

# Magnetic Properties of Nanocrystalline $\text{Mn}_{54}\text{Al}_{46}$ Powders

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## **ABSTRACT**

$\text{Mn}_{54}\text{Al}_{46}$  samples were cast into ingots and subsequently mechanically milled for 2-6 hours. The milled  $\epsilon$  phase powders were then annealed at temperatures ranging from 375-450° C to produce the ferromagnetic  $\tau$  phase. Bulk  $\text{Mn}_{54}\text{Al}_{46}$  samples were also annealed for comparison. Magnetic properties of the  $\tau$  phase powders were investigated. It was determined that the fraction of  $\tau$  phase and grain size, and thus the magnetic properties, were strongly dependent on milling time and temperature of annealing. Peak saturation magnetization ( $M_s$ ) and coercivity ( $H_c$ ) values were achieved when annealing at 400-415° C and milling for 3-4 hours, which in this study produced an approximate grain size of 25 nm. In addition, it was discovered that the inverse relationship between grain size and coercivity no longer holds when the grain size approaches 25-30 nm.

## **OBJECTIVE**

The goal of this study was to investigate the magnetic properties of  $\text{Mn}_{54}\text{Al}_{46}$  powders as a function of grain size, determined by ball milling, and anneal temperature.

## INTRODUCTION

High-performance permanent magnets are desirable for technological applications such as computer hard drives. Current solutions such as  $\text{Nd}_2\text{Fe}_{14}\text{B}$ <sup>1</sup> and  $\text{SmCo}_5$ <sup>2</sup> are based on rare earth elements, whose high costs prevents widespread commercial usage. The ferromagnetic metastable  $\tau$  phase in  $\text{MnAl}$ , first reported by Kono<sup>3</sup> and Koch et al<sup>4</sup>, is a cost-effective alternative. The  $\tau$  phase is usually achieved by way of quenching the high temperature  $\varepsilon$  phase and then annealing at a strict range of temperatures; prolonged annealing results in decomposition to the nonmagnetic  $\gamma_2$  and  $\beta$  phases. A recent study showed that mechanical milling followed by isothermal annealing of  $\text{Mn}_{54}\text{Al}_{46}$  can obtain high  $M_s$  and  $H_c$  values<sup>5</sup>. Mechanical milling is used to produce a nanocrystalline structure that improves magnetic properties. In this study we report on the optimal milling and annealing parameters for these permanent magnetic properties.

## EXPERIMENTAL METHODS

$\text{Mn}_{54}\text{Al}_{46}$  alloys were prepared by arc-melting the requisite masses of elementary manganese and aluminum in an arc furnace under an argon atmosphere. The ingots were prepared in a copper crucible, and flipped three times to ensure complete melting. Efforts were taken to avoid oxygen contamination. The ingots were then heated to  $1050^\circ\text{C}$  for

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<sup>1</sup> Q. Zeng, Y. F. Xiao, et al, J. Mater. Engn. Perf., 8(3), 305 (1999).

<sup>2</sup> Q. Zeng, Y. Zhang and G.C. Hadjipanayis, Proceedings of the 17<sup>th</sup> International Workshop on Rare Earth Magnets and Their Applications, P.961-966, 2002, Delaware, USA

<sup>3</sup> K.J. Kono, J. Phys. Soc. Jpn 13, 1444 (1958).

<sup>4</sup> A.J.J. Koch, P. Hokkelling, M.G. Van der Steeg et al, J. Appl. Phys., 31, 75S (1960).

<sup>5</sup> Q. Zeng, I. Baker, J.B. Cui, Z.C. Yan, "Structural and magnetic properties of nanostructured Mn-Al-C magnetic materials", Journal of magnetism and magnetic materials, in press 12 July 2006.

