



Super Saturated Solid Solution Fe-50wt. % Cu by High Energy Ball Milling (Attritor)

Hannora AE, Hanna FF*, Marie LK

Suez University, Faculty of Petroleum and Mining Engineering, Science and Mathematics Department, Suez, Egypt

Abstract Mechanical milling (attritor) was performed to synthesize Cu-50wt.% Fe super saturated solid solution at room temperature. The mechanically alloyed samples have been milled for 24 hrs and examined by X-ray diffraction (XRD) to investigate its microstructure. As a result of mechanical deformation a higher defect concentration generated in the powder and thus the crystallinity decreases as well as crystallite size. The magnetic properties assessments of as-milled samples were carried out using vibrating sample magnetometer (VSM). The magnetization decreases with milling time while the coercivity increases up to 12 hrs milling and then decreases.

Keywords Fe-Cu, Mechanical milling, magnetic properties

Introduction

The Iron Copper binary system is known to have low solid miscibility, and solubility is limited to only 3 % [1-2]. The majority of research concentrated on the formation of metastable phases sings to phase of Cu-Fe produced from the elemental powder blends with a positive heat of mixing. A wider range as well equiatomic composition have been explore and there phases formation and stability reported is depend to large extent on the different processing techniques used to produce the alloys. In spite the extensive studies on the system, there are many disagreement on the literature concerning the formation of single phase solid solution with homogeneous structure is possible or not [3-4]

The magnetism of iron is related to its crystal structure, and it is well known, that Fe is ferromagnetic up to 1043 K when the conventional body centered cubic (bcc) structure is maintained, while Fe in face centered cubic (fcc) structure, stable at high temperature (above 1183 K), is non-magnetic [5]. Moreover, the stabilization of Fe fcc structure, the so called γ -Fe, at room temperature (RT), can be achieved by substituting Fe atoms in a simple fcc lattice, such as fcc-Fe-TM those of some pure metals (Ni, Cu, Pt, Pd). When one of the immiscible Fe is ferromagnetic, the decomposition, by mechanical alloying (MA), of the supersaturated phases can allow development of low-cost new magnetic materials with large magneto resistance and coercivities, unusually strong magnetocaloric effects, and high thermal/electrical conductivities usually unattainable in permanent magnet [6].

The aim of this work was to study the structural transformation taking place during mechanical alloying of Cu₅₀Fe₅₀ mixture in a high energy ball mill. The produced structures of the milling were evaluated using XRD as well as scan electron microscopy. The type of the magnetic properties of the new materials was also examined.

Materials and Methods

Iron 99% and copper 99.9% -325 mesh powders (Alfa Asar) were placed into high energy ball milling modified attritor, rotating with 500 rpm. The powders were treated with hard steel balls at different milling times with the optimum balls to powder ratio equals to 10:1. XRD was performed using D5000 powder diffractometer using Cu K α radiation (wavelength $\lambda = 0.15406$ nm) with a nickel filter at 40 kV and 30 mA. The diffractometer was operated within range of $10^\circ < 2\theta < 100^\circ$ with one second step-time and 0.05 degree step-size. Diffraction signal intensity throughout the scan was monitored and processed with DIFFRAC plus software. Topas 2.1 Profile fit software was used to extract the peak parameters and the Pseudo Voigt function was used to model the peak



shape. The XRD patterns of the synthesized samples were compared with ICDD (JCPDS) standard cards, Iron (01-1267) cubic phase with space group Im3m (229) and copper (85-1326) with space group Fm3m (225). The magnetic properties of the specimen were measured by a Vibrating Sample Magnetometer Lake Shore model 7410 (USA).

Results and Discussion:

