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# Synthesis of mixed ferrite with spinel-type structure from a stainless steelmaking solid waste

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## Abstract

Acid recovery plant powder, a solid by-product of the stainless steel industry with high iron, chromium and nickel content, was used to synthesise a nanocrystalline zinc–chromium–nickel ferrite in order to recover the total metal content of this waste as a valuable ferric product. $Zn^{2+}$ was provided by dissolving ZnO in $HNO_3$ and precipitation with 1M *n*-butylamine solution. The cubic spinel-type ferrite obtained, at temperature as low as 350°C, was characterised by X-ray powder diffraction, scanning and transmission electron microscopy.

*Keywords:* Stainless steelmaking; Acids recovery plant powder; Zinc–chromium–nickel ferrite; Nanocrystalline

## 1. Introduction

Ferrites are an important family of materials whose surface area properties, particle size and chemical and crystallographic composition make their use possible in many technological applications. Ferrites with spinel-type structure may be described by the general formula $MFe_2O_4$, where M is a divalent cation. The unit cell contains eight formula units and is usually referred to as space group $Fd3m$ ($O_h^7$) with cations occupying special positions 8a and 16d. The ideal structure consists of cubic close packing of oxygen atoms (32e) in which one-eighth of the tetrahedral and half of the octahedral interstices are occupied. In the case of a ''normal'' spinel such as zinc ferrite, $Zn^{2+}$ cations usually prefer to occupy the tetrahedral sites and $Fe^{3+}$ cations the octahedral sites. The partial replacement of $Zn^{2+}$ and $Fe^{3+}$ by other metals in different oxidation states yields to mixed ferrites with different magnetic properties [1]. Numerous studies have involved the synthesis of different mixed ferrites. Traditionally, the ceramic method, which involves very high reaction temperatures, has been used for their synthesis. In contrast, current research efforts are focused on the development of low temperature synthesis methods [2,3] in order to obtain materials whose surface area and particle size can be easily designed.

At present, pure reagents are used to synthesize such materials, but previous investigations by the present authors have reported the low temperature synthesis of spinel-type materials by co-precipitation of the corresponding cations at room temperature using a 1M solution of *n*-butylamine at a pH of up to 10.5, a method which has recently been employed to synthesize pure, nanocrystalline powders of zinc ferrite spinel $ZnFe_2O_4$ from an industrial liquid waste [4].

The aim of the present investigation was to attempt low temperature synthesis of a mixed nickel–chromium–zinc ferrite from a solid by-product of the stainless steel industry.

Stainless steel finishing operations involve several surface cleaning processes which eliminate dust, scale and metallic oxides. These processes are performed by immersion of the steel in acidic solutions, generally prepared by mixing nitric and hydrofluorhydric acids. After re-use, the acidic solution finally becomes exhausted and its replacement becomes necessary. The exhausted solution, named spent pickling liquor (SPL), is taken to an acid regeneration plant where both nitric and hydrofluorhydric acids are recovered by means of pyrohydrolysis, APU resins [5] and OPAR processes [6]. The regenerated acids are thus recycled and returned to the plant. As a result of this

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process a solid waste, acid regeneration plant powder (ARPP), of very high valuable metal content (Fe, Ni, Cr and Mn) is obtained as a by-product. ARPP was employed in the present work to synthesize the mixed nickel–chromium–zinc ferrite $(Zn_{0.646}Fe_{0.354})(Fe_{1.335}Cr_{0.291}Ni_{0.354}Mn_{0.022})O_4$. The cation distribution and ionic configuration were established by X-ray analysis. Morphological analysis was performed by transmission and scanning electron microscopy.

## 2. Materials and methods

### 2.1. Materials

ARPP was used as the raw material to synthesize a mixed cubic ferrite. The chemical composition of the as-received solid is shown in Table 1.

### 2.2. Synthesis of spinel phase.

ARPP were suspended in distilled water. $Zn^{2+}$ was added by dissolving ZnO in a 1M $HNO_3$ solution in the necessary quantity to form, after heating, a zinc–chromium–nickel ferrite with cubic spinel-type structure as a single phase. Dissolved $Zn^{2+}$ was precipitated with a 1M *n*-butylamine solution (pH up to 10.5). After precipitation, the aqueous phase was composed of a butylammonium nitrate solution. The solid, precursor material, was washed three times in distilled water, centrifuged and dried at 80°C. This material was subjected to different thermal treatments in an air atmosphere. The detailed description of this synthesis method has recently been published [2,3].