12 h to ensure pure  $\epsilon$  phase, followed by water quenching to retain the structure. The ingots were then manually crushed to powder in a stainless steel mortar and pestle, and subsequently milled for varying times in a SPEX 8000 mill. The powders were placed in a hardened steel vial along with steel balls with a ball-to-sample weight ratio of 4:1. The vials were sealed under argon to limit oxidation. 1.250 grams of sample were milled at a time. Both the milled powders and the quenched bulk samples were annealed at temperatures from 375-450° C for 15 min to produce the ferromagnetic  $\tau$  phase.

The magnetic properties were measured at room temperature using a LakeShore 7300 vibrating sample magnetometer (VSM) under an external magnetic induction field of 5 and 10 kOe. Grain size and phase fraction analysis was performed using a Siemens D5000 diffractometer with a Cu x-ray tube and a KeVex solid state detector set to record Cu  $K\alpha$  X-rays.

## RESULTS

Measuring  $M_s$  as a function of anneal temperature of samples milled for different times showed that maximum values were obtained at 400° C. As was evident from Fig. 1,  $M_s$  dropped off rapidly at higher anneal temperatures. This suggested that the  $\epsilon \rightarrow \tau$  :  $\tau \rightarrow \gamma_2, \beta$  phase transformation ratio was highest there. In addition,  $M_s$  also decreased as milling time was increased. This was consistent with the observation of decomposition of  $\tau$  phase into nonmagnetic  $\gamma_2$  and  $\beta$  phases, as shown in the X-ray diffraction curves (see Fig. 7).

Fig. 2 showed that  $H_c$  values behave similarly as the anneal temperature was varied, peaking at 400° C. As milling time was increased,  $H_c$  first increased and then

decreased. This suggested a threshold grain size at which domain wall pinning is no longer a dominant mechanism (see Fig. 6). Note that although grain size decreased with increasing anneal temperature, below 400° C the  $\tau$  grains were not fully formed and so their effect on coercivity was not yet maximized.

To verify the 400° C optimal anneal temperature, a differential scanning calorimetry curve of a 2-hr milled  $\text{Mn}_{54}\text{Al}_{46}$  sample was taken (Fig. 3). The aberration at 400° C corresponded to the endothermic  $\varepsilon \rightarrow \tau$  phase transformation. Below this critical temperature,  $\text{Mn}_{54}\text{Al}_{46}$  existed largely in the  $\varepsilon$  phase, and in the  $\gamma_2$  and  $\beta$  phases when too much above it. This supported the peak  $M_s$  and  $H_c$  values at 400° C seen in Figs. 1 and 2.

Fig 4. showed hysteresis curves for bulk and 2-hr milled  $\text{Mn}_{54}\text{Al}_{46}$  annealed at 400° C. The reduced magnetization of the milled sample was due to a lower  $\tau$  phase fraction, suggesting that the smaller  $\varepsilon$  grains formed by milling had an adverse effect on the  $\varepsilon \rightarrow \tau$  phase transformation. On the other hand, the increased coercivity of the milled sample was due to the smaller  $\tau$  grain size.

Fig. 5 showed grain sizes for samples of different milling duration. These were calculated by the Scherrer method, using the characteristic  $\tau$  peak of the x-ray diffraction curves. As expected, milling reduced the  $\varepsilon$  phase grain size, which in turn reduced  $\tau$  phase grain size. Note that all mills were carried out with 1.250 g sample and a 4:1 ball:sample ratio. Modifying these parameters would result in different grain size values. When observing coercivity as a function of  $\tau$  grain size, an inverse relation for larger grain size values was apparent. However, Fig. 6 showed a decrease in coercivity between 28 and 15 nm. This was possibly the result of a loss of strict crystalline structure as the material approached an amorphous state.