Figure (1) presents the X-ray diffraction patterns of ball milled Cu-50wt.%Fe powder mixture. The mixture was milled for different periods up to 24 hrs. The XRD pattern of the elemental powder mixture before MM/MA shows only sharp peaks corresponding to the both metal mixture. The $Fe_{50}Cu_{50}$ samples set as a function of milling time are shown in Fig. (1). A notable intensity reductions occur as a result of severe plastic deformation after two hours milling. No additional possible new phases were detected throughout the MA process up to 7hrs. The peaks of Fe phase essentially disappear after 17 hrs milling while very broad peaks closed to (111) Cu phase developed with milling time. This implies that Cu has the lowest alloying rate among the mechanically milled elements. Moreover, disappearing of the Fe diffraction lines can be taken as indication that iron is integrated in the fcc-Cu structure and possible given rise to the formation of solid solution phase leading to diffraction peaks shift to lower angles progressively with milling time with increasing Fe-solubility in Cu. Following mechanical milling for 12 hrs, the main peak (110) intensities of bccFe-phase is enhanced while fccCu-phase main peak (111) decreases. Such an increase of (110) - Fe peaks started after 7 hrs milling could be attributed to the relative high dislocation density reach a saturation value, and the existing dislocation rearrange and some may be annihilated. Therefore, with further milling, the lattice strain on iron peak decreases and become sharper and even the peak position may change in reverse order. On the other hand, the (111) peak continuous to further broadening and reduced in intensities which indicate a higher work hardening rate for copper compare to the second mixed element iron. Therefore, copper continuous deformed with milling with subsequent increases in lattice strain and rather the newly formed solid solution particle refinement. A 24 hours milling is needed for the powder finally transforms into very fine structure and or amorphous as a result of the accumulated energy stored produced by milling.

The relative crystallinity was roughly calculated by comparing the integrated area intensity under peaks, of the MA powder with the as-received powders as a reference. From the results of the profile fitting, the relative crystallinity of the fcc Cu-phase was sharply decreased after 2 hrs of MA. The bcc Fe-phase shows relative crystallinity enhancement after 7hrs of MA and then decreases to the minimum value after 17hrs.

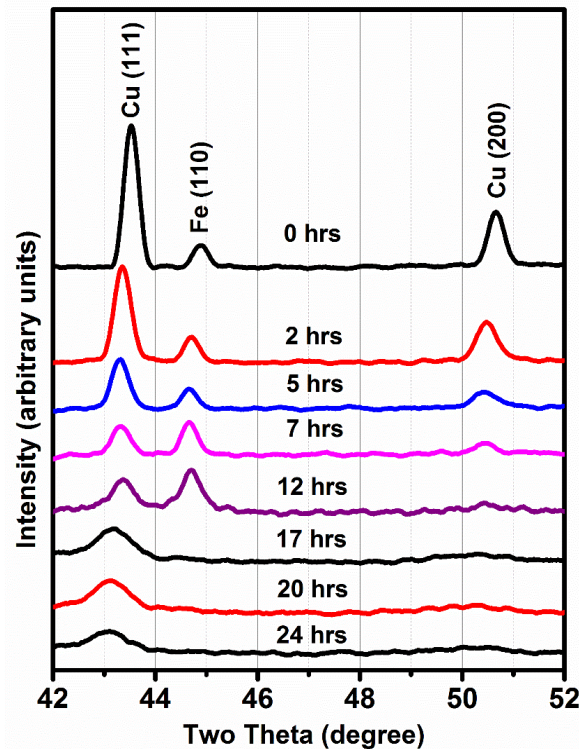


Figure 1: X-ray diffraction patterns of mechanically milled Cu-50wt.%Fe powder at different milling time.



The analysis of the produced phases after different stages of milling the Cu-Fe elements powder can be in general divided into two parts.

The elements Fe and Cu are known to be immiscible and there is no intermediate phase exists on the equilibrium diagram. Moreover, the Cu elements are unique case where they differ only by 1.5 % in atomic radius and they are very close in electron negativity, 1.9 Cu and 1.8 Fe, with a solubility limit near 0.3 % at room temperature. To monitor the alloying process after the various stages of milling, The XRD results are examined and used to calculate the change of the d-spacing values as shown in Fig. (2).