The spinel phase was also prepared following a traditional ceramic method so that the two might be compared. To this end, the required quantity of ARPP was thoroughly mixed with ZnO (Merck, analytical grade). Individual portions of this mixture were heated to 450, 600, 800 and 1100°C respectively, and maintained at these temperatures for 5 h. Thereafter they were cooled to room temperature.

Table 1
Chemical composition of acid recovery plant powders (ARPP)

| Compounds | Percentage (%w/w) |
|---|---|
| NiO | 12.72 |
| $Fe_2O_3$ | 64.95 |
| $Cr_2O_3$ | 10.65 |
| MnO | 0.72 |
| C | 0.16 |
| $SO_4^{2-}$ | 1.76 |
| $NO_3^-$ | 1.50 |
| $F^-$ | 3.52 |
| $H_2O$ | 2.94 |
| Mass losses (25–600°C) | 5.90 |
| Mass Losses (600–1000°C) | 2.78 |
| Total | 98.82 |

### 2.3. Techniques

Characterization of the materials obtained was performed by X-ray powder diffraction techniques (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray powder diffraction (XRD) patterns were recorded using a Siemens D-501 diffractometer with monochromatized Cu Kα radiation. Patterns were recorded in the step scanning mode using a 0.025° ($2\theta$) step and 2s counting time. Least-squares structure refinements of the crystalline materials were performed by the full-profile Rietveld-type method, program DBWS-9006PC [7].

Morphological analysis of samples was performed by scanning electron microscopy (SEM) using a Zeiss DSM 960 microscope, and by transmission electron microscopy (TEM) using a Jeol TEM 2010 model. Conducting samples for SEM were prepared by subjecting powder and compact specimens to gold sputtering. For TEM observations, drops of fine particle solid powder suspended in pure ethanol were deposited on carbon support film 400 mesh copper grids.

## 3. Results

### 3.1. Precursor characterization and spinel phase formation

Fig. 1 shows the XRD pattern for the ARPP. Several broad diffraction bands can be seen, indicating the low crystallinity of the identified phases: hematite ($\alpha$-$Fe_2O_3$) and a cubic spinel. This latter phase has a cell parameter $a_c$~8.32 Å, consistent with a nickel–chromium ferrite spinel [1].

Taking into account the initial chemical composition of the ARPP (Table 1), the hypothetical crystallochemical formula for a single phase cubic spinel, would be the following:

$$[Fe^{3+}_{0.451}Fe^{2+}_{0.549}]_A[Fe^{3+}_{1.151}Cr^{3+}_{0.371}Ni^{2+}_{0.451}Mn^{3+}_{0.027}]_BO_4$$

Since $Ni^{2+}$ and $Cr^{3+}$ show a very strong preference for octahedral B-sites [8,9] and considering the mass and charge balances, this hypothetical spinel would present ~55% $Fe^{2+}$ in A-sites.

Under the oxidant conditions for ARPP formation in the plant, it is not possible to obtain a ferrite spinel with $Fe^{2+}$. This fact justifies the segregation of the hematite. To avoid the iron (III) segregations –and considering that all iron must be in the form of $Fe^{3+}$ and located in both A and B-sites– it is necessary to introduce a cation with a very strong preference for tetrahedral A-sites. Since the cation

