

# Influence of the heat treatment conditions on the formation of $\text{CuFe}_2\text{O}_4$ from mechanical milled precursors oxides

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CEEC-TAC1 Conference Special Issue  
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**Abstract** Stoichiometric mixture of  $\text{CuO}$  and  $\alpha\text{-Fe}_2\text{O}_3$  milled in air up to 30 h was subjected to different heat treatments. The evolution of the heat treated milled powders was investigated by X-ray diffraction (XRD). The  $\text{CuFe}_2\text{O}_4$  was partially obtained by milling, the material consisting in a mixture of phases. By applying different heat treatments in air and in vacuum, for 2–6 h, in 500–800 °C temperature range the phases composition of the milled samples is changed. A heat treatment at 500 °C in vacuum favours the formation of delafossite ( $\text{CuFeO}_2$ ) and tenorite ( $\text{CuO}$ ) phases. If the same heat treatment is made in air, the  $\text{CuFe}_2\text{O}_4$  phase formation with a cubic structure is favoured. Differential scanning calorimetry (DSC) investigation realised in Ar atmosphere revealed two large exothermic peaks. The first one is associated with the formation of the delafossite and tenorite phases and the second one with the formation of  $\text{CuFe}_2\text{O}_4$ . The XRD patterns of the samples subjected to the DSC measurements present maxima corresponding to the delafossite and cuprospinel ( $\text{CuFe}_2\text{O}_4$ ) phases. For the heat treatment at 600 °C in air the phases present in the sample are the same as for the annealing performed at 500 °C:  $\text{CuFe}_2\text{O}_4$ ,  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{CuO}$ . The heat treatment in air at 800 °C leads to the complete reaction between the different phases and the formation of  $\text{CuFe}_2\text{O}_4$  phase in whole the sample

volume. The  $\text{CuFe}_2\text{O}_4$  ferrite crystallises after this heat treatment in two crystal systems: cubic and tetragonal.

**Keywords** Reactive milling · Differential scanning calorimetry · Copper ferrite · Delafossite · Heat treatment

## Introduction

The spinel ferrites,  $\text{MeFe}_2\text{O}_4$  (where Me is a metallic element or a group of metallic elements), are from decades in the centre of many researches all over the world due to the different and interesting properties which they own if they are synthesized in vary form and size such as: powder and pellet or nanocrystalline and nanosized state [1–7]. The ferrites are synthesized classically by ceramic method which involves the reaction of the oxides ( $\text{MeO}$  and  $\text{Fe}_2\text{O}_3$ ) precursors in solid state at relatively high temperature [1]. Beside the classical ceramic route many other routes are used such as: sol–gel [8, 9], co-precipitation [10, 11] or mechanosynthesis (mechanochemical route) [12–14]. In order to synthesize ferrites so called combined routes have also been reported amongst these methods one can mention co-precipitation/mechanical milling [15]. The synthesis of ferrites using these routes is achieved starting from various precursors. Using those methods the state of material is changed, the material is in nanocrystalline or nanostructured state and the properties of the material are changed. The spinel ferrites crystallize in cubic structure, space group— $\text{Fd}\bar{3}\text{m}$ . They are ionic compounds in which the  $\text{Me}^{2+}$  cations and  $\text{Fe}^{3+}$  cations are surrounded by  $\text{O}^{2-}$  anions in two types of crystallographic positions corresponding to tetrahedral and octahedral sites [1]. One of the most interesting ferrites is copper ferrite,  $\text{CuFe}_2\text{O}_4$ . The copper–iron oxide ( $\text{CuFe}_2\text{O}_4$ ), as all the spinel ferrites, crystallizes in the cubic

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spinel structure in some condition and is called cuprospinel. Beside this system, there is another possibility for crystallisation of this oxide, the tetragonal structure, spatial group— $I4_1amd$ . The crystallisation of the  $CuFe_2O_4$  in a structure or another depends upon the synthesis condition [1, 16]. Typically, for the copper–iron oxide, a synthesis by ceramic route followed by a quench from above  $760\text{ }^\circ\text{C}$ , leads to a cubic spinel structure with the  $Cu^{2+}$  cations in octahedral sites and  $Fe^{3+}$  cations distributed between the tetrahedral and octahedral sites [1]. If the samples are slowly cooled it becomes tetragonal and the copper and iron cations occupy similar crystallographic sites as for the cubic spinel. In both cases the structure of  $CuFe_2O_4$  is an inverse spinel [16]. The synthesis of the  $CuFe_2O_4$  using mechanochemical synthesis route starting from a stoichiometric mixture of oxides,  $CuO$  and  $\alpha\text{-Fe}_2O_3$ , has some drawbacks since the  $Cu\text{-O-Fe}$  system has a large reversibility [17]. The formation of a  $CuO\text{-Fe}_2O_3$  solid solution between the starting oxides mixture has been reported to occur during milling, the solid solution has corundum structure [18, 19]. The synthesis of the copper ferrite was achieved by mechanical milling of the precursors oxides followed by annealing treatment [20].