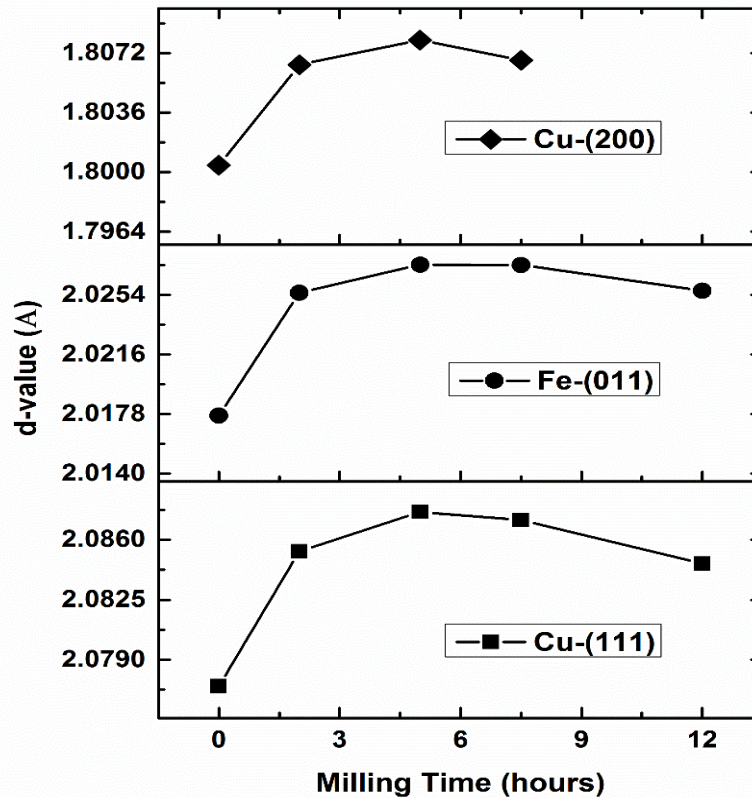


Figure 2: d-values variation after mechanical alloying with different time.

The results indicate that the peaks intensities reduction are associated with shift in peaks position as milling time increase and lead to a subsequent reduction of particle size of both elements, Fe and Cu. This stage of milling continuous up to 12 hrs and the observed changes could be related mainly to the increase of heterogeneous strain on the lattice of both Fe and Cu as a result of high milling energy. The continuous changes in peak profiles, broadening and displacement, are a demonstration that Fe have gradually react with Cu to form a super-saturated Cu(Fe) limited solid solution phase. The present result suggested that the fcc on lattice is expanded, with milling time up to 12 hrs, by incorporation of iron atom and resulted in an increase of the lattice parameter from 0.3615 nm to 0.3451 nm for Cu(Fe) solid solution. This result is in agreement with previously obtained values [7,8], in spite the fact that iron-atomic size is slightly larger by regard to copper. It is therefore, possible to conclude that at end of this milling stage 17 hrs, a mixture of an Cu(Fe) supersaturated phase is formed in addition to fcc (Cu) and both have a nanometer particle size.

Mössboure spectroscopy analysis is also used by several authors to examine the possible local atomic alloying after milling CuFe mixtures [1, 9, and 10]. In general their results indicated that after the stages of milling up to 20 hrs, two nonmagnetic spectra are observed and attributed to the Fe(Cu) solid solution and a fcc (Fe) phase attached to the fcc (Cu) matrix. The results confirm the presence of more than one phase, but it differ in suggesting a transformation of bcc (Fe) rich in copper to an fcc (Fe) structure take place during this stage of milling. Moreover, it is important to indicate that a maximum of 3at.%Cu concentration is estimated in fcc (Fe) phase. Such transit phase is not detected up to 17 hrs of milling, where all possible Fe-peak completely disappears which could be due to the formation of a small amount of such bcc (Fe) phase in addition to the expected broadening due to lattice strain. Under such condition it would rather difficult to identify the presence of such phase. Malt et al [11] indicated that based on bond measurement between Cu and Fe that neither a very

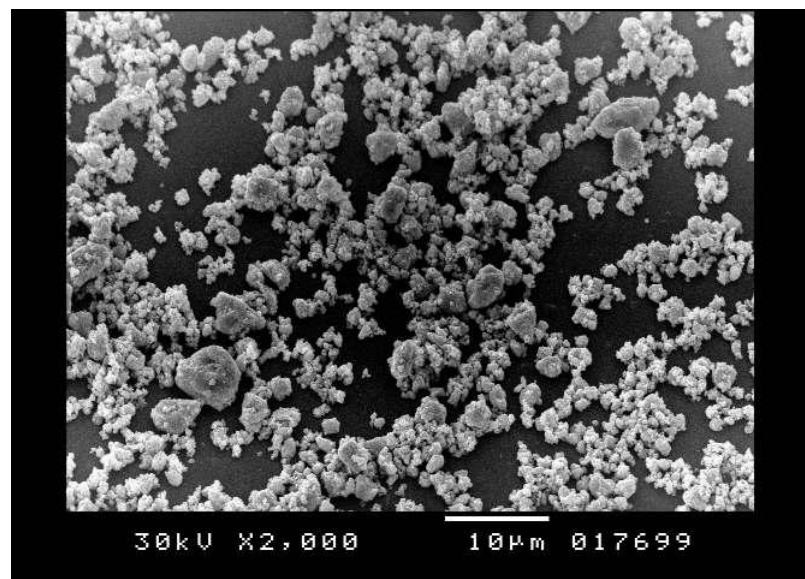


weak interaction nor repulsion exist between unlike neighbor of Cu and Fe atoms and been attributed to the positive heat of mixing in this system.