X-ray diffraction data was shown in Fig. 7 for bulk  $\epsilon$   $\text{Mn}_{54}\text{Al}_{46}$  as well as for bulk and milled  $\tau$  samples. All  $\tau$  samples were annealed at optimal  $400^\circ\text{C}$ . The volume fraction of  $\tau$  phase decreased as a function of milling time, as seen by the relative intensities of characteristic  $\tau$  and  $\beta$  peaks in the  $40\text{-}44\ 2\Theta$  region. Increased milling time also caused broadening of the  $\tau$  peaks, corresponding to decreased grain size. This microstructural characterization confirmed previously-discussed trends of milling time and anneal temperature.

Fig. 8a) and 8b) showed 150x and 350x scanning electron microscope images of a 2-hr milled sample. 8c) and 8d) show the same for a 6-hr milled sample. Of note was the decrease in average particle size between milling times. The haphazard size distribution in the 2-hr milled sample was due to the manual grinding of solid samples to produce powder for milling. After six hours of milling, the particles were much more uniformly sized.

## CONCLUSION

The saturation magnetization and coercivity of the  $\tau$  phase in the  $\text{Mn}_{54}\text{Al}_{46}$  alloy were determined to be influenced directly by milling time and anneal temperature. Peak values were achieved when annealing at  $400\text{-}415^\circ\text{C}$  and milling for 3-4 hours, which under the experimental conditions produced an approximate grain size of 25 nm. In addition, it was established that maximum coercivity is achieved when the grain size reaches the 25-30 nm range.

Further studies in the Mn-Al system might focus on differential scanning calorimetry tests of  $\epsilon \rightarrow \tau$  transformation temperatures as a function of grain size, as well

as the separation of individual phase transformations. Furthermore, the grain size threshold at which coercivity was maximized warrants additional focus.

## FIGURE CAPTIONS

Fig. 1.  $M_s$  values at varying anneal temperatures for a) bulk  $Mn_{54}Al_{46}$  b) 2-hr milled sample and c) 6-hr milled sample, under an external field of 10 kOe.

Fig. 2.  $H_c$  values at varying anneal temperatures for a) bulk  $Mn_{54}Al_{46}$ , b) 2-hr milled sample and c) 6-hr milled sample, under an external field of 5 kOe.

Fig. 3. Differential scanning calorimetry curve of a 2-hr milled  $Mn_{54}Al_{46}$  sample.

Fig. 4. Hysteresis curves for 400° C annealed a) bulk  $Mn_{54}Al_{46}$  and b) 2-hr milled  $Mn_{54}Al_{46}$ .

Fig. 5. Grain size values for samples of different milling duration. Values calculated using Scherrer method.

Fig. 6. Coercivity as a function of  $\tau$  grain size.

Fig. 7. X-ray diffraction curves for a) bulk  $\epsilon$   $Mn_{54}Al_{46}$ , b) bulk  $\tau$  sample, c) 2-hr milled  $\tau$  sample and d) 6-hr milled  $\tau$  sample. All  $\tau$  samples were annealed at 400° C.

Fig. 8a) and 8b) 150x and 350x scanning electron microscope images of a 2-hr milled sample. 8c) and 8d) are the same for a 6-hr milled sample.

