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OXIDATION MECHANISM OF Ni–P ALLOYS

R. Gajerski, A. Małecki, B. Prochowska-Klisch and
M. Wierzbicka

Faculty of Materials Science and Ceramics, University of Mining and Metallurgy,
al. Mickiewicza 30–059 Cracow, Poland

Abstract

The powders of Ni–P alloys containing 13% of phosphorus were obtained by precipitation from the solution. The oxidation of Ni–P alloys in polythermal conditions was studied. It was found that oxidation of Ni–P alloys goes through stages and that intermediate products of the oxidation are: Ni_2P and $Ni_2P_2O_7$. The final products of oxidation process are NiO and $Ni_3(PO_4)_2$. The sequence of chemical reactions describing the oxidation of Ni–P alloys was proposed.

Keywords: Ni–P alloys, oxidation

Introduction

The Ni–P alloys with phosphorus content of 7–15% in form of coatings deposited on the surfaces of different materials are used as anticorrosion protection as well as to increase hardness of these surfaces. Also Ni–P alloys in powder form have attracted considerable attention recently because of their potential practical application. These alloys are obtained from aqueous solutions by reduction of Ni^{2+} ions with sodium hypophosphite, as amorphous or microcrystalline material [1]. Full crystallization of Ni–P alloys occur at about 500 K and then they can be considered as solid solutions of Ni_3P in metallic nickel [2]. The presence of phosphorus in the nickel matrix increases the temperature of oxidation of these alloys in respect of metallic nickel. Therefore lately Ni–P alloys are used in electronics for contacts and conducting paths working in raised temperatures [3]. However the mechanism of the oxidation of Ni–P alloys is still unknown. In the present paper the attempt to explain the oxidation mechanism of considered alloys is made.

Experimental

In the investigations the powder samples of Ni–P alloys were used. The Ni–P powder was prepared by precipitation from the solutions which contained

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nickel(II) sulfate ($NiSO_4 \cdot 7H_2O$–29 g/dm^3), sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$ –33.7 g/dm^3) acetic acid (CH_3COOH 80%–21.9 g/dm^3), malic acid (HOOC–CH(OH)–CH_2–COOH–10.5 g/dm^3) and citric acid (HOOC–CH_2–C(OH)COOH–CH_2–COOH–5.25 g/dm^3). The precipitation of Ni–P alloys is a result of the following reactions:

$$H_2PO_2^- + H_2O \rightarrow HPO_3^{2-} + H^+ + 2H$$

$$H_2PO_2^- + H \rightarrow P + OH^- + H_2O$$

$$Ni^{2+} + 2H \rightarrow Ni + 2H^+$$

The first reaction occurs when a small amount of $PdCl_2$ is added to the bath and then reaction goes on autocatalytically. Precipitation of Ni–P powders was carried out at 80–90 °C and *pH* of solution was about 4.7. The powders were filtered, washed with distilled water and dried at room temperature (Fig. 1). To avoid influence of crystallization on the oxidation process the amorphous Ni–P powders were initially crystallized in vacuum at about 600°C during 1 h. Prepared samples have contained 13 wt.% of P which was determined by photometric analysis. The grain size was <1 μm.

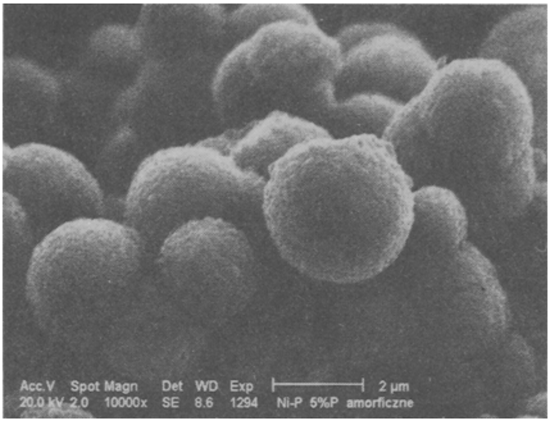

Fig. 1 Microphotograph of Ni–P alloy powder after precipitation

The oxidation of Ni–P samples was carried out in polythermal conditions in derivatograph apparatus of Paulik-Paulik-Erdey system in air, at atmospheric pressure. The sample mass was about 180 mg. TG and DTA curves were recorded for different heating rates 1.25–10 deg·min^{-1}. Identification of phases formed during oxidation was made on partially and completely oxidized samples using XRD and IR techniques.

