

Magnetic and structural properties of electrodeposited $\text{Co}_{1-x}\text{P}_x$ amorphous ribbons

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The specific magnetic moment, coercive force, anisotropy field, and saturation magnetostriction constant have been measured in $\text{Co}_{1-x}\text{P}_x$ amorphous ribbons with $0.04 < x < 0.27$. Differential scanning calorimetry, x-ray diffraction, and transmission electron microscopy analysis have been made in order to study the transition from the amorphous state to the crystalline one. Results suggest that transition takes place when x decreases from 0.19.

INTRODUCTION

The study of magnetic and structural properties of $\text{Co}_{1-x}\text{P}_x$ amorphous alloy, obtained by electrodeposition, has been the goal of many efforts in the last two decades.¹⁻⁵ The behavior of saturation magnetization, coercive field, electrical resistivity, and differential scanning calorimetry (DSC) and x-ray analysis suggests that the alloy is amorphous when sample compositions range from $x=0.04$ to 0.27. However, most recent studies on nanocrystalline magnetic alloys have shown that magnetic and structural properties are similar to those of the amorphous state. Lanote and Porreca⁵ have reported two different behaviors of saturation magnetization, coercive field, and magnetostriction constant for compositions $0.04 < x < 0.12$ and $x > 0.12$. They suggest the existence of an intermediate (microcrystalline) state between crystalline and amorphous ones. This result has been obtained on samples electrodeposited on Al substrates.

In this work we have studied the behavior of the above parameters in samples electrodeposited on Cu substrates. DSC thermographs as well as x-ray and transmission electron microscopy (TEM) analysis have been carried out in order to study the transition from the amorphous state to the crystalline one.

EXPERIMENTAL PROCEDURE

$\text{Co}_{1-x}\text{P}_x$ amorphous alloys were obtained by electrodeposition from the bath reported by Brenner¹ on Cu substrate at temperature of 70 °C with electrolytic current density between 1 and 0.07 A/cm². The samples were 75 mm long, 2 mm wide, and about 30 μm in thickness. Chemical composition was determined by inductively cou-

pled plasma atomic emission spectrometry and ranges from $x=0.04$ to 0.27.

X-ray-diffraction patterns were recorded for all samples as deposited and after a thermal treatment on a DSC, using a D-500 diffractometer with Cu $K\alpha$ radiation. Typical DSC scans have been performed on all the samples with a heating rate of 10 °C/min from 100 to 510 °C, under a flowing N₂ atmosphere. In addition, a study by electron diffraction and microscopy was carried out on a JEOL 2000 FX electron microscope by working at 200 kV.

Different techniques have been used for magnetic measurements. Specific magnetic moments of samples have been measured by using a vibrating sample magnetometer, with a sensitivity of 10^{-3} emu. Anisotropy fields have been measured from hysteresis loops by using a conventional setup for flux density measurements, applying an ac magnetic field at a frequency of 5×10^{-2} Hz and maximum value of 500 Oe. Coercive fields were measured from the derivatives of hysteresis loops by means of a PM 3335 Digital Oscilloscope at a frequency of 17.5 Hz. Finally, measurements of the saturation magnetostriction constants have been made through the small-angle magnetization rotation (SAMR) method by using a HP 35660A Dynamic Signal Analyzer and EGG 5209 lock-in amplifier. Special emphasis has been taken to achieve technical saturation of samples in these measurements, otherwise, important errors may be introduced by this method, not only in the absolute value of λ_s , but also in its sign.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the dependence on P content (4%–27%) of the specific magnetic moment M_s , coercive field H_c , anisotropy field H_a , and saturation magnetostriction

constant λ_s . As can be seen in Fig. 1(a), M_s changes linearly with composition between 19 to 27 at. % P. A rough extrapolation gives a value near to the hcp Co polycrystal for zero P content, and a value near zero for a composition of 33–34 at. % P, corresponding to the Co_2P phase. When the P content decreases below 19 at. % P, M_s presents a different behavior, increasing roughly linearly with a lower slope. The same change of behavior is seen for H_c , H_k , and λ_s . All these parameters also change linearly with composition between 19% and 27%. In the case of λ_s it should be noted that no change in sign has been observed, as other authors have reported.⁵

There is, however, a change in slope for all the parameters studied, which occurs at P content ($x \leq 0.19$), for which a third peak of crystallization is observed in DSC thermographs, as shown in Fig. 2. This peak corresponds to crystallization of fcc Co according to x-ray-diffraction pattern. When x decreases below 0.19, the latent heat corresponding to the first and third peaks (hcp Co and fcc Co from x-ray patterns) increases, and the latent heat of the second peak (Co_2P) decreases. When x increases from 0.20, the peak corresponding to hcp Co crystallization de-

