COMPOSITIONAL DEPENDENCE OF MICROHARDNESS AND CRYSTALLIZATION BEHAVIOR IN ELECTRODEPOSITED Ni-P AMORPHOUS ALLOYS

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ABSTRACT

In this work differential thermal analysis and microhardness tests were carried out on a series of electrodeposited Ni-P alloys with different phosphorus content. The effects of both aging and heat treatment on the stress relaxation of these alloys were also studied. A nearly similar pattern was observed in the compositional dependence of microhardness and thermal properties of the amorphous alloys. The results obtained are discussed in relation to the cluster model and the degree of structural disorder in the different compositions as revealed by x-ray studies .

Keywords: Amorphous alloys, Nickel-Phosphorus, Composition, Crystallization,Hardness.

1. INTRODUCTION

Ni-P alloys of certain compositions are typical metallic glasses that lack long range order in their atomic structure and which have many industrial applications. This is due to their excellent corrosion resistance, wear resistance and non-magnetic properties. Extensive studies are, therefore, directed towards the structure and crystallization behavior of these alloys. Because of the low solubility limit of phosphorus in crystalline nickel, Ni-P alloys of low phosphorus content are considered as P-supersaturated solid solutions in which the lattice becomes more and more strained by increasing the P content [1]. On the other hand, deposits with high phosphorus content are considered amorphous structures in a metastable state and the stability of which is expected to depend strongly on composition. In general, the structure of as-deposited Ni-P alloys with high phosphorus content has been reported to be either amorphous or microcrystalline in nature [1,2].

X-ray techniques have been used to study the structure of electrodeposited Ni-P alloys and the atomic arrangements in these alloys may be described in terms of a radial distribution function [2]. The interference function of these alloys, in particular with high phosphorus content, can be depicted by the dense random packing of hard sphere model [3]. On the other hand, cluster model was applied using computer modeling and revealed that the cohesion energy of small clusters of Ni-P depends on the P content of the system [4]. This was observed for both compact cluster classes and for the seven and thirteen atoms as well. There is, however, certain limitations on structural models as applied to Ni-P or to other noncrystalline metallic alloys.

There is also certain discrepancy concerning the behavior of amorphous Ni-P deposits and the exact mechanisms involved in their co-deposition. Such discrepancy has been attributed by some authors [5] to the presence of structural inhomogeneities in the prepared samples which mask any composition dependence. The existence of microscopic and macroscopic inhomogeneities of samples may be tested by the crystallization behavior as well as the dependence of other measured parameters on the composition.

Generally, the composition dependence of Ni-P alloys having P content up to 25 at % can be divided into two regions[1]. For deposits having P < 20 at %, the crystallization of amorphous alloys leads to the precipitation of fine Ni crystallites in a matrix of Ni_3P phase. For alloys with P content > 20 at %, the crystallization process leads to various metastable

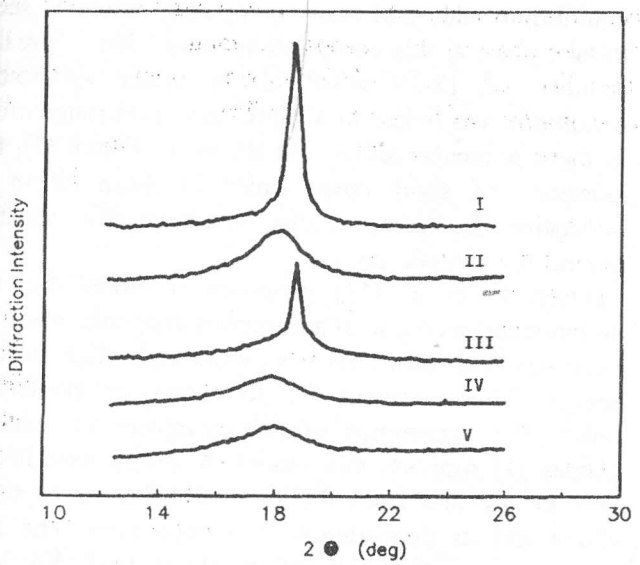

Figure 1a. X-ray diffraction scans for the five compositions of Ni-P alloys:
I: 15.2 at% P II: 18.6 at%P III: 21.1 at%P
IV: 24 at%P V: 26.2 at%P.

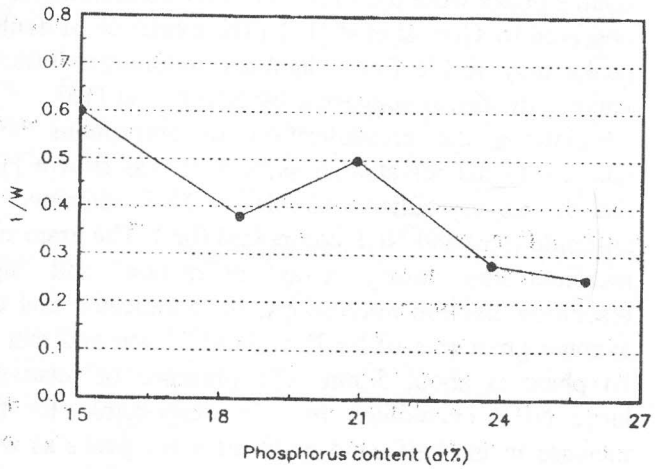

Figure 1b. The reciprocal of half band width of XRD peaks as a function of P content.