This article presents results of the investigation of the influence of the heat treatments condition on the formation of  $CuFe_2O_4$  from mechanical milled precursor oxides,  $CuO$  and  $\alpha\text{-Fe}_2O_3$ .

## Experimental

A stoichiometric mixture of high purity commercial oxides powders (Alpha Aesar), copper oxide ( $CuO$ —tenorite) and

iron oxide ( $\alpha\text{-Fe}_2O_3$ —hematite) was used as starting sample (ss) for the reactive milling (RM). The stainless steel vials and balls were used. The milling conditions are similar with the ones used previously and described elsewhere [21]. After this milling, in order to obtain  $CuFe_2O_4$  several heat treatments have been applied. The heat treatments were realized in air and in vacuum at  $350\text{--}800\text{ }^\circ\text{C}$  temperature range and for times between 2 to 6 h.

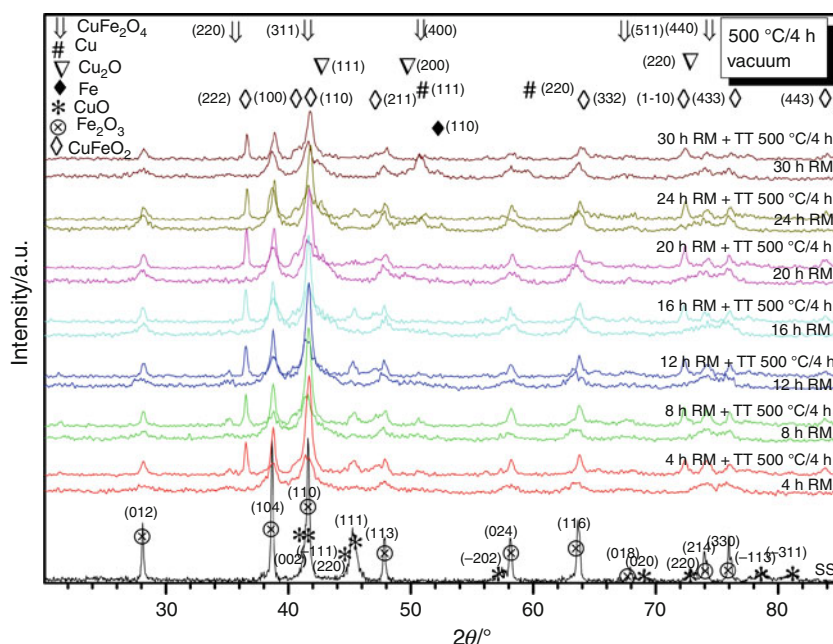
The formation of copper ferrite by milling and heat treatment and the evolution of the other phases during milling have been investigated by X-ray diffraction (XRD). A Siemens D5000 diffractometer which operates in reflection with  $Co\text{ K}_\alpha$  radiation ( $\lambda = 1.7903\text{ \AA}$ ) was used.

The differential scanning calorimetry (DSC) measurements were realized using NETZSCH–DSC 404S apparatus and as reference an alumina sample. We used a heating/cooling speed of  $10\text{ }^\circ\text{C}/\text{min}$  and the temperature range was between 25 and  $1,000\text{ }^\circ\text{C}$ . The measurements were performed in Ar atmosphere.

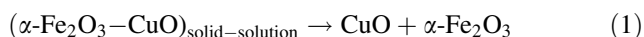
## Results and discussion

The XRD patterns of the ss (stoichiometric mixture of  $CuO$  and  $\alpha\text{-Fe}_2O_3$ ), as-milled samples (4, 8, 12, 16, 20, 24 and 30 h of milling) and the milled and subsequently annealed ( $500\text{ }^\circ\text{C}/4\text{ h}$  in vacuum) samples are shown in the Fig. 1. For the as-milled samples, the phases observed in the material are very different depending upon the milling time, as reported in our previous study [19]. After 4 h of milling a mixture of  $CuO\text{-}\alpha\text{-Fe}_2O_3$  solid solution and cubic  $CuFe_2O_4$  phase is observed. These results confirm the

