

## THE DETAILED MECHANISM OF OXIDATION OF Ni-P ALLOYS

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### Abstract

DTA in conjunction with X-ray diffraction analysis with a high-temperature camera and infrared spectroscopy was employed to determine the mechanism of oxidation of Ni-P alloys. Amorphous Ni-P powders were obtained from a nickel(II) sulphate bath as a nickel source and sodium dihydrophosphate(I) as a reducing agent. The crystallization product is composed of two phases: (f.c.c.) Ni and (b.c.t.) Ni<sub>3</sub>P. The amorphous to crystalline transformation takes place in the temperature range 280–330°C. Ni<sub>3</sub>P samples were heated from room temperature to 1050°C in air atmosphere at 5°C min<sup>-1</sup>. It was found that the first stage of oxidation of Ni<sub>3</sub>P goes through the intermediate phase of Ni<sub>12</sub>P<sub>5</sub> formation to Ni<sub>12</sub>P. Some exothermic reactions were observed. Heating runs were interrupted after each reaction for crystal structure determination by IR spectrometry. Infrared spectra are reported and it is shown that the structure units present in the amorphous products at about 700°C were the oxoanions PO<sub>3</sub><sup>-</sup> and P<sub>2</sub>O<sub>7</sub><sup>4-</sup>. The final products of the oxidation process are NiO and Ni<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.

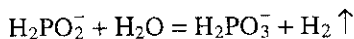
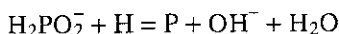
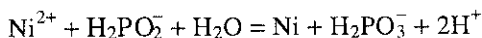
**Keywords:** nickel phosphates, nickel phosphides, Ni-P alloys, oxidation

### Introduction

Ni-P alloys can be prepared by different techniques, such as rapid quenching from the melt, vapour deposition, and electroless or electrolytic deposition. The ultrafine amorphous Ni-P alloy particles produced by chemical reaction are a new class of materials [1]. The ultrafine particles with uniform size are of importance for modelling and quantitative experiments. By applying chemical methods, it is possible to produce a large amount of material in powder form, which can be utilized in powder metallurgy, magnetic recording and catalysis, for example. In the present work, a new method of preparing ultrafine amorphous Ni-P alloy particles and the behaviour at elevated temperatures are presented. The powder was precipitated from aqueous solution by reduction of nickel(II) sulphate with sodium dihydrophosphate(I) initiated with PdCl<sub>2</sub> solution at 80–90°C. This reaction is well known in electroless plating. The mechanism of

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the reaction between nickel and hypophosphate ions involves several oxidation-reduction reactions, as follows:



The structures and properties of Ni–P alloy powders depend on several factors, the most significant of which are pH, temperature, nickel ion concentration and dihydrophosphate(I) concentration. After precipitation, the Ni–P powders were filtered, washed with distilled water and dried at room temperature in air. The P contents of the alloy powders were determined by using the molybdophosphoric acid method. The prepared samples contained 8–22 at.% of P. The amorphous Ni–P particles are in alloy form, not in the form of separate Ni and P domains since there is just one broad peak in the XRD pattern.

The Ni–P binary phase diagram shows that the equilibrium structure in the range 0–25 at.% P corresponds to Ni and Ni<sub>3</sub>P. In addition, the solubility of P in Ni is negligible. The heat treatment of as-prepared samples causes a transformation from the amorphous to the crystalline phase. Crystallization of the amorphous alloys Ni–P leads to various metastable phases, which are subsequently transformed to stable phases. After this phase transformation, face-centred cubic (f.c.c.) Ni austenite and body-centred tetragonal (b.c.t.) Ni<sub>3</sub>P are present. This indicates a possible high reactivity with respect to oxygen. The amorphous to crystalline transformations in the studied samples were found to be complete at 350°C and dependent on the P content.

## Experimental

Oxidation studies on the Ni–P samples were carried out under non-isothermal conditions in air in the temperature range 300–1050°C. Heat treatments were carried out in a derivatograph of the Paulik-Paulik-Erdey system. TG and DTA curves were recorded at a heating rate of 5°C min<sup>-1</sup>.

The oxidation products were examined by X-ray diffraction analysis with a high-temperature camera, DTA and IR spectroscopy. TG and DTA runs were interrupted at various stages of oxidation for the determination of product structures.