Figure (2) shows the following:

i- DTA curves of amorphous alloys produced, at least, one of two main exothermic peaks as shown in Figure (2a). The first peak occurs at about 618 K while the second peak occurs at about 678 K.

ii- The variation of the position of the maximum corresponding to the two main crystallization peaks as a function of P at% is shown in Figure (2b).

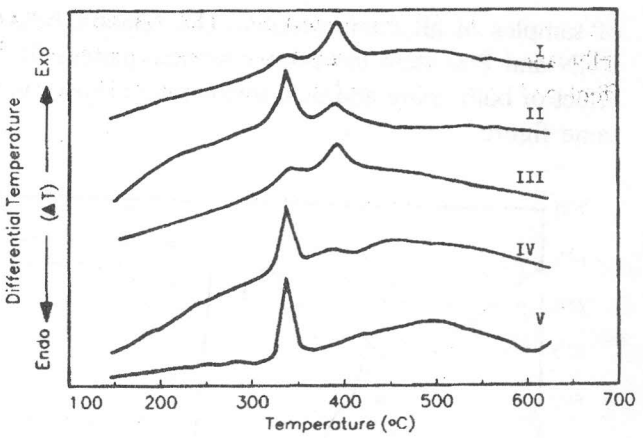

Figure 2a. DTA scans of the five compositions of Ni-P alloys.
I: 15.2 at%P II: 18.6 at%P III: 21.1 at%P
IV: 24 at%P V: 26.2 at%P.

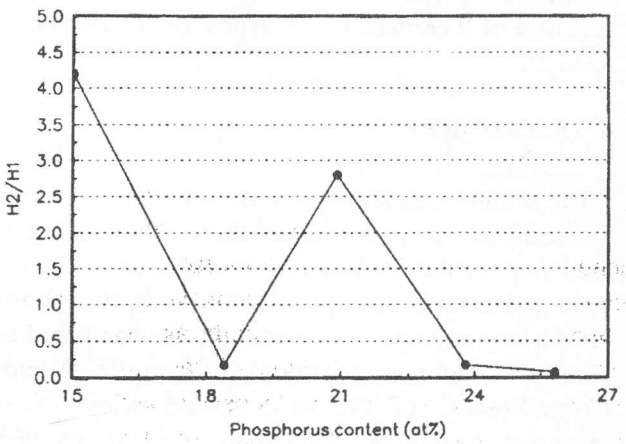

Figure 2b. The relative height of DTA peaks as a function of P content.

3-3. *Microhardness Measurements*

As shown in Figure (3), the VHN for as-deposited Ni-P alloys generally decreases with the increase in P content. However, aging Ni-P samples for 16 months increases the VHN. Such increase is relatively higher for alloys having higher P content and is maximum near the eutectic composition. On the other hand, mild heat treatment of samples at 473 K for about 2 hours also produced a general increase in the microhardness

of samples at all compositions. The relation between VHN and P content indicates a similar pattern for the effect of both aging and heat treatment as shown in the same figure.

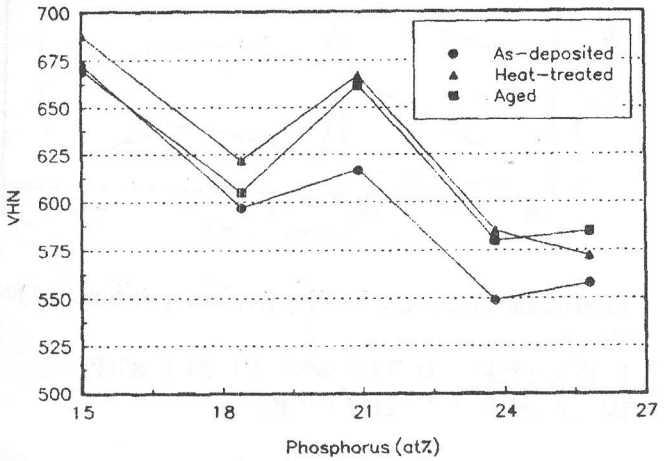

Figure 3. Vicker's Hardeners number (VHN) as a function of P content for as-deposited, heat-treated and aged alloys.

