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THERMAL OXIDATION KINETICS OF $Ni_{100-x}P_x$ POWDERS

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Abstract

The oxidation of $Ni_{100-x}P_x$ (7.3 at%<x<25.0 at%) powders in air in the temperature range 350–450°C was determined by kinetics and X-ray diffraction. The isothermal kinetics was modeled using the Ginstling–Brounstein equations. The oxidation process was found to be thermally activated with activation energy 127.8 kJ mol^{-1} for x=7.3 at% to 157.7 kJ mol^{-1} for x=25.0 at% It was found that the rate constants for x=7.3 at% were approximately 100 times lower than those for x=25.0 at%.

Keywords: kinetic models, nickel phosphides, Ni–P alloy, oxidation

Introduction

For an amorphous alloy system the investigation of oxidation kinetics is very important in order to understand the nature of the oxidation processes more deeply. The oxidation process of Ni–P system is very complex, and controversial results have been reported. To our knowledge, there have been no recent or detailed studies of the kinetic of the thermal oxidation of Ni–P powders. In addition, because previous investigators have been primarily concerned with the oxidation kinetics of electroless Ni–P coatings at temperatures >600° [1–3], there is a need for data below this temperature.

The kinetics of thermal oxidation of $Ni_{100-x}P_x$ (7.3 at%<x<25.0 at%) in 0.14 atm of oxygen in the temperature range 350–450°C using the isothermal thermogravimetric analysis. X-ray diffraction was used to identify the phases formed during oxidation. In this investigation, nano-size amorphous powders were used. Such a fine particle size makes its easier to study the early stages of oxidation.

Experimental

Sample characterization

$Ni_{100-x}P_x$ (7.3 at%<x<25.0 at%) ultrafine amorphous alloy particles have been prepared by chemical reduction of Ni(II) ions by phosphate(I) ions ($H_2PO_2^-$). This autocatalytic reaction goes on, when a small amount of $PdCl_2$ is added to the solution. The powders were prepared at 80–90°C. The black slurry obtained was washed by

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deionized water and collected in a filter, then dried in a vacuum dryer at 90°C. A stable powder sample was obtained. The composition of the powders was determined by chemical analysis. Seven samples of $Ni_{100-x}P_x$ of phosphorus content equal to: 7.3, 10.6, 15.2, 19.8, 22.4 and 25.0 at% were obtained. They have an almost spherical morphology with diameters decreasing with the increase phosphorous contents. The preparation method, the fundamental properties, and the crystallization behavior of $Ni_{100-x}P_x$ ultrafine amorphous particles were described in our earlier papers [4–6].

Oxidation kinetics

The powder specimens (~34 mg each) were suspended in the thermal gravimetric analyzer (TGA) (SDT 2960 TA Instruments) in platinum crucibles. During isothermal studies, specimens were heated at a rate of 50°C min^{-1}. At 250°C they were held for 3 min to thermally equilibrate the system, at the desired temperature 350 to 450°C – for 60 to 240 min, and finally at 550°C for 300 min to reach the oxidation process completed. Mass change data were collected every 10 s during all TG experiments. The flow rates of synthetic air were held constant at 100 cm^3 min^{-1}.

Results

Figures 1 and 2 show the representative isothermal TG curves for $Ni_{100-x}P_x$ (x=25.0 at%) and $Ni_{100-x}P_x$ (x=7.3 at%) powders, respectively. The same oxidation behavior was observed for all studied alloys compositions. The high phosphorus samples exhibited less mass gain. As the powders were heated, there was some mass loss (about 0.5 mass%) observed due to the loss of adsorbed water. At temperature 550°C oxidation process is completed for all samples and no significant mass changes took place.

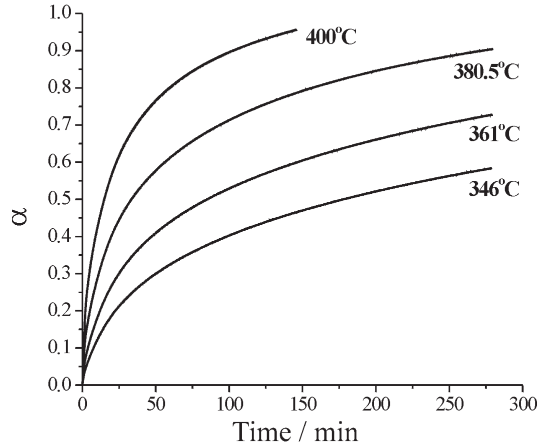

Fig. 1 Isothermal TG curves for for $Ni_{100-x}P_x$ (x=25.0 at%)

