

## NiCoMn nanostructured powders used for wastewater treatment

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(Received: 01 November 2023, Accepted: 13 November 2023)

(2nd International Conference on Contemporary Academic Research ICCAR 2023, November 4-5, 2023)

**ATIF/REFERENCE:** Dadda, K., Djerad, S., Alleg, S., Dadda, N. & Hlil, E. (2023). NiCoMn nanostructured powders used for wastewater treatment. *International Journal of Advanced Natural Sciences and Engineering Researches*, 7(10), 171-174.

**Abstract** – This study uses mechanical alloying to prepare nanostructured Co<sub>27</sub>Mn<sub>13</sub>Ni<sub>60</sub> (wt.%) powders. 24 h of milling leads to the formation of a single fcc-solid solution that undergoes ferromagnetic-paramagnetic transition at a Curie temperature of about 790 K. Powders were tested for Fenton catalysis, and their performance was investigated for methylene blue discoloration.

**Keywords** – NiCoMn Powders; XRD; Fenton-Like Process; Methylene Blue.

### I. INTRODUCTION

Nano-produced powders have attracted much attention due to their promising application in different fields. These powders can be elaborated by several methods, such as the mechanical alloying technique (MA). The MA is a solid-state process based on repetitive fracture, cold solder, and agglomeration phenomena of powder particles. The high-energy ball-powder-ball and/or ball-powder-vials impacts reduce the particle size to a nanometric scale and introduce many structural defects' origins of extraordinary applications such as soft magnetic character, catalysts, sensors, etc. Arc melting and MA techniques [1]–[5] were used to elaborate disordered face-centered cubic and body-centered cubic CoNi-based solid solution with soft-magnetic

character. The solid solution is used in an oxidation reaction *via* a heterogeneous Fenton-like process.

The Fenton reaction is an effective oxidation system used for water treatment by forming hydroxyl radicals ( $\bullet$ OH) [6] responsible for dye degradation.

### II. MATERIALS AND METHOD

The nominal composition of Co<sub>27</sub>Mn<sub>13</sub>Ni<sub>60</sub> (wt.%) powders was prepared from pure elements of Co (99.5%), Mn (99.95%), and Ni (99.9%) by using a high energy planetary ball mill (FRITSH Pulversitte 7) at 400 rpm, under an argon atmosphere, at ambient temperature. The ball-to-powder weight ratio was 12/1. 24 h of milling was set with an interruption of 15 min each 30 min of

milling. Morphology, structure, and microstructure measurements were investigated using scanning electron microscopy (FEI Quantum 250) and X-ray diffractometry (PANalytical Empyrean diffractometer). Magnetic measurements were carried out by BS2 magnetometer and vibrating sample magnetometer (LakeShore 7404) at room temperature.

A. Methylene blue discoloration experiments

The concentration of methylene blue was determined by using a JENWAY 675UV/Vis spectrometer at 665 nm. The reaction solution was composed of 30 mg of powders and 100 mL of acidic solution of methylene blue ( $5 \cdot 10^{-5}$  M, pH = 3). A volume of about 3 mL of the reaction solution was collected with a syringe at regular time intervals for absorbance measurements and then they were returned to the solution. The experiments were carried out at 60°C under different stirring conditions.

III. RESULTS

The powder morphology (Fig. 1) shows irregular shape and size. The large particle size is due to the nature of the starting materials as all elements have a strong tendency to form agglomerates.

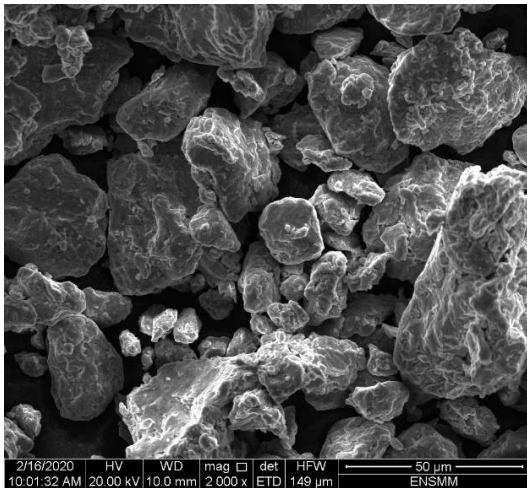


Fig. 1 SEM micrograph of NiCoMn powder mixture.