## Results and discussion

### *Differential thermal analysis*

Figure 1 shows DTA, TG and DTG curves for a Ni<sub>3</sub>P sample. The sample was heated at 5°C min<sup>-1</sup> in air atmosphere. The oxidation process is seen to proceed

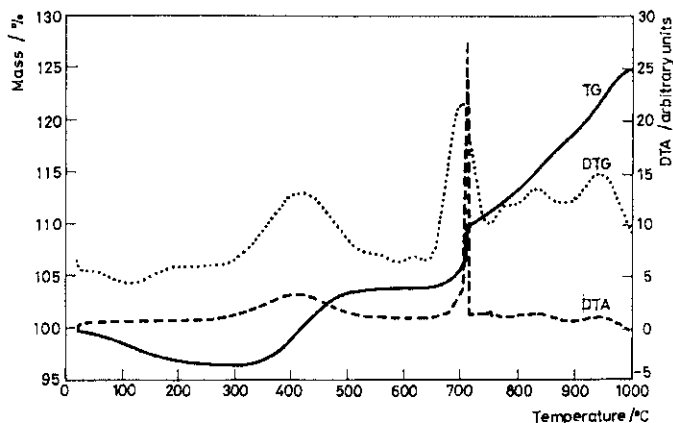


Fig. 1 DTA, TG and DTG curves of oxidation of  $\text{Ni}_3\text{P}$  in air,  $V_T=5^\circ\text{C min}^{-1}$ ,  $m=75$  mg

through three stages. The first is well separated from the second one, but stages II and III overlap. The four exothermic peaks observed are ascribed to stages I, II and III. The sharp and very strong exothermic peak in the DTA curve is observed at  $\sim 700^\circ\text{C}$  in stage II of the oxidation process.

### X-ray diffraction analysis

The oxidation products at various stages during the oxidation of the Ni-P samples were examined by means of X-ray diffraction with a high-temperature camera. Figure 2 shows XRD results on the oxidation of  $\text{Ni}_3\text{P}$ . It illustrates phase

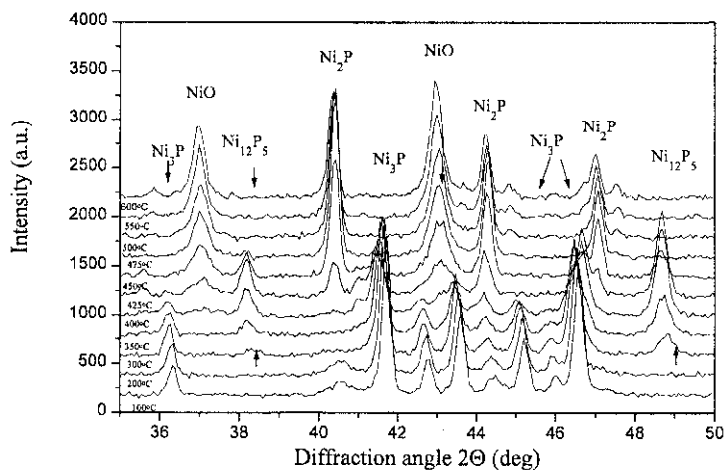
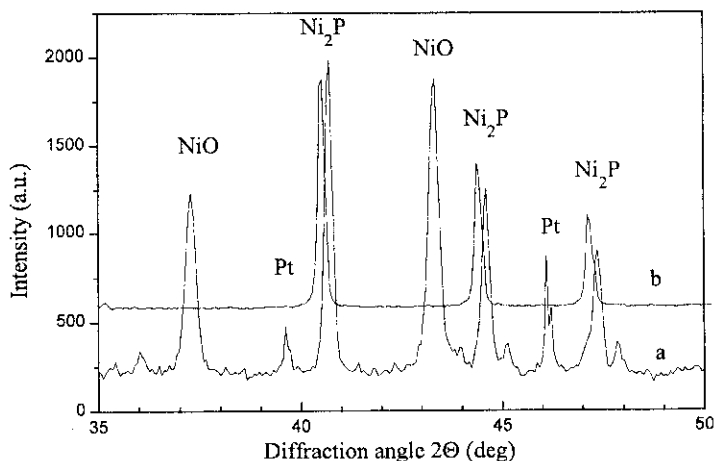
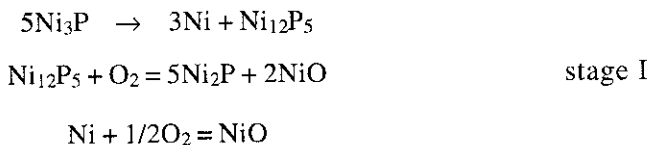


Fig. 2 X-ray diffraction patterns of  $\text{Ni}_3\text{P}$  oxidized in a high-temperature camera in air (heating rate:  $5^\circ\text{C min}^{-1}$ )



**Fig. 3** X-ray diffraction patterns of (a) a  $\text{Ni}_3\text{P}$  sample after the first oxidation stage at  $600^\circ\text{C}$ , (b) a  $\text{Ni}_2\text{P}$  sample

identification for the temperature range up to  $600^\circ\text{C}$ . It is easily established that the first exothermic DTA peak corresponds to the formation of  $\text{NiO}$  and  $\text{Ni}_2\text{P}$ . The intermediate phase  $\text{Ni}_{12}\text{P}_5$  was observed in the temperature range  $350\text{--}500^\circ\text{C}$ . Figure 3 shows XRD patterns for (a) a  $\text{Ni}_3\text{P}$  sample after the first oxidation stage at  $600^\circ\text{C}$  and (b) a  $\text{Ni}_2\text{P}$  sample. The first oxidation process may be described as follows:



The above reactions correspond well with the mass increase of the oxidation of the sample for the first stage:  $\Delta m = 7.7\%$ .

