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Crystallization temperature of amorphous electroless nickel–phosphorus alloys

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Abstract

Amorphous alloy is thermodynamically unstable, and it crystallizes after heat treatment. Considering ordered clusters as crystalline nuclei in amorphous electroless nickel–phosphorus alloy, crystallization thermodynamics and growth controlled by diffusion of nuclei were studied in detail. Crystallization temperature is determined when the size of nuclei is equal to the critical grain size at a heating rate. The simulated crystallization temperatures of alloys with various phosphorus contents are examined by experiment and other investigations under like conditions.

Keywords: Electroless nickel–phosphorus alloys; Crystallization temperature; Growth of crystalline nuclei; Phosphorus content

1. Introduction

Electroless nickel alloys have drawn attention and have been applied in various industries since the first discovery by Brenner and Riddell in 1944 due to their unique properties such as wear and corrosion resistance, solderability, and uniformity of coating thickness [1–3]. Lu prepared nanocrystalline alloys characterized by ultrafine grains and a large volume fraction of interfaces by complete crystallization, which make amorphous alloys more useful [4,5].

Amorphous nickel–phosphorus (Ni–P) alloys can be prepared by electroless plating using hypophosphite as reducing agent. Generally speaking, Ni–P alloys are classified by phosphorus (P) content into three kinds: low P (about 2–7 at.% P), medium P (about 8–12 at.% P and 13–18 at.% P), and high P (more than 19 at.% P) alloys. Although there is argument about the microstructure of Ni–P alloys, it is accepted that low P alloys are phosphorus-supersaturated solid solutions of nickel nanocrystalline, but high P alloys exhibit a fully amorphous structure, while medium P alloys are a mixture of nanocrystalline and amorphous structures [6–9].

Electroless Ni–P alloys are thermodynamically unstable and eventually form stable structures of face-centred cubic Ni crystal and body-centred tetragonal nickel phosphide (Ni_3P) compounds. Different results were reported regarding the microstructures in the as-deposited condition and the stable phases after heat treatments. For low P and medium P alloys, nickel crystal precipitated firstly and Ni_3P followed; however, Ni_3P and (or) Ni_xP_y compounds such as Ni_2P, Ni_5P_2, $Ni_{12}P_5$, and Ni_7P_3 occur firstly in high P alloys [10–16].

The crystallization and phase transformation behavior of electroless-plated Ni–P deposits during thermal processing has been the subject of various investigations. It is shown that different alloy compositions and heat treatment conditions could affect both the microstructural characteristics and crystallization behavior of the deposit [17–20].

Crystallization temperature is crucial in the application of amorphous Ni–P alloys and complete crystallization process. In this study, crystallization temperature will be simulated by thermodynamic and kinetic analysis, exam-

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ined by experiments of amorphous Ni–P alloys with various phosphorus contents prepared by electroless plating, which may shed light on other more complex systems.

2. Microstructure of electroless Ni–P alloys as-deposited

With phosphorus content increase in electroless Ni–P alloys as-deposited, the microstructure changed from nanocrystalline to amorphous continuously, owing to P atoms disturbing the regular arrangement of Ni atoms. There are short-range orderings in all of Ni–P alloys (i.e., Ni–Ni clusters and Ni–P clusters), as shown in Fig. 1a [21]. After structural relaxation, P was segregated by short-range movement during the heating process; meanwhile the size of ordered clusters increases. These clusters may act as crystalline embryos or even crystalline nuclei. Nickel crystallite will occur as followed, which can be seen in Fig. 1b. It is noted that there are nickel crystallites in low P alloy as-deposited. So we can take ordered clusters and crystallites as crystalline nuclei, whose size d^* in Ni–P alloy with various P contents (η) can be approximately expressed as [22]:

$$d^* = \delta \Big/ \left\{ 1 - \left[(C_{gb} - \eta) / (C_{gb} - C_g) \right]^{1/3} \right\} \quad (1)$$

where δ is the thickness of nuclei boundary, considered independent with grain size, which is 0.8–1 nm for electroless Ni–P alloys; C_{gb} and C_g stand, respectively, for P concentration of that solute inside the nuclei and at the matrix at a very large distance compared to the radius of the nuclei.