4. DISCUSSION

The results obtained from x-ray data show that, within the composition range under study, there is a general tendency for the formation of amorphous state as the P content increases. Sample III, however, was shown to have a higher degree of crystallinity as compared to the other two close compositions of samples II and IV. Crystallization of the as-deposited alloys by heat treatment causes the appearance of two exothermic peaks which were assigned to the crystallization of two different types of crystallites. The first peak occurred due to the crystallization of pure Ni and the second peak as due to the precipitation of a mixture of Ni and Ni_3P.

The half band width of x-ray peaks depends on i) the degree of crystallinity and ii) the size of crystallites which precipitate from the matrix. Because of the relatively large size of Ni_3P crystals [11] , their presence in the amorphous matrix causes a considerable degree of broadening of x-ray peaks. The relatively sharp x-ray peak at a composition of 21.1 at%P may reflect the overall tendency of the alloy to precipitate at compositions close to the eutectic point. Flechon et al [12] deduced that Ni-P alloys in the vicinity of the eutectic composition are directly close to the metastable equilibrium state and many competing reactions seem to take place at this composition range. The greater stability of 18-19 at%P alloys under metastable conditions was linked to a significant short range order in these particular alloys. As shown in Figure (1), the existence of short range order in these alloys is noticeable for compositions symmetrically situated around the eutectic point.

D'Acapito et al [13] proposed a model for the inhomogeneous phase of amorphous materials, in which micro-crystals form with correspondingly high surface energy. These prevent the formation of crystalline order. The occurrence of polymorphism in metallic glasses [1] supports this model. A similar conclusion may be reached from the thermal behavior of these alloys and its dependence on composition. The low temperature peak observed at about (618 K), was assigned by some workers [1,14] to the crystallization of Ni and reorganization of the amorphous matrix while the high temperature peak around 678 K was explained as due to the formation of Ni plus Ni_3P crystallites. No double peaks were found in our DTA measurements as observed by Grewal et al [15] . The existence of double peaks may result from chemical inhomogeneities at varying depths as suggested by Szasz et al [16].

Following the crystallization of amorphous Ni-P alloys into nanocrystalline system, it was shown [11] that the as- crystallized samples of Ni-P contained Ni austenite (fcc) and Ni_3P compound (bct). The grain size measurements, using x-ray diffraction and high resolution electron microscopy, have indicated that the average grain size of Ni_3P is about 12 nm and that of Ni phase is about 5 nm. The presence of relatively large Ni3P crystallites may be responsible for the increase in the half band width of x-ray peaks as well as the increase in the relative intensity of the second DTA crystallization peak.

A correlation between the mechanical and thermal behavior of amorphous alloys was noted by several workers. Chang et al [10] observed an increase in the microhardness on heating the amorphous alloy. The increase in hardness of the alloys upon heat treatment may be attributed to the dissociation of the metastable solid solution into the equilibrium two phase alloy. Similar findings were observed on the heat treatment of Co-P amorphous alloys [17]. The increase in microhardness with heat treatment was found to follow a two stage process. In the first, a structural relaxation

occurs in which the reduction of free volume of the devitrification process produces a slight microhardness increase. The second stage was attributed to the precipitation of Co and Co_3P crystalline phases.

Results of the transformation thermodynamics [11] have also shown that the interfaces in the nanocrystalline material contain more spaces and consequently are more disordered and more defective compared to normal crystalline phases. Using the cluster model, it was assumed [18] that the crystallization process may involve the trapping of clusters by the growing crystals followed by the dissolution of the trapped clusters with a subsequent change in the composition with increasing crystal diameter.

On the other hand, the slight increase in microhardness following isothermal annealing at 473 K may be due to changes in the cluster structure as depicted from thermodynamic analysis [6,11]. The presence of microcrystallites or nanocrystallites leads to a more disordered and a more strained interfaces. Prolonged aging at room temperature seems to produce a similar behavior. It is reasonable therefore to assume that there is a noticeable correlation between the relative increase in microhardness and the existence of certain crystalline phases within the amorphous matrix. This may explain the obvious correspondence found for the dependence of both x-ray, thermal and microhardness data on composition. The presence of certain microcrystallites such as Ni_3P and or free nickel within the amorphous matrix, even without heat-treatment, may be responsible for the relatively high value of microhardness observed for sample I and to a less extent for sample III.

5. CONCLUSION

In this work, the behavior of a series of Ni-P alloys with compositions situated around the eutectic point has been characterized using different experimental techniques. A significant x-ray peak broadening was noted for compositions with high P content (higher than 21 at% P). Crystallization of alloys by heat treatment causes the appearance of two exothermic peaks which were assigned to the crystallization of pure Ni and a mixture of Ni and Ni_3P. The presence of the crystalline phases within the amorphous matrix leads to an increase in the microhardness of these alloys. However aging samples up to 16 months or annealing at 200 °C for 2 hours seem to induce only weak relaxations with a corresponding slight increase in the value of microhardness .

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