Fig. 1

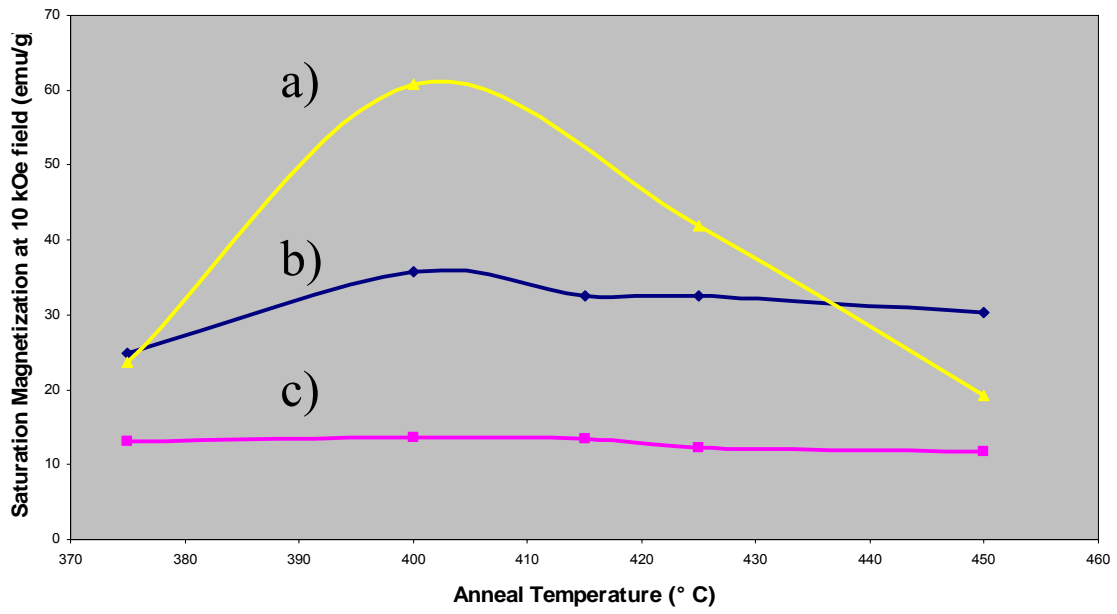


Fig. 2

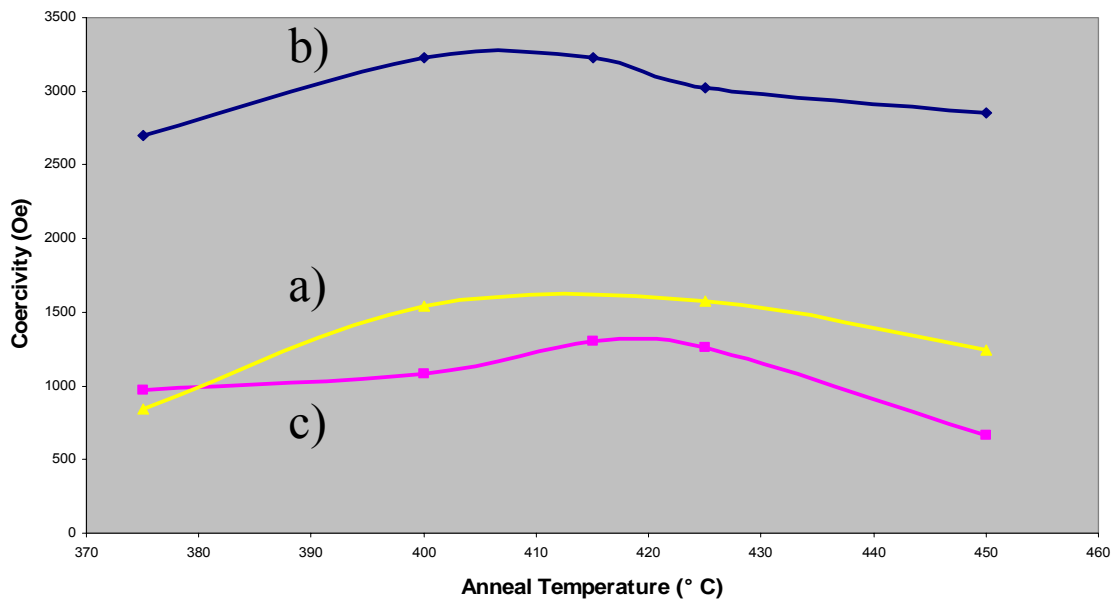