**Fig. 1** XRD patterns recorded for the ss (stoichiometric mixture of  $CuO$  and  $\alpha\text{-Fe}_2O_3$ ), as-milled samples (4, 8, 12, 16, 20, 24 and 30 h of RM) and the milled and annealed at  $500\text{ }^\circ\text{C}/4\text{ h}$  in vacuum samples. The diffraction patterns were vertically shifted, for clarity



formation of a solid solution between precursor oxides as was reported also in [18, 19]. For the 8, 12 and 16 h milled samples, another phase is formed beside the solid solution and copper ferrite, cuprite—Cu<sub>2</sub>O. The XRD patterns of the samples milled for 20, 24 and 30 h contain the (110) Bragg reflection of elemental iron. This is due to the powder contamination by the vials and balls during milling [21, 22]. One cannot exclude that the powder contamination occurs even earlier, but in such a case the amount of elemental iron is too small to be detected by XRD (that is to say below a few percents). Further milling, for 24 and 30 h, leads to the dissociation of Cu from the oxides as can be seen from the appearance of Bragg peaks attributed to elemental copper in the diffraction patterns. After annealing at 500 °C for 4 h in vacuum new phases are formed in the material. For the 4 h milled and subsequently annealed sample the diffraction pattern exhibit new maxima assigned to the delafossite CuFeO<sub>2</sub> and tenorite CuO phases. For CuFeO<sub>2</sub> the following reflection are noticed in the diffraction pattern: (222), (100), (110), (211), (332), (110), (433) and (443). The most intense Bragg peak of this oxide, attributed to the (110) reflection, is overlapping with the (311) one of CuFe<sub>2</sub>O<sub>4</sub> (110) of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and (110) and (002) of CuO. The (111) and (220) Bragg peaks of CuO are very close and cannot be distinguished from one another. The delafossite phase is forming from the transformation of a part of solid solution CuO–Fe<sub>2</sub>O<sub>3</sub> in CuFeO<sub>2</sub>. The transformation of CuFe<sub>2</sub>O<sub>4</sub> into CuFeO<sub>2</sub> can be excluded due to the fact that the (220) reflection of the copper ferrite (which is not the most intense) is present in the diffraction patterns and is more intense compared with the as-milled sample. The transformation of the solid solution of CuO–Fe<sub>2</sub>O<sub>3</sub> into CuFeO<sub>2</sub> does not respect the stoichiometry. In CuO–Fe<sub>2</sub>O<sub>3</sub> solid solution the expected ratio between the metallic elements and oxygen (assuming that there was no release of oxygen during milling) is 3:4, whereas in the delafossite phase this ratio is 1:1. This suggests also a release of oxygen during the milling. Another explanation is that the delafossite phase which is formed has metallic vacancies, Cu<sub>1-x</sub>Fe<sub>1-y</sub>O<sub>2</sub> (where *x* represent the Cu vacancies and *y* the Fe vacancies). One can remark that the formed oxide probably does not respect the Cu:Fe ratio of 1:1 expected for CuFeO<sub>2</sub> delafossite due to the excess iron cations which are provided by the iron richer solid solution CuO–Fe<sub>2</sub>O<sub>3</sub>. Practically the chemical formula of the delafossite formed here can be written as: Cu<sub>1-x-s</sub>Fe<sub>1-y+s</sub>O<sub>2</sub>, where *s* represent the Cu cations replaced by Fe cations. The formation of CuO is occurs most probably from the decomposition of the CuO–Fe<sub>2</sub>O<sub>3</sub> solid solution.

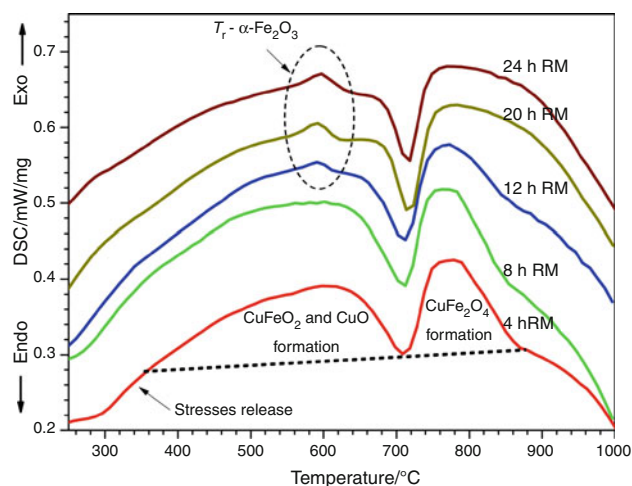


It is worth to mention that the CuO Bragg peak can be better seen by refining the structure (removing the stresses

and/or defects and increasing the crystallite size) of the non-reacted CuO.