Figure (1), shows that further milling time between 17 to 24 hrs, only a single peak broad and relatively strong in intensity can be observed. This peak is broad enough to include all the remaining of (110)-Fe peak. At this stage of high milling time, further refinement of the microstructure is expected due to the increase in defect density as well as an increase of interface area of particles. Under such condition in the diffusion between Cu and Fe will be more favorable and could result in alloying between elements particles on the atomic level. Simulation calculation results suggested that the formation of solid solution is possible for a system with positive heats of mixing at a relative moderate shearing rate [12].

There is some disagreement in the literature over the occurrence of a complete atomic level solid solution in the processing CuFe powder by mechanical alloying. The confliction could be mainly associated with difficulties in analysis XRD results; the existing of high defect crystallites with a few nanosize contributing to further broadening, which make it hard to identify the peaks. In that respect, scan electron microscopy image has been used for microstructure clarification. Figure (3) show example for FeCu particle after 7 hrs milling, where an almost homogeneous particles distribution can be observed with a nanosize particle size conforming the XRD results. At a higher magnification, it is possible to observe the flat layer nature of the particles as formed by milling, a very fine particles in the order of a few micro scan can be also observed inside the larger particles mainly at the center. This microstructure observation can indicate that due the continuous increased deformation during milling harder Fe compare to Cu particles will be fragment to very small particles as the one observed in the scan micro graph. This arrangement has been indicated by both Yavari et al [2] and Genete et al [13], to be much favorable site for atoms to be continuous dissolve under deformation. They further estimated the enthalpy associated with generated very fine dissolve particles and they concluded that for such small size particles the formation of solid solution can energetically possible. However, there are a disagreement on the nature of the interface between element component formed after dissolution, it either coherent or incoherent.

A more recent study using high resolution TEM, confirmed the formation of dual phase microstructure rather than a single Cu(Fe) solid solution. A clusters of atoms are found to be distributed randomly in the Cu(Fe) solid solution matrix [3]. Therefore, it is possible to conclude the Fe(Cu) particle formed inside the supersaturated Cu-rich in Fe solid solution after milling in the high energy ball-mill after 24 hrs.



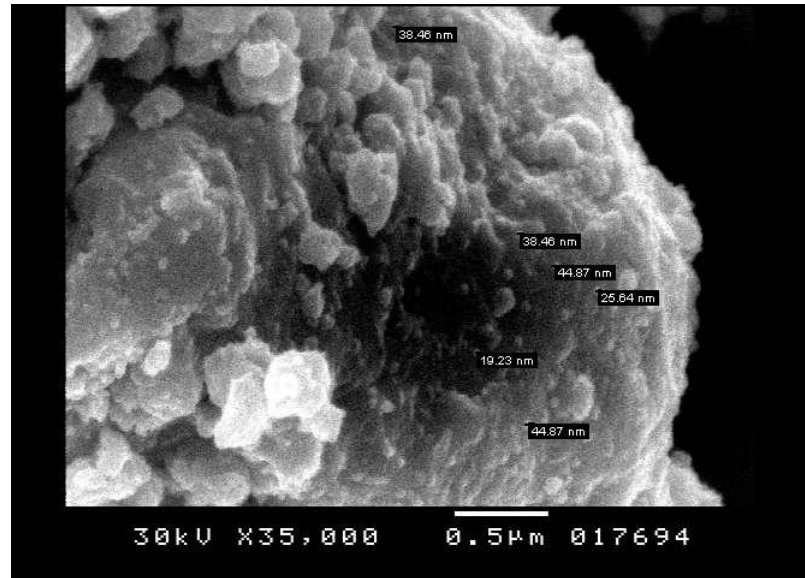


Fig. 3: SEM images of mechanical alloyed Fe-50wt.%Cu for 7 hrs.