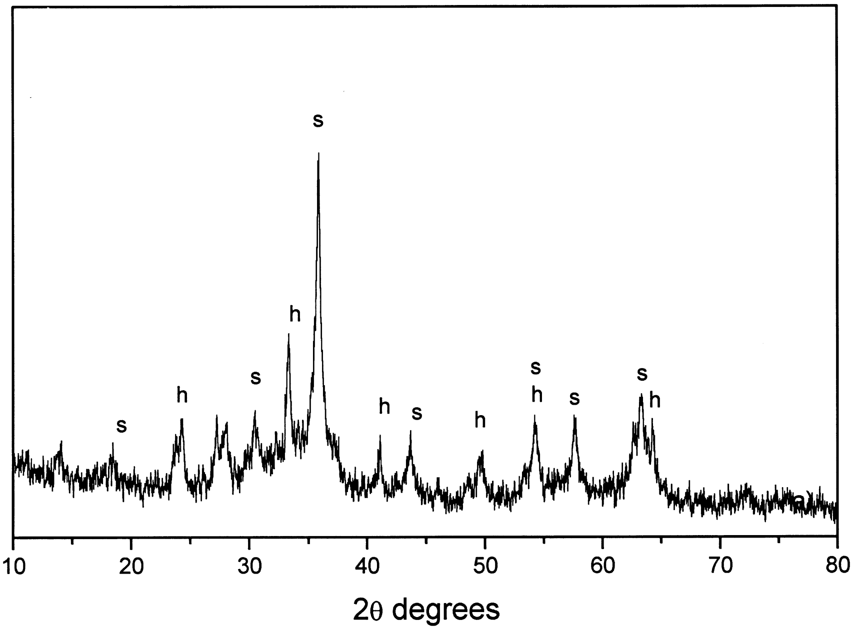

Fig. 1. X-ray powder diffraction pattern for the acid recovery plant powder (ARPP). (h: hematite, s: cubic spinel).

with the greatest affinity for this site is $Zn^{2+}$, ARPP powders were suspended in a 1M $HNO_3$ solution containing dissolved ZnO in the quantity necessary to form a cubic spinel ferrite with no other segregated phase.

In order to obtain the charge-balanced spinel ferrite phase, the next condition: $[Zn^{2+}]_A = 1 - [Ni^{2+}]_B$, is required, since $[Fe^{3+}]_A = [Ni^{2+}]_B$. On the basis of ARPP cationic composition (Table 1), it was calculated that 1.27 g ZnO had to be dissolved in a 1M $HNO_3$ solution containing 5 g of ARPP. Dissolved $Zn^{2+}$ was then precipitated with a 1M *n*-butylamine solution to pH of up to 10.5.

X-ray powder diffration patterns for this material at room and other temperatures are shown in Fig. 2. Fig. 2a shows the XRD pattern of the precursor material obtained from the initial ARPP with added $Zn^{2+}$ and precipitated. This pattern corresponds to a mixture of hematite, a cubic spinel phases with a very low crystallinity and zinc (II) hydroxinitrate $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ [10] (identified only by the sharp 001 reflection line at 7.3 Å). This solid becomes the precursor material of a single phase spinel. When this mixture was heated at 350ºC a cubic single phase spinel with very low crystallite size was obtained. After heating at 600°C, the cell parameter of this cubic single phase spinel was $a_c = 8.3708(9)$ Å (Fig. 2b). Finally, after heating at 1100°C for 2.5 h the cell parameter increased slightly up to 8.3795(1) Å and a sinterization process took place (Fig. 2c).

Taking into account the cationic composition of ARPP and the quantity of zinc precipitated, the following spinel formula was calculated:

$$[Zn^{2+}_{0.646}Fe^{3+}_{0.354}]_A[Fe^{3+}_{1.335}Cr^{3+}_{0.291}Ni^{2+}_{0.354}Mn^{3+}_{0.022}]_BO_4$$