For the 8, 12, 16, 20 and 24 h milled and annealed samples the same phases are observed in the obtained material as for the 4 h milled and annealed sample. For these milling times Cu<sub>2</sub>O was present in the as-milled sample, whereas this phase disappears upon annealing, this indicates that this oxide reacted during the heat treatment. Similarly, the elemental Fe and Cu observed for the long milling times (20, 24 and 30 h) have also reacted during the annealing treatment. For the 30 h milled sample the (111) and (220) Bragg peaks of CuO are much less intense in comparison with the other samples and only a shoulder of the (111) diffraction line of Cu<sub>2</sub>O is noticed in Fig. 1. We mentioned above as suggested in our previous work [19] that a release of some oxygen during milling from the processed powder is also possible. The presence of the Cu<sub>2</sub>O in the 30 h milled and subsequent annealed sample confirms somehow this assumption. Due to the lack of oxygen for the 30 h milled and subsequent annealed sample the amount of CuO is less and a small amount of Cu<sub>2</sub>O remains in the sample. We interpret this as resulting of a lack of oxygen to oxidize the Cu<sub>2</sub>O.

The DSC curves recorded during heating up to 1,000 °C in Ar atmosphere for the CuO +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> samples milled for 4, 8, 12, 20 and 24 h are presented in the Fig. 2. For all the samples the heat released up to 350 °C is associated with the release of the internal stresses induced in the samples by the milling process. For the 4 and 8 h milled samples, two large exothermic peaks are remarked. The first exothermic peak is associated with the formation of the CuFeO<sub>2</sub> and CuO and the second peak with the formation of the CuFe<sub>2</sub>O<sub>4</sub>. The XRD pattern recorded for the milled and annealed at 500 °C/4 h samples indicate the



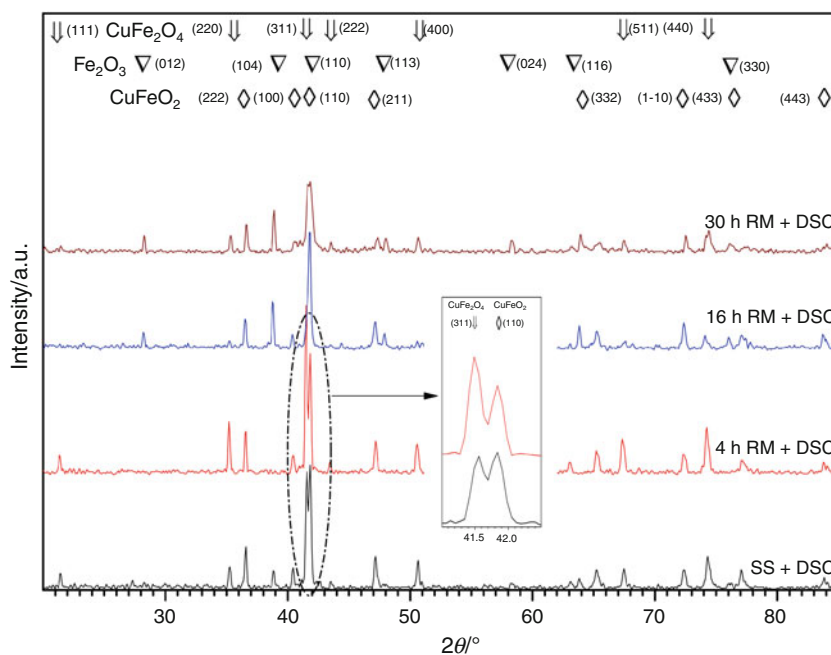
**Fig. 2** DSC curves recorded during heating up to 1,000 °C in Ar atmosphere for the CuO +  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> samples milled 4, 8, 12, 20 and 24 h of RM