The equilibrium solid solubility of P in Ni alloy is 0.32 at.%, however, which increases to 1 at.% because of lattice stained in nanocrystallines [23,24]. C_{gb} is adopted as 15 at.% by Farber et al., which is not considerable especially for Ni–P alloy with P content of 15–19 at.%. So let us take C_{gb} as 19 at.% and C_g as 1 at.% in this study [25]. The nuclei/crystallite sizes of Ni–P alloy with various P contents calculated by Eq. (1) are shown in Fig. 2,

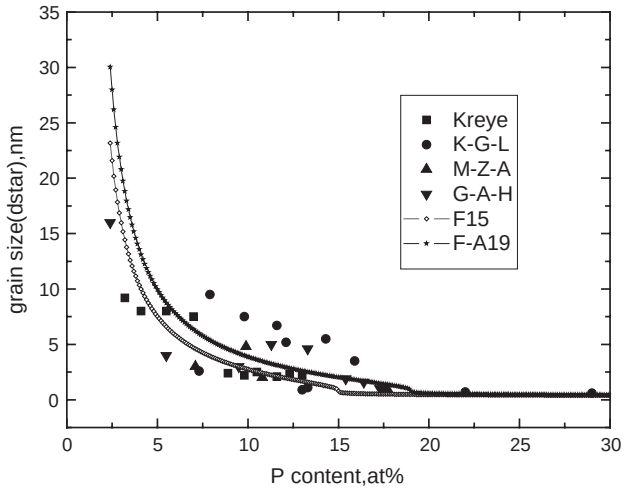

Fig. 2. Grain size of Ni–P alloys as-deposited with various P contents.

compared with results of other investigators. Results of Kreye ('Kreye'), Kumar, Graham, and Lu ('K–G–L'), Mahoney, Zhang, and Allen ('M–Z–A'), and Guo, Apachitei, and Hur ('G–A–H') are shown in the figure as scatter spots [6,8,14,17,25–30]. The grain size in the as-deposited condition was found to decrease with the increase of P content. It demonstrated that curve 'F-A19' with a C_{gb} of 19 at.% is accepted also compared with curve 'F-15' with a C_{gb} of 15 at.%.

3. Crystallization behavior of amorphous Ni–P alloys

Crystallization behavior of amorphous electroless Ni–P alloys under certain temperatures is determined by their composition (i.e., primary, eutectic, and polymorphic crystallization for hypoeutectic, eutectic, and hypereutectic alloys, respectively).

There are two structural components in Ni–P alloys after complete crystallization: nanometer-sized crystallites and interfaces between crystallites. The volume faction of interfacial components will be much enhanced when the grain size is reduced to the nanometer scale. Supposing the

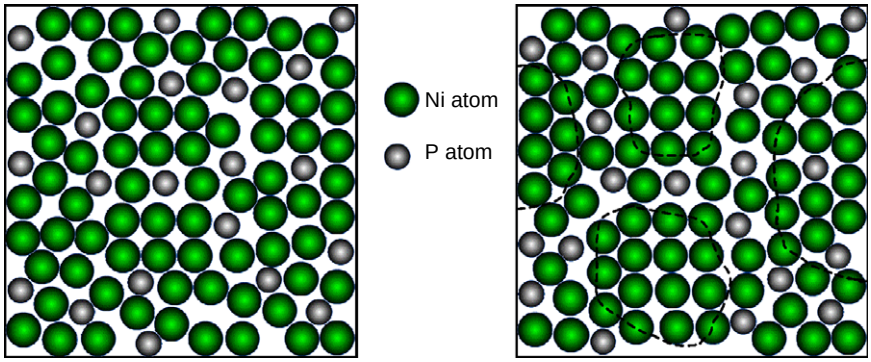

Fig. 1. Schematic diagrams illustrating nuclei growth of Ni–P alloy in two dimensions (20 at.% P). (a) Ordered clusters of as-deposited coating. (b) Crystalline nuclei in the alloy after P segregation.