Fig. 3

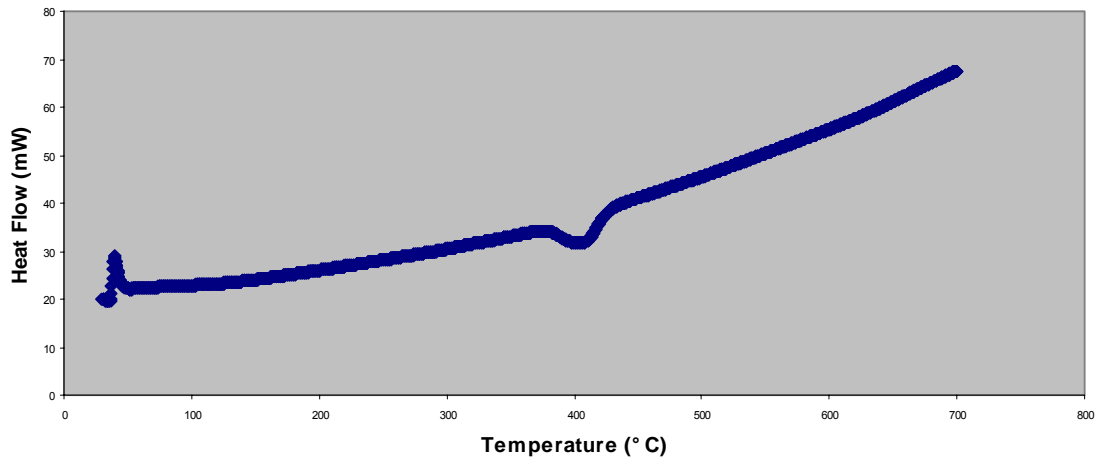


Fig. 4

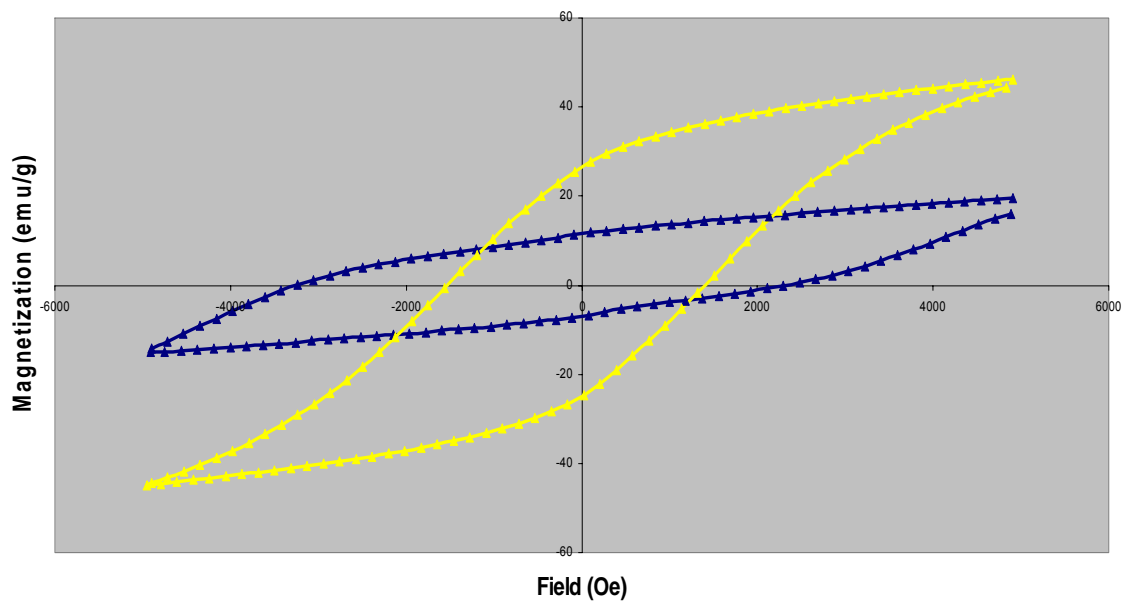