formation of delafossite at this temperature. The first exothermic peak started after 350 °C and is finished at about 707 °C for the 4 h milled sample and at 711 °C for the 8 h milled samples. The formation of the  $\text{CuFe}_2\text{O}_4$  phase begins immediately after the end of the delafossite formation and it is finished at about 870 °C. The peak associated with the formation of  $\text{CuFeO}_2$  ended at higher temperature (712, 715 and 720 °C for sample milled for 12, 20 and 24 h respectively) for these samples compared with the samples milled for 4 or 8 h. This can be due to the existence of several phases in the milled material. Furthermore, the formation of the  $\text{CuFe}_2\text{O}_4$  seems to begin and end at higher temperatures; this could be also the results of the lack of oxygen. During the heating the  $\text{CuFeO}_2$  it is transformed in copper ferrite with oxygen vacancies— $\text{CuFe}_2\text{O}_{4-\gamma}$  (where  $\gamma$  represents the oxygen vacancies). The formation of the copper spinel with oxygen vacancies was previously reported by Goya and Rechenberg [17]. The other exothermic peak present in the sample milled for 12, 20 and 24 h is associated with the recrystallisation of the  $\text{Fe}_2\text{O}_3$  and is observed at about 593 °C for the 12 and 20 h milled samples recrystallisation and at 596 °C for the 24 h milled sample [23]. The recrystallisation process of the hematite is probably also present in the 4 and 8 h milled samples but is masked due to the presence of the other processes. The recrystallisation process is more obvious for these samples due to the partial decomposition of the solid solution during milling, and consequently the recrystallisation is more easy. The association of the heat released up to 350 °C with the stress release is confirmed by the XRD patterns recorded for the samples milled and subsequently

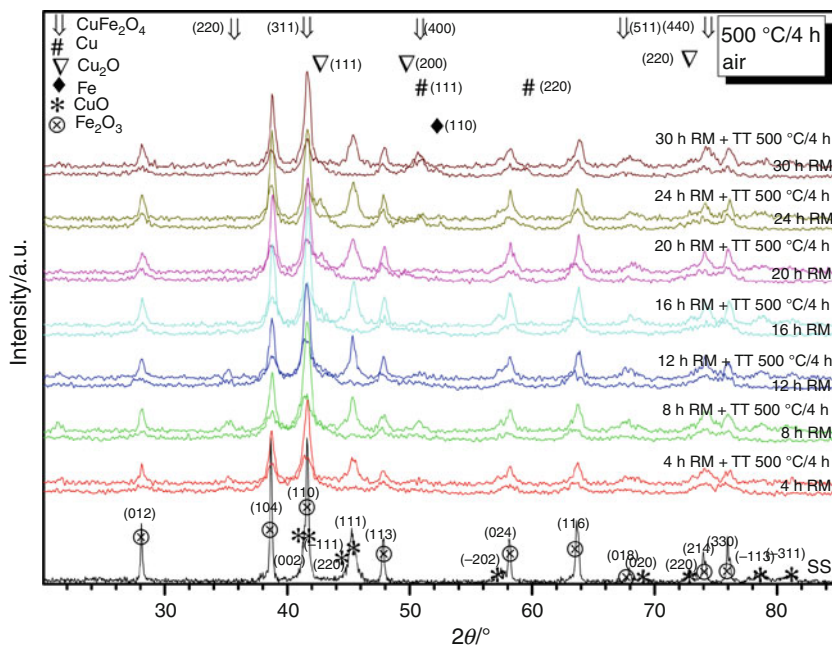
annealed at 350 °C/4 h in vacuum. In these milled and annealed samples (350 °C/4 h) there is no evidence of formation of  $\text{CuFeO}_2$  and the diffraction peaks are better defined and less broadened.

The assignment of the second exothermic peak to the formation of  $\text{CuFe}_2\text{O}_4$  is sustained also by XRD investigation made after the DSC measurements. In the Fig. 3 are presented the XRD patterns recorded for the ss, as well as for the as-milled for 4, 16 and 30 h subjected to DSC measurements up to 1,000 °C in Ar samples. During the DSC measurement in the ss and in the 16 and 30 h milled samples are formed three phases: cubic  $\text{CuFe}_2\text{O}_4$ ,  $\text{CuFeO}_2$  and  $\alpha\text{-Fe}_2\text{O}_3$ . The 4 h milled and subjected to DSC sample present two phases: cubic  $\text{CuFe}_2\text{O}_4$  and  $\text{CuFeO}_2$ . The existence of the  $\text{Fe}_2\text{O}_3\text{-CuO}$  solid solution in this sample is favourable to the formation of the cuprospinel— $\text{CuFe}_2\text{O}_4$ . The presence of the delafossite after the DSC treatment in these samples is due to the lack of oxygen which favours the formation of this phase instead of cuprospinel. The amount of  $\text{CuFe}_2\text{O}_4$  seems to be higher in the 4 h milled sample subjected to DSC compared with the amount of  $\text{CuFeO}_2$  whilst the ratio between the intensities of the most intense Bragg peak of the cubic spinel copper ferrite to that of the most intense maxima of the delafossite is 1.47. For the ss subjected to DSC this ratio is 0.96, the amount of each phase seems to be the same (see the inset of the Fig. 3). For the 4 h milled sample the major part of the  $\text{Fe}_2\text{O}_3\text{-CuO}$  solid solution is transformed into  $\text{CuFe}_2\text{O}_4$  during DSC treatment and for the 16 and 30 milled sample, after DSC the amount of the hematite is higher, the formation of  $\text{Cu}_2\text{O}$  and the presence of elemental Cu and Fe

