopy of residues after thermal treatment revealed the substructure of the bulk material to consist of a fine three-dimensional network of interconnected smaller metal particles. These particles were all about 0.5 μm in size but smaller particles were also observed. Shapes of individual particles are irregular and dendritic. Loosely bound metal agglomerates are obtained if the samples are not calcined at too high a temperature. The thermal decomposition of  $N_2H_5[Ni(N_2H_3COO)_3] \cdot H_2O$  is complete in inert atmosphere at 400°C. Loosely bound nickel powder can be seen in Fig. 4: individual ag-

glomerates are up to 200  $\mu\text{m}$  long, but these break down easily to smaller particles during handling. Sizes of the basic particles forming these agglomerate are about 0.2  $\mu\text{m}$ . In Fig. 4, voids due to exit of evolved gases can clearly be seen. Decomposition in vacuum (Fig. 5) produces larger particles (approximate diameter 0.5  $\mu\text{m}$ ). At higher temperatures these particles tend to sinter and the product as a whole exhibits a higher rigidity. Products obtained at temperatures of about 900°C are compact with appreciably less porosity. Specific surfaces of products at 400°C are up to 4  $\text{m}^2/\text{g}$ , but only 0.5–1  $\text{m}^2/\text{g}$  at 600°C.

## Conclusion

Preparation of metal powders through thermal treatment of iron, cobalt, nickel and copper hydrazidocarbonates is possible. Agglomerates of fine metal particles forming larger metal grains are obtained, which resemble shapes of the original crystals. Substantial mass losses of up to 82% are observed.

The very high reactivity of the products suggests use as catalysts, either alone or in combination with an inert carrier, as oxygen scavengers, or in batteries and fuel cells.

## References

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**Zusammenfassung** — Das beschriebene Verfahren zur Metallpulverherstellung beinhaltet eine Kombination von Zersetzungs- und Reduktionsprozessen. Der große Masseverlust bei der Freisetzung von gasförmigen Produkten hinterläßt Agglomerate eines feinkörnigen dreidimensionalen Netzwerkes aus Metallpartikeln der Größe 0.2 bis 1  $\mu\text{m}$ .