Figures 4 and 5 show the XRD results on  $\text{Ni}_2\text{P}$  oxidation during stages II and III. It can be seen that only the crystalline phases  $\text{NiO}$  and  $\text{Ni}_3(\text{PO}_4)_2$  were formed at about  $700$  and  $850^\circ\text{C}$ . The above results do not explain the origin of the sharp peak at  $\sim 700^\circ\text{C}$  in the DTA curve. The final products at  $1050^\circ\text{C}$  were  $\text{NiO}$  and  $\text{Ni}_3(\text{PO}_4)_2$ .

### Infrared spectra

A detailed study of oxidation mechanism would not have been possible without the use of vibrational spectroscopy for nickel phosphates. Infrared spectra were obtained to clarify the structural changes which take place in the phosphate anions during stages II and III of the oxidation. IR spectra were recorded by the

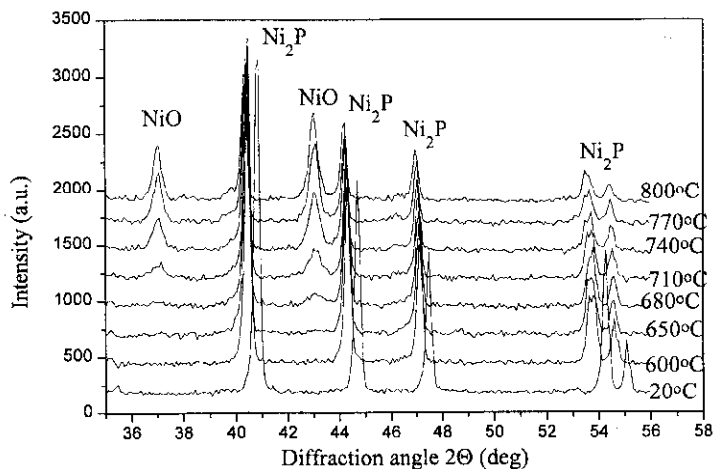


Fig. 4 X-ray diffraction patterns of  $\text{Ni}_3\text{P}$  oxidized in a high-temperature camera in air (heating rate:  $5^\circ\text{C min}^{-1}$ )

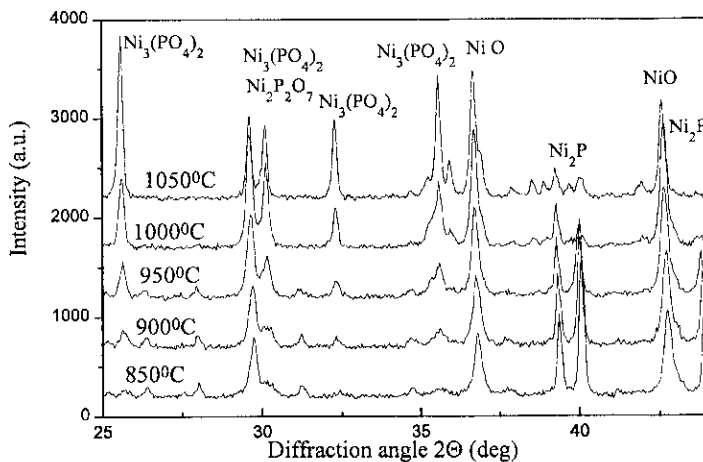


Fig. 5 X-ray diffraction patterns of  $\text{Ni}_2\text{P}$  oxidized in a high-temperature camera in air (heating rate:  $5^\circ\text{C min}^{-1}$ )

KBr method at room temperature after treatments at various temperatures. Nickel phosphates were prepared by solid-state reactions from the starting materials  $\text{NiCO}_3$ ,  $[\text{Ni}(\text{OH})_2]_2 \cdot n\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ . The synthesized phosphates are of use as reference substances for the IR spectra. Figures 6 and 7 show the IR spectra of  $\text{Ni}_2\text{P}$  oxidation products for the temperature range  $600\text{--}1050^\circ\text{C}$  and crystals in the system  $\text{NiO}\text{--}\text{P}_2\text{O}_5$ , respectively. Figure 7 reveals many characteristic peaks for the crystals, whose spectra were measured as references for the spectra of the amorphous phosphates.