**Fig. 3** XRD patterns recorded for the ss, samples milled 4, 16 and 30 h and subjected to DSC measurement up to 1,000 °C in Ar. In the figure RM means reactive milling



**Fig. 4** XRD patterns recorded for the ss, as-milled samples (4, 8, 12, 16, 20, 24 and 30 h of milling) and the milled and subsequently annealed samples at 500 °C for 4 h in air



leads to a high amount of  $\text{Fe}_2\text{O}_3$  after DSC. The copper ferrite formed after the DSC treatment exhibits cubic symmetry for all the studied samples.

Changing the annealing atmosphere from vacuum to air and maintaining the temperature of the treatment at 500 °C and the annealing time at the same 4 h, leads to different phases present in the material. In the Fig. 4 are shown the XRD patterns of the ss, of the as-milled samples (4, 8, 12, 16, 20, 24 and 30 h of milling) and of the samples milled and annealed at 500 °C/4 h in air. During this heat treatment in air there are no evidences of the formation of the delafossite phase. For all the samples milled and annealed at 500 °C/4 h in air, the samples are containing the following phases:  $\text{CuFe}_2\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{CuO}$ . The  $\text{CuO}$  phase is formed from the dissolution of the  $\text{Fe}_2\text{O}_3$ – $\text{CuO}$  and from the crystallisation of the amorphous  $\text{CuO}$  for the sample milled 4 and 8 h. For the rest of the sample the formation of the  $\text{CuO}$  can be attributed also to the oxidation of the  $\text{Cu}_2\text{O}$ :



For the samples milled 24 and 30 h another possibility of the formation of the tenorite is the copper provided by the reduction of the  $\text{Cu}_2\text{O}$  [19]:



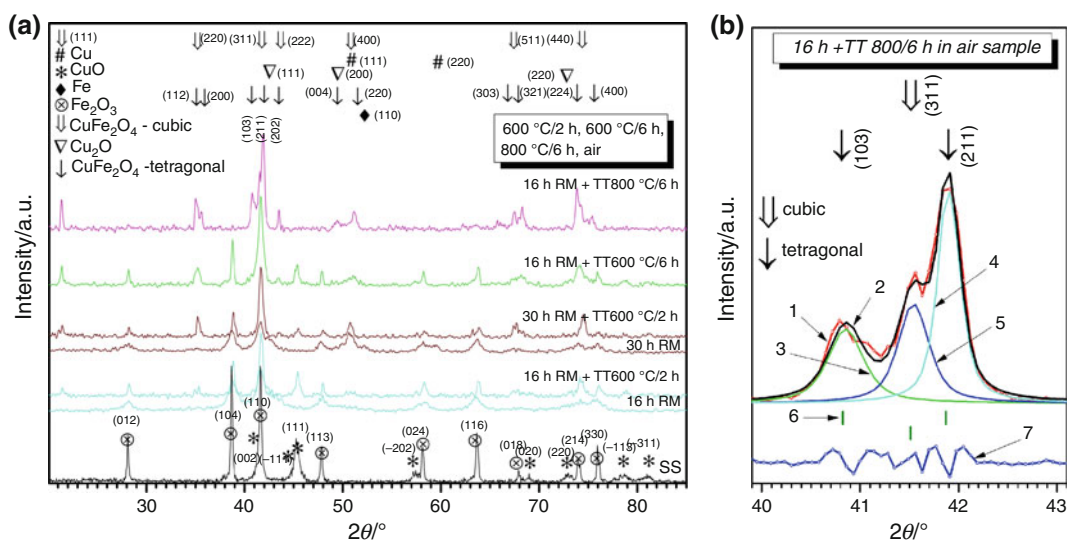
In addition, one must keep in mind that during this heat treatment the excess of Fe, coming from contamination during milling process, will react to form oxide. The Bragg peaks of  $\text{CuFe}_2\text{O}_4$  were attributed to the cubic spinel structure.