Fig. 5

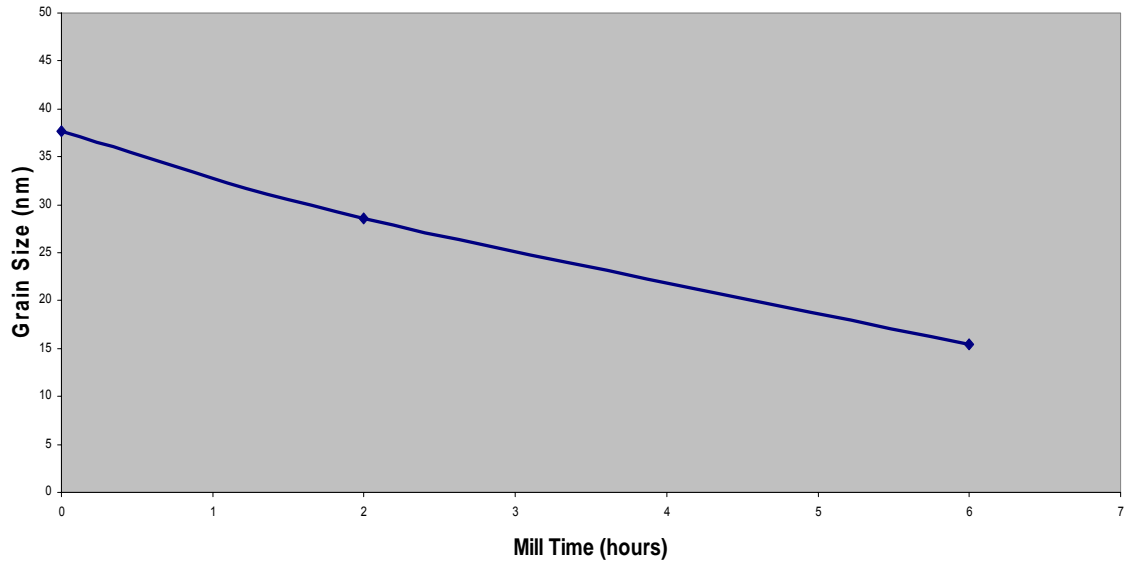


Fig. 6