The refinement of the X-ray diffraction pattern (Fig. 2) has been performed using the MAUD program, which is based on the Rietveld method [7]. The best refinement is achieved by introducing a single solid solution, labeled (NiCoMn)-SS, with a lattice parameter of  $a = 3.542 \text{ \AA}$ , average crystallite size of about 60 nm, and microstrains of 1.5%.

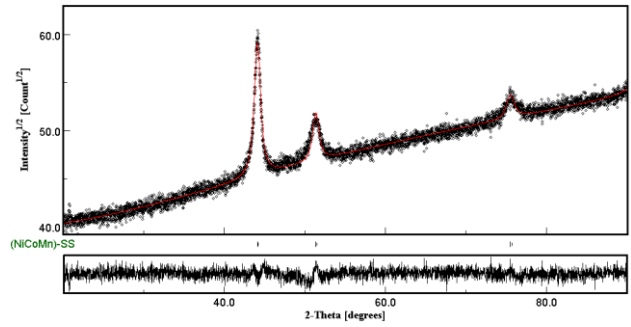


Fig. 2: Rietveld refinement of the X-ray diffraction patterns of NiCoMn powder mixture (Reliability parameters: GoF = 0.89, Rwp = 1.87; Rb = 147, Rexp = 2.08).

The magnetization-field (M–H) hysteresis loop (Fig. 3) recorded at room temperature under varying magnetic field up to 10 kOe show that the M-H curve exhibits narrowed and sigmoidal-shaped hysteresis loops typical to the soft magnetic character.

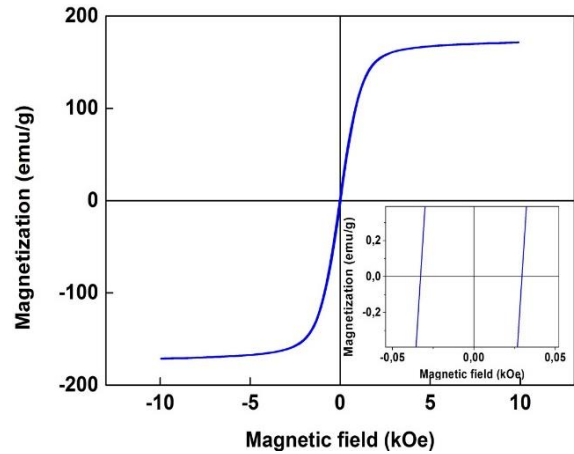


Fig. 3: Hysteresis loop of the ball-milled powders. The inset shows a zoom of the central part region.

The low field of 500 Oe measurements of the magnetization to temperature dependence (M–T) curve, evaluated in the temperature range of 200–850 K, reveals that the as-formed solid solution undergoes a magnetic ferromagnetic–paramagnetic phase transition at a Curie temperature of  $T_c = 790 \text{ K}$  (Fig. 4).

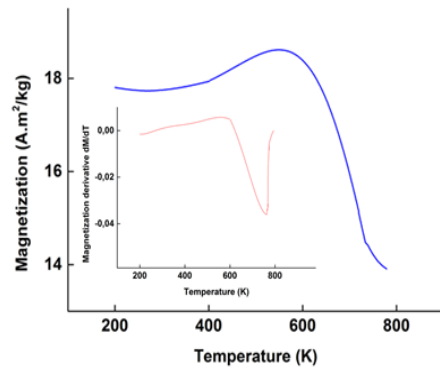


Fig. 4: M–T curve of NiCoMn powder mixture. The inset shows the first derivative.