Increasing the temperature of the heat treatment at 600 °C and reducing the treatment time at 2 h we obtained

an increase of the amount of the  $\text{CuFe}_2\text{O}_4$ . In Fig. 5a are presented XRD patterns recorded for the ss, the 16 and 30 h milled samples and the samples milled for 16 and 30 h followed by heat treated at 600 °C/2 h in air samples. In the same figure are presented the XRD patterns recorded for the 16 h milled and heat treated in air samples at 600 and 800 °C/6 h, respectively. For both heat treated samples at 600 °C for 2 h, the phases present in the material are the same as for the treatment performed at 500 °C for 4 h in air:  $\text{CuFe}_2\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{CuO}$ . This heat treatment is favourable to the formation of the cubic  $\text{CuFe}_2\text{O}_4$ ; the Bragg peaks corresponding to this phase are better defined due to the higher annealing temperature.

For example, the (220) diffraction line of the copper spinel was difficult to identify in the diffraction pattern of the sample milled 30 h and heat treated at 500 °C/4 h in air. After this treatment at 600 °C, the (220) maximum of the copper spinel is of similar intensity as the most intense maxima of the hematite. The  $\text{CuO}$  maxima are reduced in intensity as a result of the reaction of this phase by reacting with  $\text{Fe}_2\text{O}_3$ . The higher milling time is also more favourable to the formation of this phase, the maxima of the copper spinel are much more intense in comparison with the other phases in the diffraction pattern of the 30 h milled sample compared with the 16 h milled sample.

In order to increase the amount of  $\text{CuFe}_2\text{O}_4$ , the temperature and the duration of the heat treatment were increased. By increasing the heat treatment time from 2 to 6 h for the 16 h milled sample the amount of the  $\text{CuFe}_2\text{O}_4$  increases, the cubic spinel XRD lines are more intense comparison with the other oxides lines. A new Bragg peak is observed in the diffraction pattern after this heat



**Fig. 5** **a** XRD patterns of the ss, 16 and 30 h milled samples, 16 and 30 h milled and heat treated at 600 °C/2 h in air samples, 16 h milled and heat treated at 600 and 800 °C/6 h samples and **b** fit and deconvolution of the experimental XRD pattern of the tetragonal (103) and (211) and cubic (311) reflections of  $\text{CuFe}_2\text{O}_4$  for the 16 h

milled and heat treated at 800 °C for 6 h. 1 Experimental points, 2 fitted curve of experimental points, 3 (103) peak of tetragonal  $\text{CuFe}_2\text{O}_4$ , 4 (211) peak of tetragonal  $\text{CuFe}_2\text{O}_4$ , 5 (311) Bragg peak of cubic  $\text{CuFe}_2\text{O}_4$ , 6 positions of the Bragg peaks, 7 difference between the experimental points and the corresponding fit

treatment. This corresponds to the (103) diffraction line of  $\text{CuFe}_2\text{O}_4$  with tetragonal structure. During heat treatment a part of  $\text{CuFe}_2\text{O}_4$  with cubic structure is transformed into  $\text{CuFe}_2\text{O}_4$  with tetragonal structure. Another possibility of the tetragonal  $\text{CuFe}_2\text{O}_4$  formation is the reaction of a part of the  $\text{Fe}_2\text{O}_3$  and  $\text{CuO}$  amount during annealing in the range of 2–6 h (after 2 h of heat treatment the tetragonal structure was not evidenced). By increasing the temperature of the heat treatment at 800 °C and maintaining the treatment duration at 6 h for the 16 h milled sample only  $\text{CuFe}_2\text{O}_4$  was obtained. During this heat treatment the solid solution  $\text{Fe}_2\text{O}_3\text{--CuO}$  and the  $\text{Cu}_2\text{O}$  fully reacts in the presence of the oxygen forming the  $\text{CuFe}_2\text{O}_4$ . After this heat treatment the obtained  $\text{CuFe}_2\text{O}_4$  powder is also crystallised in two crystal symmetries: cubic and tetragonal. The maxima of both  $\text{CuFe}_2\text{O}_4$ —tetragonal and  $\text{CuFe}_2\text{O}_4$ —cubic are present in the diffraction pattern, but the maxima of the tetragonal phase are more enhanced compared with the maxima of the cubic phase and the amount of the material crystallised in the tetragonal system is larger. The fit and deconvolution of the tetragonal  $\text{CuFe}_2\text{O}_4$  (103) and (211) lines and cubic  $\text{CuFe}_2\text{O}_4$  (311) reflection for the 16 h milled and subsequently annealed at 800 °C/6 h is presented in Fig. 5b. The ratio between the most intense peak of the tetragonal structure (211) and the most intense maxima of cubic structure (311) is 1.6, which means an amount of 62% tetragonal  $\text{CuFe}_2\text{O}_4$  and respectively 38% cubic  $\text{CuFe}_2\text{O}_4$ . The copper ferrite structure seems to be sensitive to this heat treatment temperature and mainly changes its crystal structure type from cubic to tetragonal.