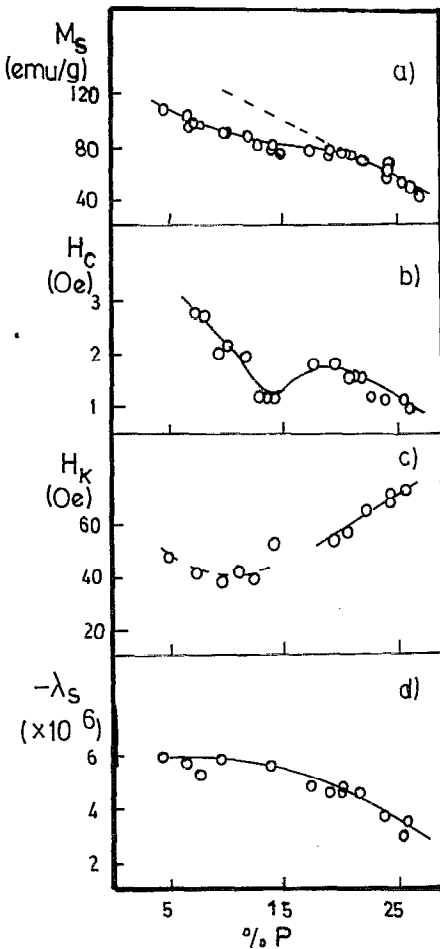


FIG. 1. Behavior of magnetic properties vs at. % P. (a) Specific magnetic moment M_s , (b) coercive field H_c , (c) anisotropy field H_k , and (d) saturation magnetostriction constant λ_s .

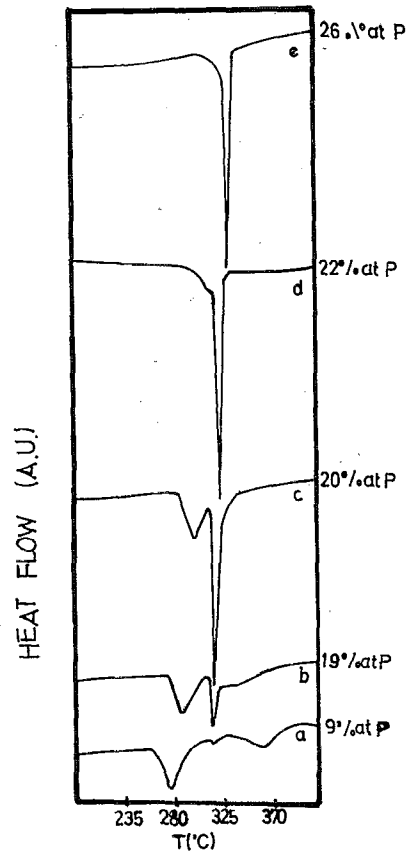
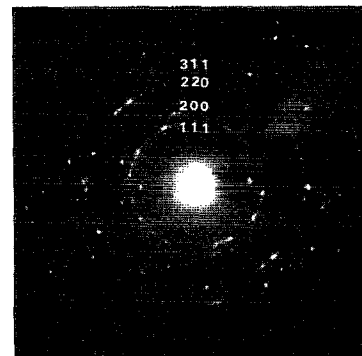
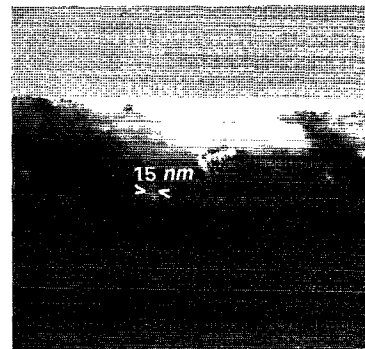


FIG. 2. Differential scanning calorimetry output on heating at $10^\circ\text{C}/\text{min}$ for different compositions. (a) $x=0.09$, (b) $x=0.19$, (c) $x=0.20$, (d) $x=0.22$, and (e) $x=0.26$.



a)



b)

FIG. 3. (a) Electron-diffraction patterns and (b) electromicrograph for $x < 0.12$.

creases, while the peak corresponding to Co_2P phase increases, which has been confirmed by x-ray diffraction. The x-ray diffraction on samples as cast, with $x \geq 0.06$, shows no evidence of crystallinity. Only for samples with lower x value, a smooth broad peak with small peaks of crystallization was detected. However, TEM analysis of samples with x below 0.12 shows electron-diffraction ring patterns characteristic of polycrystalline materials, as can be seen in Fig. 3(a). The rings have the ratio of the square roots of 3,4,8,11,12,... and can be indexed on the basis of the cubic cell characteristic of fcc Co with parameter $a = 3.54 \text{ \AA}$. The corresponding electromicrograph [Fig. 3(b)] shows the presence of very small crystallites (10–15 nm) dispersed on an amorphous matrix, for a sample with $x = 0.075$.

The experimental results from DSC thermographs, x-ray diffraction, and magnetic measurements suggest that for $x \geq 0.19$, the material is amorphous with local order similar to the hcp Co and Co_2P crystalline phases, in a ratio that decreases as P content increases. However, this state changes for x below 0.19, where the transition from

pure amorphous to crystalline states is achieved as local ordered units increase in number and size, in a gradual way. While x-ray analysis indicates an amorphous state up to about 6 at. % P, the TEM technique shows the existence of small crystallites for x below 0.12. Moreover, magnetic measurements suggest incipient nucleation can even appear for larger P concentration ($x < 0.19$).

Consequently, it can be concluded that below $x = 0.19$ the boundary between amorphous and crystalline states depends on the discrimination of the selected experimental technique.

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