Figure (4) shows the VSM results of the Fe₅₀Cu₅₀ milled samples after different milling times, which consists of ferromagnetic iron in Cu matrix at short time of mechanical alloying. A super-paramagnetic behavior was observed after higher time of milling and could be related to the fine structure formation (very small domain).

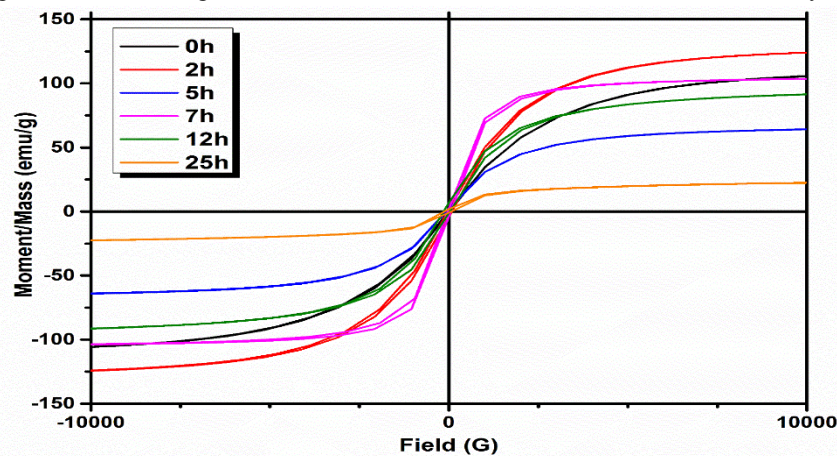


Figure 4: Hysteresis curves of mechanically alloyed Fe-50wt.% Cu powder with different times.

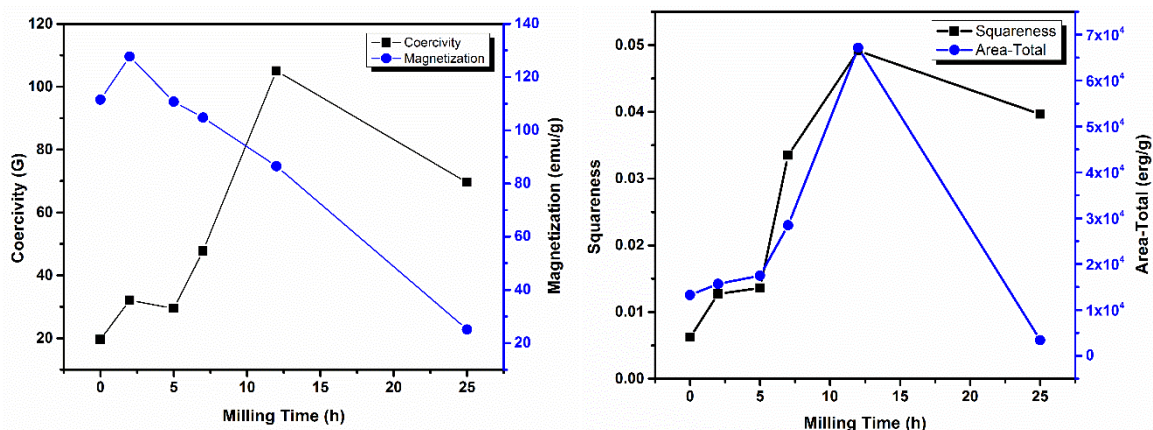


Figure 5: Milling Time dependence of mechanically alloyed Fe-50wt.% Cu powder; (a) Coercivity and magnetization and (b) Squareness and Area-Total.

Figure (5a) presents the variations of both the coercivity and magnetization at room temperature of Fe-50wt.% Cu powder with milling time. The coercivity and magnetization values at 0, 2, and 5 hrs milling time can be attributed to the solid solution refinement stage. Following further milling between 5 to 12 hrs, a relative higher rate of coercivity increases are obtained, from ~20 to ~105 G respectively. In similar accordance the magnetization values presented a decrease in its values with milling time, from ~ 127 to ~25 emu/g. The dependence of both coercivity and magnetization of the Fe-50wt.% Cu powder are in agreement with the XRD results, i. e. to the formation of a super-saturated Cu(Fe) limited solid solution phase.