The as-formed solid solution was tested in the discoloration reaction of methylene blue under three different stirring conditions (Fig. 5): magnetic stirring (mag) and mechanical stirring (mec). One can observe that the degradation efficiency using the magnetic stir (~95%) is more enhanced than that for the mechanical (~75%) one.

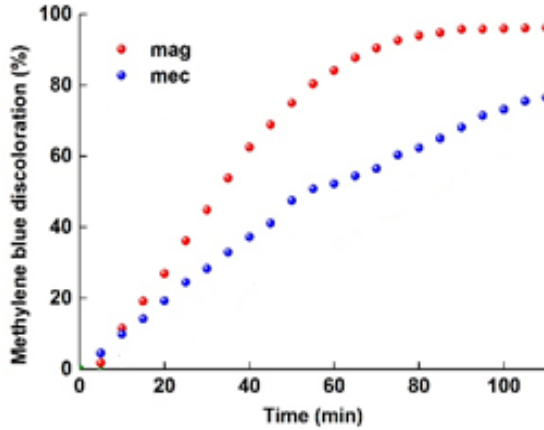


Fig. 5: Discoloration reaction of NiCoMn powder mixture under two different stirring conditions: magnetic stirring (mag) and mechanical stirring (mec).

The discoloration process during the oxidation of methylene blue may be described as a pseudo-first-order reaction kinetic by using the following relation:

$$\ln \frac{A_0}{A} = k \cdot t \quad (3)$$

The rate constant  $k$  values extracted from the slopes of the straight lines of  $\left(\ln \frac{A_0}{A}\right)$  versus  $t$  curves were, respectively, 0.011 and 0.013  $\text{min}^{-1}$  for mag and mec stirring where the reaction registered one stage.

#### IV. DISCUSSION

The MA technique is an easy process to produce solid solutions that can be stabilized when the atomic size mismatch  $\delta$  is valued at  $\delta \leq 6.6\%$  and the ratio between the entropy and enthalpy of mixing  $\Omega$  is  $\Omega \geq 1.1$  [8]. The two characteristic factors are given by:

$$\delta = \sqrt{\sum_1^n c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \quad (1)$$

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \quad (2)$$

where  $c_i$  is the atomic proportion of the  $i$ -th element,  $r_i$  is the atomic radius of the  $i$ -th element,  $\bar{r}$  is the average radius of the three elements,  $T_m$  is the

theoretical melting point ( $T_m = \sum_1^n (T_m)_i c_i$ ),  $\Delta S_{mix}$  is the entropy of mixing ( $\Delta S_{mix} = -R \sum_1^n (c_i \ln c_i)$ ),  $\Delta H_{mix}$  is the enthalpy of mixing ( $\Delta H_{mix} = 4 \sum_{i=1, i \neq j}^n (\Delta H_{ij} c_i c_j)$ ),  $R$  is the perfect gas constant, and  $\Delta H_{ij}$  is the enthalpy of mixing of each possible binary system calculated according to the approach of Miedema [9]. The two criteria of  $\delta = 3.1$  and  $\Omega = 1.9$  fulfil the conditions, and the stability of the as-formed solid solution is highly possible.

The coercive field value obtained from the M–H hysteresis loop,  $H_c = 490$  Oe, which ranges between 100 and 1000 Oe, confirms the soft magnetic character of the as-formed solid solution. Since the remanence to saturation magnetization ratio value ( $M_r/M_s = 0.04$ ) is less than 0.1, the powder particles are multi-domains.

Using a pitched four-blade magnetic bar for the discoloration experience, in the case of the magnetic stirring, can strew the powder particles over its entire surface, making the particles susceptible to react easily within the dye molecules and consequently accelerating the oxidation rate as it successively increased during the complete experimental period. However, the flow dynamic resulting from the mechanical stirring differs totally from that of the magnetic one. In this case (i.e. mechanical stirring), the minimum fluid velocity in the central location of the vessel and under the paddle makes the place adequate to form aggregate. This aggregation decreases the reaction of methylene blue oxidation as the exposed particles' surface to the dye molecules is reduced.