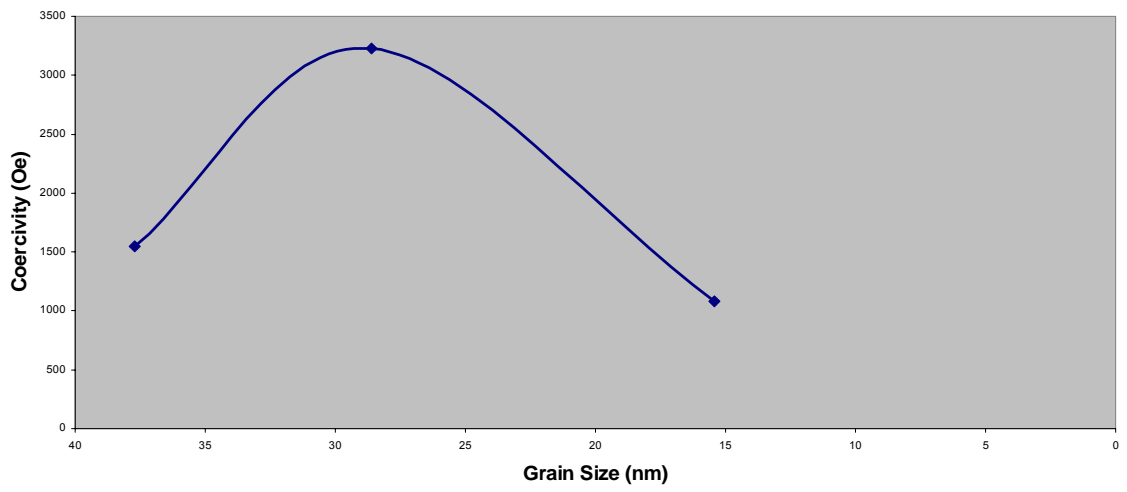


Fig. 7

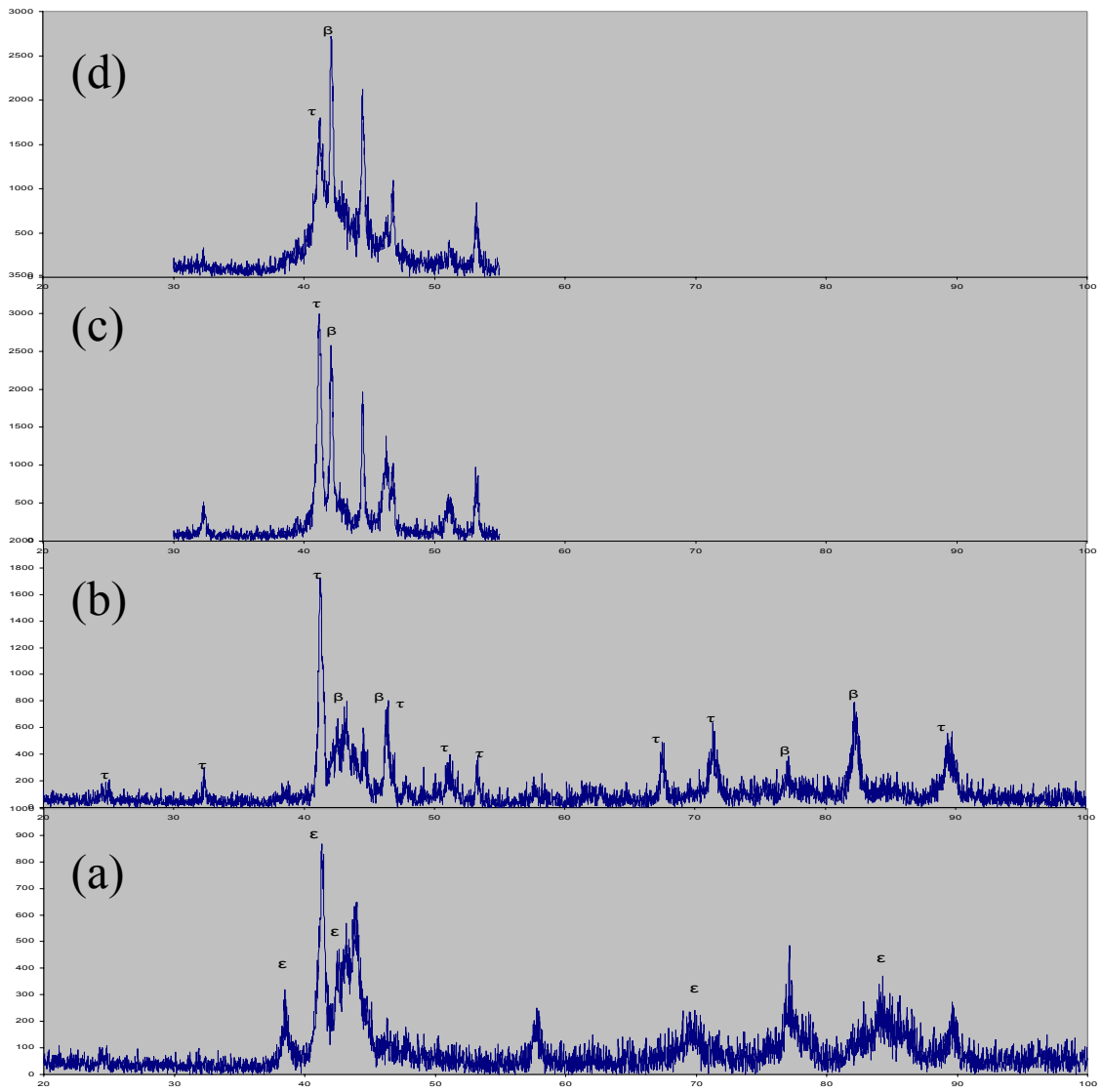


Fig. 8