Results and discussion

As it was expected initially crystallized samples consist of Ni_3P phase dispersed in metallic nickel (Fig. 2a). The representative example of TG and DTA curves obtained during the oxidation of Ni–P alloys is shown on Fig. 3. As it is seen the oxidation proceeds generally through three stages. The first stage is well separated from the second one but stages II and III overlap in some small

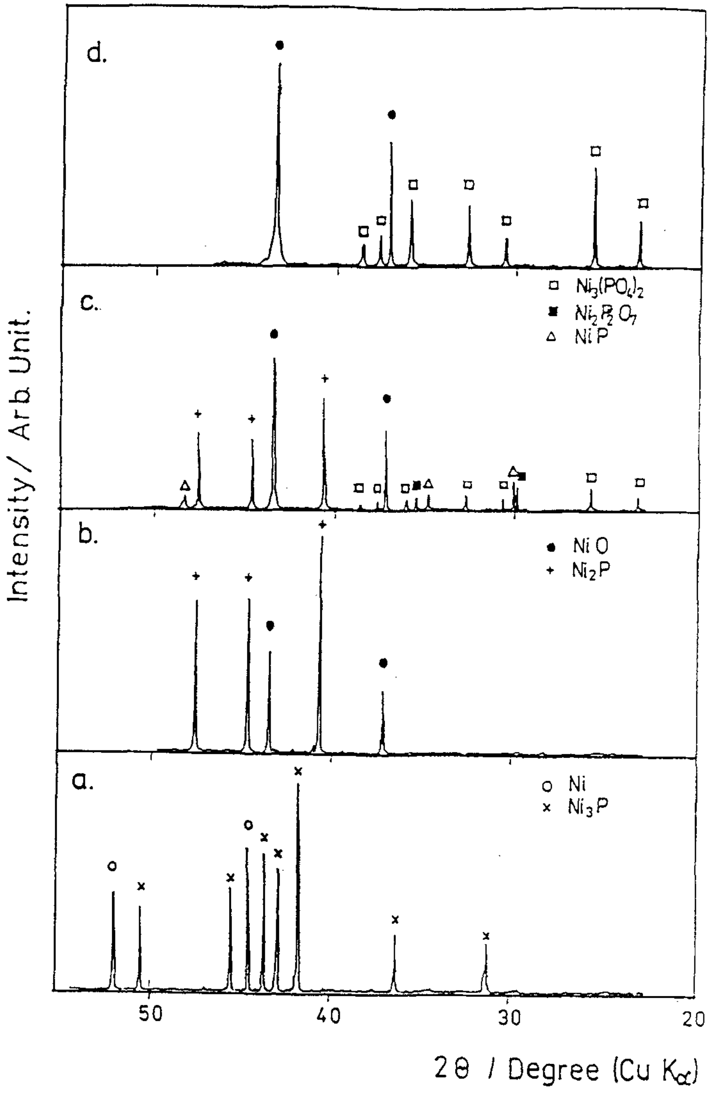

Fig. 2 XRD patterns of Ni–P alloys; a) before oxidation, b) after stage I of oxidation, c) after stage II, d) fully oxidized sample