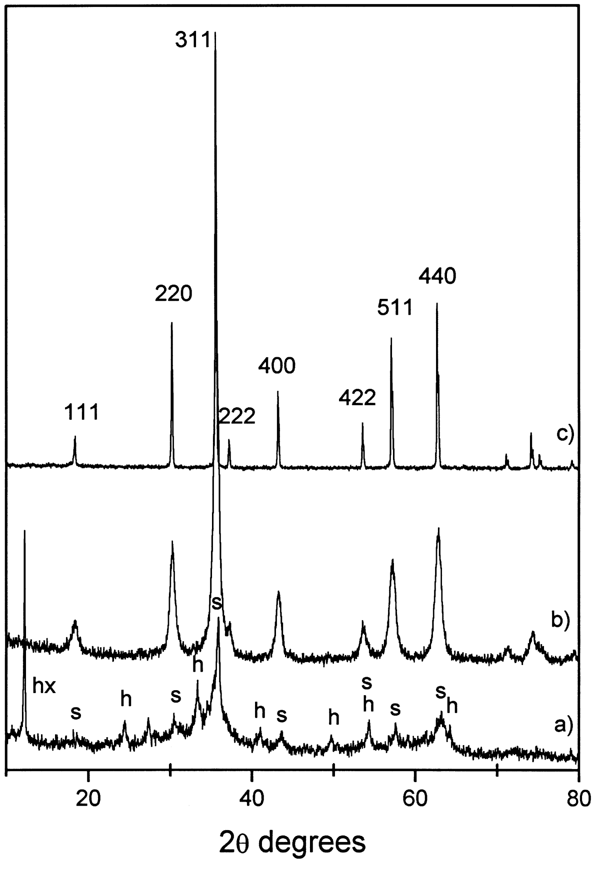

Fig. 2. X-ray powder diffraction patterns recorded on: (a) precursor material, (b) precursor heated at 600°C, 16 h and (c) precursor heated at 1100°C 2.5 h. (hx: zinc hydroxynitrate, h: hematite, s: cubic spinel).

Table 2
Crystallographic parameters obtained from Rietveld refinement for zinc–nickel–chromium ferrite synthesised from powder precursor treated at different temperatures

| $T$(°C) | 600 | 1100 |
|---|---|---|
| $a_c$ (Å) | 8.3708(9) | 8.3795(1) |
| $u$ | 0.2584(4) | 0.2595(4) |
| $d$(A–O) | 1.934(3) | 1.952(3) |
| $d$(B–O) | 2.025(3) | 2.018(3) |

Table 2 shows the cell parameter value, $a_c$, the oxygen positional parameter, $u$, and $d$(A–O) and $d$(B–O) bond distances for the cubic single phase spinel at different temperatures, as determined by Rietveld refinement method.

Theoretical bond distances for tetrahedral and octahedral sites, as derived by Poix [11,12] from systematic studies on materials with spinel type structure, are shown in Table 3. This author also established the invariant character of the cation–oxygen distances for cubic spinel-type structures. The lattice parameter $a_c$ is related to $d_A$ and $d_B$ as follows:

$$a_c = 2.0995 d_A + (5.8182 d_B^2 - 1.4107 d_A^2)^{1/2}$$

where $d_A = \Sigma n_i(\mathrm{Me}_i - \mathrm{O})_A$ and $2d_B = \Sigma n_j(\mathrm{Me}_j - \mathrm{O})_B$.

Table 3
Cation–oxygen distances [9,10] used to calculated the theoretical cell parameter of cubic ferrite

| Cation | $(\mathrm{Me}_i\text{–O})_A$ (Å) | $(\mathrm{Me}_j\text{–O})_B$ (Å) |
|---|---|---|
| $Zn^{2+}$ | 1.970 | – |
| $Fe^{3+}$ | 1.855 | 2.020 |
| $Cr^{3+}$ | – | 1.991 |
| $Ni^{2+}$ | – | 2.088 |
| $Mn^{3+}$ | – | 2.045 |

From these relationships the theoretical cell parameter value for the synthesized spinel ferrite is $a_c = 8.3781$ Å, a figure very similar to the experimentally obtained values (Table 2). These results therefore indicate that the theoretically established ionic configuration and cation distribution are correct.

As an example of Rietveld refinement, Fig. 3 shows plots of the observed, calculated and difference profile for the ferrite obtained by heating the precursor at 1100°C for 2.5 h.

With respect to the synthesis of this material following the ceramic method, XRD powder diffraction patterns of thoroughly mixed powder of ARPP and ZnO at room temperature, 600 and 1100°C are shown in Fig. 4. Fig. 4a shows the XRD pattern of initial mixture, in which may be identified a cubic spinel with of very low crystallinity ($a_c \approx 8.33$ Å), hematite and zincite (ZnO). When this mixture was heated at 600°C (Fig. 4b) and 800°C for 5 h, a gradual fall in hematite and zincite content, accompanied by an increase in quantity and crystallinity of cubic spinel, was observed. Only after heating at 1100°C for 5 h a pure cubic spinel was obtained (Fig. 4c).