For the milled samples, the preferred crystallographic structure of the copper ferrite seems to be cubic symmetry [24]. Similar behaviour has been reported by Berbenni et al. [20], which obtained the tetragonal structure of  $\text{CuFe}_2\text{O}_4$  after the heat treatment at 750–800 °C of the mechanically milled precursors. The change of crystallographic system has been also observed by Stewart et al. [25] for a copper ferrite synthesized by co-precipitation. Indeed they observed a heat treatment induced change from cubic to tetragonal.

The lattice parameter calculated for both tetragonal and cubic symmetries are in good correlation with the previously reported results [1, 26, 27]. We obtained a value for the lattice parameter of 8.369 Å for the cubic structure. This value of the lattice parameter is very close to the one from the JCPDS file 77-0010, 8.37 Å. For the tetragonal structure the value for the lattice parameters, where  $c = 8.575$  Å and  $a = 5.850$  Å and these values are in good agreement with the JCPDS file 34-0425,  $c = 8.630$  Å and  $a = 5.844$  Å. The difference between the calculated values of the lattice parameters and the ones from the reference file could be related to different cation distribution in the spinel structure. Indeed, if the obtained copper ferrite has a cations distribution which do not respect the arrangement of an inverse spinel ( $\text{Cu}^{2+}$  cations in octahedral sites) it is possible to have a mixed spinel structure (part of  $\text{Cu}^{2+}$  cations in tetragonal sites). In this case the formula of the copper spinel taking into account the oxygen release and mixed spinel structure becomes:  $(\text{Cu}_{1-\delta}\text{Fe}_\delta)^{\text{tetra}}(\text{Fe}_{2-\delta}\text{Cu}_\delta)^{\text{octa}}\text{O}_{4-\gamma}$ , where  $\gamma$  represent the oxygen vacancies.

## Conclusions

The influence of the heat treatment, in vacuum and in air, over the formation of the  $\text{CuFe}_2\text{O}_4$  from the mechanically milled precursor oxides has been evidenced. The RM of the stoichiometric mixture of precursor oxides ( $\text{CuO}$  and  $\alpha\text{-Fe}_2\text{O}_3$ ) leads to the formation of various phases in the as-milled samples, depending upon milling time. The heat treatment in vacuum at  $500\text{ }^\circ\text{C}$  is favourable to the formation of the delafossite phase, also during this heat treatment is forming  $\text{CuO}$ . The DSC analyses in Ar revealed two exothermic peaks, one associated with the formation of  $\text{CuFeO}_2$  and  $\text{CuO}$ , and the second at temperature higher than  $700\text{ }^\circ\text{C}$  associated with the formation of  $\text{CuFe}_2\text{O}_4$ . The heat treatments in air are more favourable to the formation of the  $\text{CuFe}_2\text{O}_4$  due to the oxygen contribution. After the heat treatment at  $500$  and  $600\text{ }^\circ\text{C}$  the sample  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{CuO}$  phases beside the  $\text{CuFe}_2\text{O}_4$  phase. For the samples milled for longer milling time the amount of the  $\text{CuFe}_2\text{O}_4$  which is forming is bigger. For heat treatment temperature of  $800\text{ }^\circ\text{C}$  a complete reaction between the precursors was obtained and in the material the  $\text{CuFe}_2\text{O}_4$  phase is the only one observed. The  $\text{CuFe}_2\text{O}_4$  formed after this heat treatment has two types of symmetries: tetragonal (in majority) and cubic. The lattice parameter obtained for the tetragonal  $\text{CuFe}_2\text{O}_4$  indicates that  $a$  is lower and  $c$  is larger comparison with the reference and this was attributed to the cation distribution.

**Acknowledgements** This study was supported by CNCSIS—UEFISCSU, project number PNII—IDEI code 1519/2008.

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