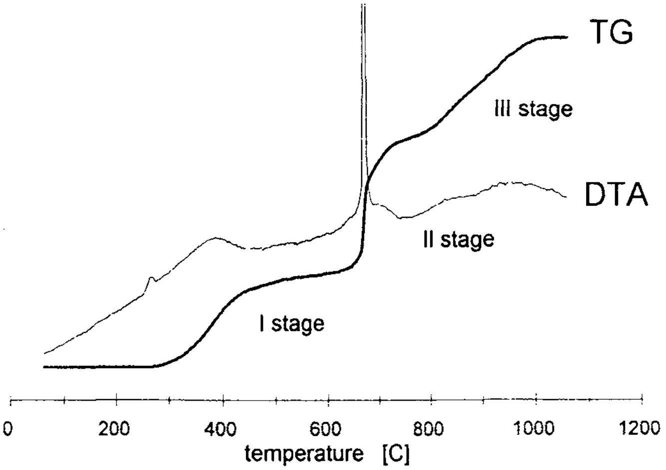

Fig. 3 TG and DTA curves for Ni–P alloys oxidation (heating rate: 5 deg·min^{-1})

region. The separation of last two steps depends on the conditions of experiment, first of all depends on the heating rate. The IR spectra (Fig. 4b) and XRD patterns (Fig. 2b) of the samples after stage I of the oxidation show that in the first stage Ni_2P and NiO is formed and Ni_3P as well as metallic nickel disappear. As a result the following chemical reactions corresponding to the first stage of oxidation of Ni–P alloys can be written:

$$Ni + 1/2O_2 \rightarrow NiO \qquad I.1$$

$$Ni_3P + 1/2O_2 \rightarrow NiO + Ni_2P \qquad I.2$$

The above reactions well correspond with increase of mass of oxidized sample observed on TG curve.

During the second stage $Ni_2P_2O_7$, $Ni_3(PO_4)_2$ and perhaps NiP formation is observed (Fig. 2c). The XRD identification of NiP is undecided due to coincidence of NiP and $Ni_2P_2O_7$ X-ray patterns. The sharp peak on DTA curve corresponding to stage II indicates that new kind of the chemical bond is created in respect of the first stage. Because XRD patterns (Fig. 2c) and IR spectra (Fig. 4b) show the presence of nickel phosphates it is clear that the origin of this thermal effect is the creation of phosphorus-oxygen bonds. Therefore the following reactions should take place:

$$Ni_2P + 1/2O_2 \rightarrow NiP + NiO \qquad II.1$$

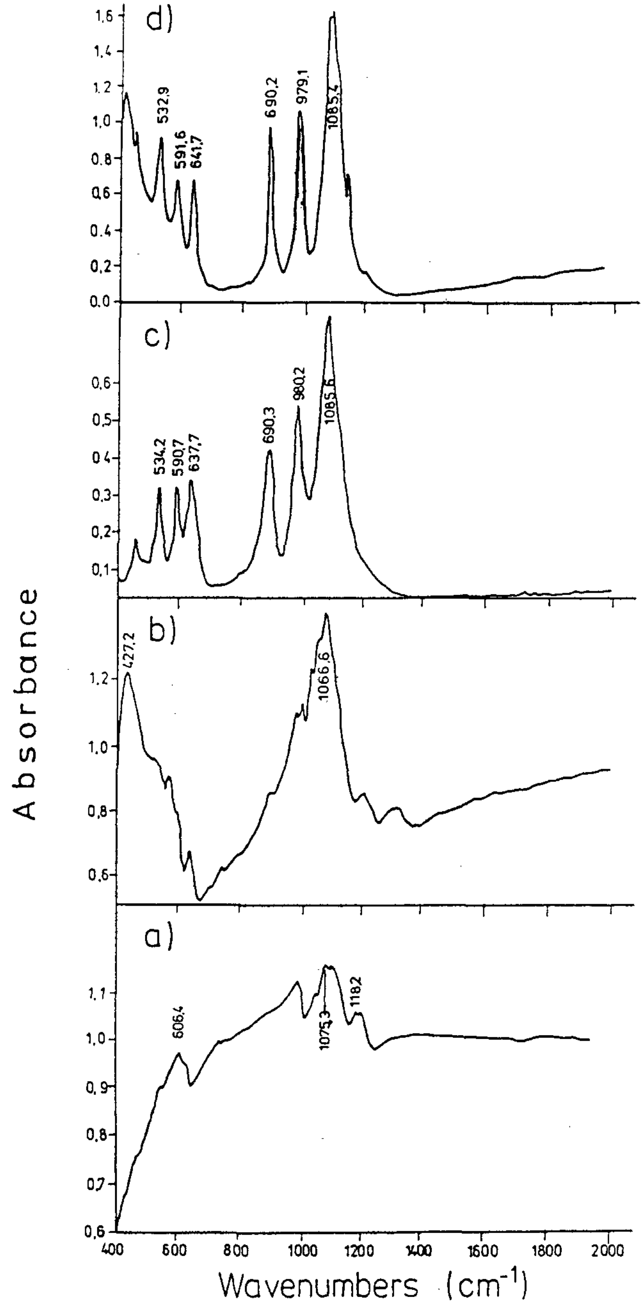

Fig. 4 IR spectra; a) before oxidation, b) after stage I of oxidation, c) fully oxidized sample, d) $Ni_3(PO_4)_2$

$$4Ni_2P + 9/2O_2 \rightarrow 2Ni_3(PO_4)_2 + 2NiO \qquad \text{II.2}$$

$$2Ni_2P + 9/2O_2 \rightarrow Ni_2P_2O_7 + 2NiO \qquad \text{II.3}$$

Ni_2P is present in reacting system to the end of oxidation process. Then one of the reason of the increase of mass observed during the second and third stage are the reactions of Ni_2P with oxygen. Decrease of oxidation rate observed between the second and third stage can be the result of:

a) kinetic inhibition of Ni_2P oxidation which relies on formation of the layer of phosphates on Ni_2P grain;

b) differences between temperature behaviour of the rate constants of the second stage reactions.

The second reason of existence of the third reaction stage can be possible NiP oxidation if, it really forms in the stage II.

$$2NiP + NiO + 7/2O_2 \rightarrow Ni_3(PO_4)_2 \qquad \text{III.1}$$

The final product of oxidation is the mixture of NiO and $Ni_3(PO_4)_2$ (Figs 2d and 4c), thus $Ni_2P_2O_7$ disappeared. The possible way of $Ni_2P_2O_7$ disappearing is reaction with NiO:

$$Ni_2P_2O_7 + NiO \rightarrow Ni_3(PO_4)_2 \qquad \text{III.2}$$

Finally during the third stage of considered reaction several processes simultaneously take place. These are for certain reactions II.2, II.3 and III.2 and perhaps III.1.

References

1 Z. Hu, J. Shen, Y. Chen, M. Lu and Y. Hsia, J. Non-crystalline Solids, 159 (1993) 88.
2 K. H. Hur, J. H. Jeong and D. N. Lee, J. Mater. Sci., 25 (1990) 2573.
3 R. Gajerski, S. Labuś, A. Małecki, J. Obłakowski and B. Prochowska-Klisch, Proc. IV Corrosion Conf. KOROZJA '93, Warsaw, Poland, 1993, pp. 425–427.

Zusammenfassung — Durch Fällen aus Lösung wurden Pulver einer Ni-P-Legierung mit einem Phosphorgehalt von 13% erhalten. Es wurde die Oxidation von Ni-P-Legierungen unter polythermen Bedingungen untersucht. Man fand, daß die Oxidation von Ni-P-Legierungen verschiedene Schritte durchlaufen und daß Ni_2P und $Ni_2P_2O_7$ Zwischenprodukte der Oxidation sind. Die Endprodukte des Oxidationsprozesses sind NiO und $Ni_3(PO_4)_2$. Es wurde ein Reaktionsschema für die Oxidation von Ni-P-Legierungen vorgeschlagen.