These results pointed out that the butylamine synthesis method allows a cubic spinel-type structure to be obtained as a single phase at a temperature around 400°C below that of the traditional ceramic method.

### 3.2. Morphology

Fig. 5 shows the morphology of initial ARPP which is composed of spherical particles between 50–200 μm in diameter. This small particle size induces high reactivity. Scanning electron micrographs of the precursor material obtained after adding $Zn^{2+}$ and precipitating with $n$-butylamine indicate that this material is composed by very

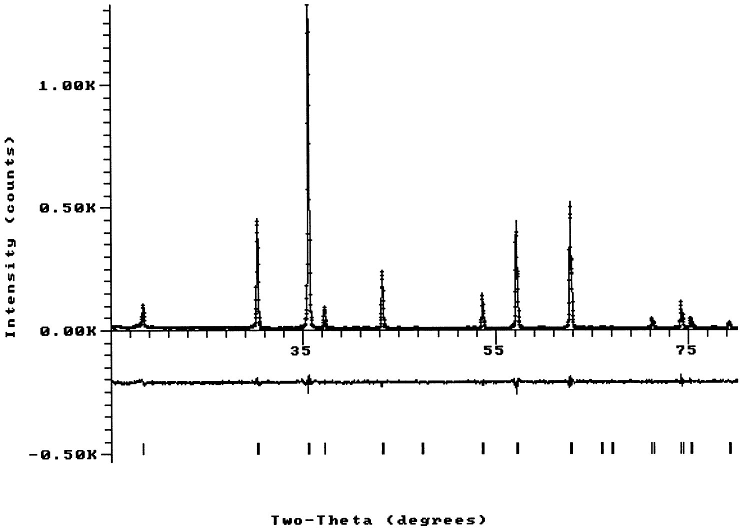

Fig. 3. Observed (cross), calculaled (continuous line) and difference profiles for the final Rietveld refinement for precursor material heated at 1100°C for 2.5 h.

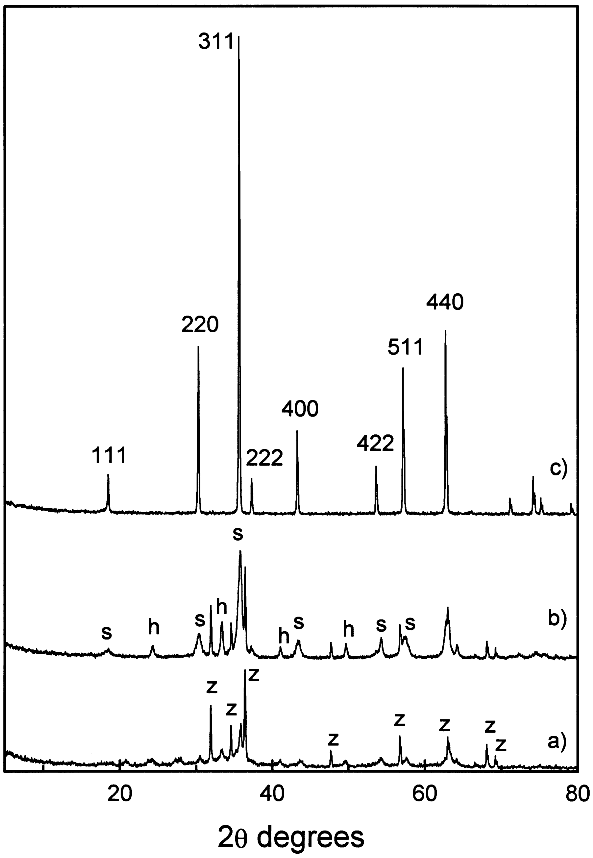

Fig. 4. X-ray powder diffraction patterns recorded on materials obtained by ceramic method: (a) mixture of ARPP and ZnO, (b) mixture heated at 600°C for 5 h and (c) mixture heated a 1100°C for 5 h. (z: zincite, h: hematite, s: cubic spinel).

small particles which tend to agglomerate (Fig. 6). When heated at 350°C for 16 h, nanoparticles of ferrite are obtained. Fig. 7 shows TEM micrographs of material thus treated. The particle diameters in Fig. 7a are estimated between 5–20 nm. In Fig. 7b where a magnification of $6\times10^5$ was achieved, apparent lattice images can be observed for several particles along with agglomerates of very small cubic particles. Lattice spacings of ~2.5 and ~8.4 Å can be observed in different particles, corresponding to the $d(311)$ and the $d(100)$ values respectively. These observations indicate the well-crystallised single phase spinel obtained at a very low temperature (350°C).