#### V. CONCLUSION

The mechanically alloyed  $\text{Co}_{27}\text{Mn}_{13}\text{Ni}_{60}$  (wt.%) powders were prepared in a high-energy planetary ball mill P7. The X-ray diffraction analysis confirmed the formation of a single disordered fcc-solid solution phase obtained after 24 h of milling that undergoes a magnetic phase transition at 790K. The powders have been tested in discoloration reaction of methylene blue under different conditions. The nanostructured  $\text{Co}_{27}\text{Mn}_{13}\text{Ni}_{60}$  powders are good candidates for water treatment applications.

#### ACKNOWLEDGMENT

DGRSDT/MESRS Algeria and l'Ecole Nationale Supérieure des Mines et Métallurgie d'Annaba (ENSMM) are gratefully acknowledged.

## REFERENCES

- [1] Y. Zhou, P. Nash, X. Dai, D. Li, A. Silva, G. Lopes Cardoso, Phase equilibria in the Co-Mn-Ni system, *J. Alloy. Compd*, Vol 777, pp 1274–1285, 2019.
- [2] N. Dadda, K. Dadda, W. Bouchelaghem, M. Medjaldi, S. Alleg, M. Bououdina, E. K. Hlil, Magnetic and Electronic Structure Studies of Nanocrystalline (Co<sub>2</sub>Mn)<sub>40</sub>Ni<sub>60</sub> Alloy, *Acta Phys. Pol.*, Vol A 140, pp 153–160, 2021.
- [3] M. Triki, H. Mechri, H. Azzaz, M. Azzaz, Characterization of nanostructured magnetic alloy based on Ni-Co-Mn produced by mechanical synthesis, *J. Magn. Magn. Mater.*, Vol 541, pp 168514, 2022.
- [4] A. Ghasemi, K. Zamani, M. Tavoosi, G.R. Gordani, Enhanced Soft Magnetic Properties of CoNi-Based High Entropy Alloys, *J. Supercond. Novel Magn.*, Vol 33, pp 3189–3196, 2020.
- [5] K. Dadda, N. Dadda, S. Djerad, S. Alleg, M. A. Oulabes, E. K. Hlil, Investigation on microstructure, magnetic and electronic structures of the mechanically alloyed (Co<sub>2</sub>Mn)<sub>100-x</sub>Ni<sub>x</sub> powders used as an oxidizing agent for methylene blue, *J. Magn. Magn. Mater.*, Vol 556, pp 169390, 2022.
- [6] Y. Tian, X. He, H. Zhou, X. Tian, Y. Nie, Z. Zhou, C. Yang, Y. Li, Efficient fenton-like degradation of ofloxacin over bimetallic Fe–Cu@Sepiolite composite, *Chemosphere* 257 (2020), 127209.
- [7] L. Lutterotti, S. Matthies, H.R. Wenk, “MAUD — A Friendly Java Program for Material Analysis Using Diffraction”, *Newslett. CPD* 21, 14 (1999).
- [8] X. Yang, Y. Zhang, Prediction of high-entropy stabilized solid-solution in multicomponent alloys, *Mater. Chem. Phys.*, Vol 132, pp 233–238, 2012.
- [9] A. Takeuchi, A. Inoue, Classification of Bulk Metallic Glasses by Atomic Size Difference, Heat of Mixing and Period of Constituent Elements and Its Application to Characterization of the Main Alloying Element, *Mater. Trans.*, Vol 46, pp 2817–2829, 2005.
- [10] Y. Li, W.P. Hesieh, R. Mahmudov, X. Wei, C.P. Huang, Combined ultrasound and Fenton (US-Fenton) process for the treatment of ammunition wastewater, *J. Hazard. Mater.*, Vol 244-245, pp 403-411, 2013.