It is reported that [14], an increase in the squareness, when going from the isolated nanocrystals to the 2D isotropic monolayer with the applied field in the surface. Then when we compare to the case of nanocrystals arranged in linear chains, the squareness is notably increased when the field is parallel to the chains. As shown in figure 5, the squareness of the hysteresis curve increases with milling time up to 12 hrs due to particle agglomeration and then decreases after particle refining.

At milling time higher than 12 hours up to 24 hours the coercivity begins gradual decreases and also the magnetization continue decreases in the same range of milling time but a different slope dependence. The measurements behavior of both coercivity and magnetization between 12 and 24 hrs milling were in agreement with results suggested by XRD that postulated a further refinement and a mixture of an Cu(Fe) supersaturated phase was formed in addition to fcc (Cu) which affected the values of coercivity and magnetization.

Conclusion

- Formation of supersaturated solid solution Fe-50wt.%Cu during High-energy ball milling has been formed.
- A super-paramagnetic behavior was observed by VSM results of the as-milled samples with higher milling time corresponds to the fine structure formation (very small domain).
- The behavior of both the coercivity and the magnetization with milling time seem to be caused by the grain size reduction in agreement with hysteresis curves of mechanically alloyed sample with different milling times.

References

1. Uenishi, K., Kobayashi, K. F., Nasu, S., Hatano, H., Ishihara, K. N., & Shingu, P. H. (1992). Mechanical alloying in the Fe-Cu system. *Zeitschrift für Metallkunde*, 83(2), 132-135.
2. Yavari, A. R., Desre, P. J., & Benameur, T. (1992). Mechanically driven alloying of immiscible elements. *Physical review letters*, 68(14), 2235.
3. Mojtahedi, M., Goodarzi, M., Aboutalebi, M. R., Ghaffari, M., & Soleimani, V. (2013). Investigation on the formation of Cu-Fe nano crystalline super-saturated solid solution developed by mechanical alloying. *Journal of Alloys and Compounds*, 550, 380-388.
4. Jiang, J. Z., Gente, C., & Bormann, R. (1998). Mechanical alloying in the Fe-Cu system. *Materials Science and Engineering: A*, 242(1), 268-277.
5. Gorria, P., Martínez-Blanco, D., Pérez, M. J., Blanco, J. A., Hernando, A., Laguna-Marco, M. A., ... & Garbarino, G. (2009). Stress-induced large Curie temperature enhancement in Fe 64 Ni 36 Invar alloy. *Physical Review B*, 80(6), 064421.
6. Drbohlav, O., & Yavari, A. R. (1995). Mechanical alloying and thermal decomposition of ferromagnetic nanocrystalline fcc-Cu 50 Fe 50. *Acta metallurgica et materialia*, 43(5), 1799-1809.
7. Crespo, P., & Hernando, A. (1999). Mechanically alloyed supersaturated Fe_xCu_{100-x} solid solutions: structural and magnetic properties. *Recent Research Developments in Nanostructures*, 1, 63-86.
8. Hong, L. B., & Fultz, B. (1998). Two-phase coexistence in Fe-Cu alloys synthesized by ball milling. *Acta materialia*, 46(8), 2937-2946.
9. Jiang, J. Z., Gonser, U., Gente, C., & Bormann, R. (1993). Thermal stability of the unstable fcc-Fe₅₀Cu₅₀ phase prepared by mechanical alloying. *Applied physics letters*, 63(8), 1056-1058.
10. Li, T., Li, Y. Z., & Zhang, Y. (1995). H., Gao, C., Wei, S.-Q. and Liu, W.-H. *Phys. Rev. B*, 52, 1120.
11. Ma, E., Sheng, H. W., He, J. H., & Schilling, P. J. (2000). Solid-state alloying in nanostructured binary systems with positive heat of mixing. *Materials Science and Engineering: A*, 286(1), 48-57
12. Bellon, P., & Averback, R. S. (1995). Nonequilibrium roughening of interfaces in crystals under shear: application to ball milling. *Physical review letters*, 74(10), 1819.
13. Gente, C., Oehring, M., & Bormann, R. (1993). Formation of thermodynamically unstable solid solutions in the Cu-Co system by mechanical alloying. *Physical Review B*, 48(18), 13244.
14. Russier, V., Petit, C., & Pileni, M. P. (2003). Hysteresis curve of magnetic nanocrystals monolayers: Influence of the structure. *Journal of applied physics*, 93(12), 10001-10010.