Fig. 5. SEM micrograph of initial acid regeneration plant powder (ARPP).

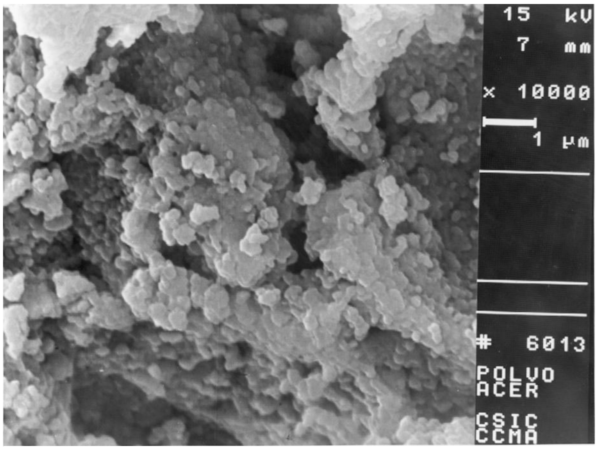

Fig. 6. SEM micrograph of the mixed ferrite obtained at 350°C.

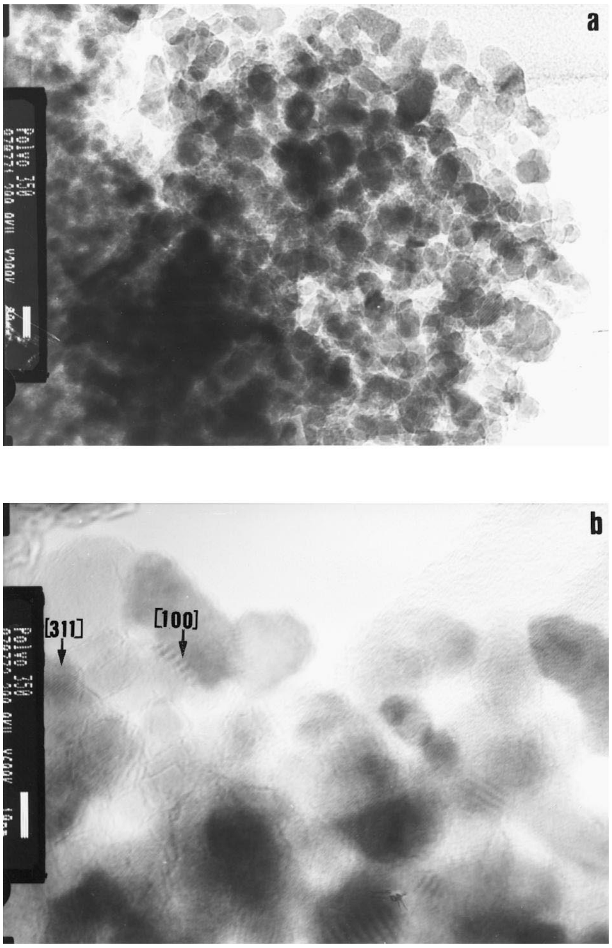

Fig. 7. TEM images of mixed ferrite obtained at 350ºC, (a) a $2\times10^5$ and (b) $6\times10^5$ magnification.

## 4. Conclusions

The butylamine synthesis method developed in this investigation affords to obtain a well-crystallized cubic mixed spinels from acids recovery plant powders and zincite. This is possible due to the small particle size (~50–200 μm) of the precursor powders and the lamellar morphology of the synthesised zinc hydroxinitrate. The high reactivity of these phases provokes the necessary ionic diffusion and spinel crystallization at a very low temperature (350°C) compared to the traditional ceramic method, which allows single phase spinel formation only at 1100°C. Moreover, this synthesis method is a low cost technology which allows the total recovery of metals from acid recovery plant powders.

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