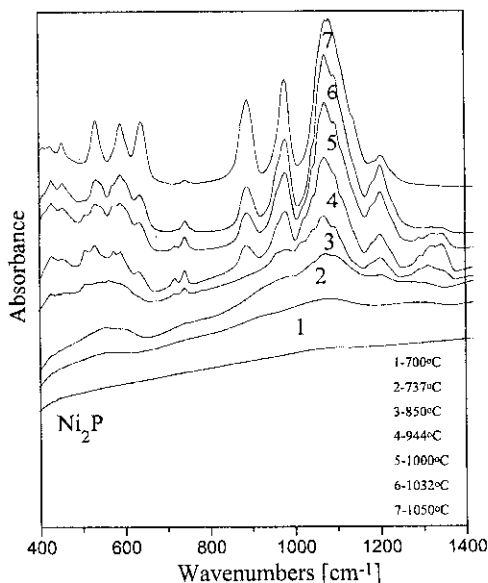


Fig. 6 Infrared spectra of  $\text{Ni}_2\text{P}$  oxidation products in the temperature range 600–1050°C

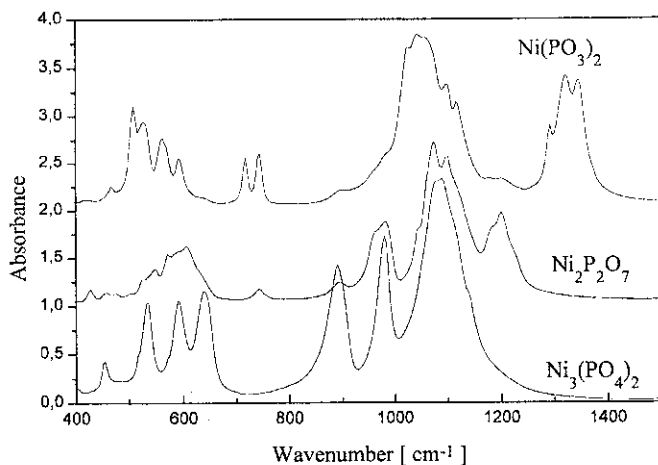
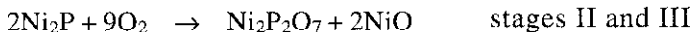
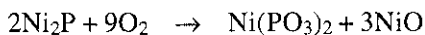


Fig. 7 Infrared spectra of crystals in the system  $\text{NiO-P}_2\text{O}_5$

The chain-type  $\text{Ni}(\text{PO}_3)_2$  crystals exhibit peaks at  $1287\text{ cm}^{-1}$  and  $1321\text{--}1340\text{ cm}^{-1}$ , which are assigned to the  $\nu_{\text{as}}(\text{PO}_2)$  mode [2]. For the pyrophosphate  $\text{Ni}_2\text{P}_2\text{O}_7$  crystals, the peak at  $1205\text{ cm}^{-1}$  is assigned to the  $\nu_{\text{as}}(\text{PO}_3^{2-})$  mode [3], and for the orthophosphate crystals, the peak at  $\sim 1080\text{ cm}^{-1}$  is assigned to the  $\nu_{\text{as}}(\text{PO}_4^{3-})$  mode [4]. In other words, the three peaks may be attributed to  $\text{PO}_4$  groups with 2, 3 and 4 nonbridging oxygens, respectively. Curves 1–7 in Fig. 6

show a very broad absorption band at about  $1300\text{ cm}^{-1}$ , assigned to the  $\nu_{\text{as}}$  mode of  $\text{PO}_2^-$  units in metaphosphate groups, which have a chain or ring structure. Moreover, the intensity of the  $\sim 1300\text{ cm}^{-1}$  band increases in the temperature range  $700\text{--}950^\circ\text{C}$ , and decreases above  $950^\circ\text{C}$ . The broad band at  $\sim 1200\text{ cm}^{-1}$  in curves 1–7 in Fig. 6 can be attributed to  $\text{PO}_3^{2-}$  terminal group vibration in nickel pyrophosphate,  $\text{Ni}_2\text{P}_2\text{O}_7$ . The same changes were observed in the intensity of the  $\sim 1200\text{ cm}^{-1}$  band. Curve 7 indicates that only crystalline  $\text{Ni}_3(\text{PO}_4)_2$  is present in the final product at  $1050^\circ\text{C}$ . The above results explain the origin of the sharp peak at  $\sim 700^\circ\text{C}$  in the DTA curve. This strong thermal effect is due to the formation of a new kind of chemical bonds, P–O bonds in amorphous meta- and pyrophosphates.

The results obtained from the IR absorption spectra are consistent with those of XRD analysis with a high-temperature camera and DTA. For the next stages of the oxidation process, we propose:



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