The mass gain is due to the formation of Ni_2P and NiO [6]:

$$Ni_{100-x}P_x(s)+\frac{100-3x}{2}O_2(g)=(100-3x)NiO(s)+xNi_2P(s) \quad (<600°C) \qquad (1)$$

To find out the underlying thermodynamic basis for the $Ni_{100-x}P_x$ oxidation, we have made some calculations using thermodynamic data from Barin [7]. The oxidation of $Ni_{100-x}P_x$ (x=25.0 at%), i.e. Ni_3P to Ni_2P and NiO can be expressed as:

$$Ni_3P(s)+0.5O_2(g)=NiO(s)+Ni_2P(s) \quad (<600°C) \qquad (2)$$

The Gibbs free energies for above reaction are –1482 and –1318 kJ for the reaction temperatures of 350 and 550°C, respectively. The formation of Ni_2P and NiO is confirmed by X-ray analysis (Fig. 3). $Ni_{100-x}P_x$ (x=7.3 at%) powder has the largest mass gain (22.6 mass%) among all seven studied powders, it is very close to

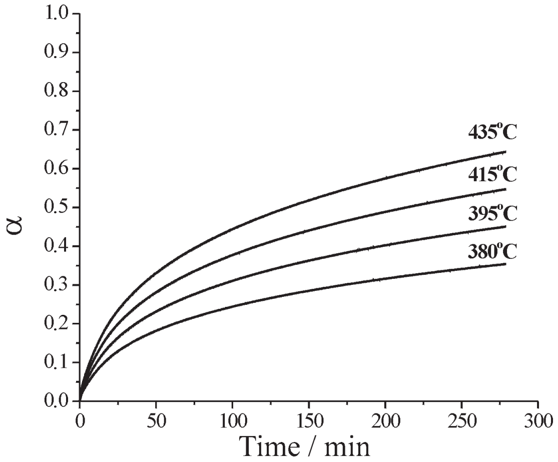

Fig. 2 Isothermal TG curves for for $Ni_{100-x}P_x$ (x=7.3 at%)

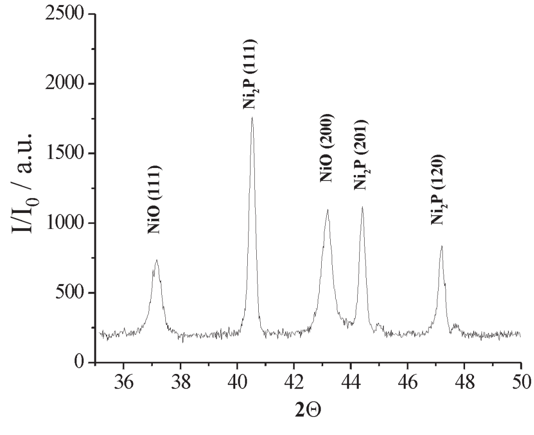

Fig. 3 X-ray diffraction patterns of $Ni_{100-x}P_x$ (x=22.4 at%) powder after oxidation at 550°C

22.1 mass%, as predicted by Eq. (1). Comparison of the mass gains calculated from Eq. (1) with the experimental results is shown in Fig. 4.

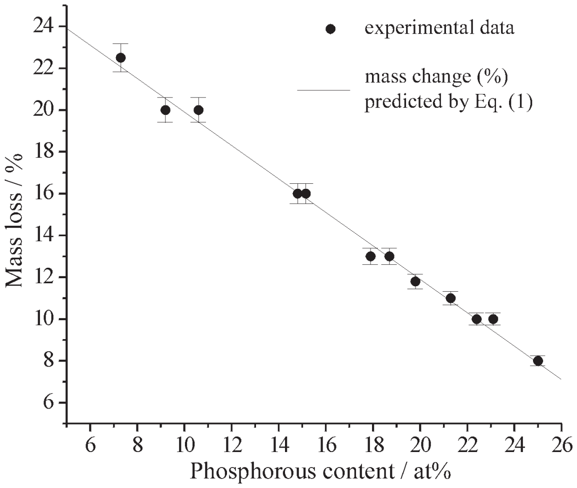

Fig. 4 Comparison of the mass gain calculated from Eq. (1) with the experimental results

Attempts were made to fit the isothermal data to a variety of kinetic models based on mechanisms, including diffusion control. All kinetics could be modeled closely at temperatures 350–450°C using diffusion-rate-limited model for reactions involving spherical particles, i.e., the Ginstling–Brounstein equation modified by Małecki [8–10]:

$$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}=kt^{n} \tag{3}$$

where k, like n are constant parameters at constant temperature, α is the fraction of powder that has reacted. The modification of the Ginstling–Brounstein model extended the range of its application to the cases where, for instance, diffusion processes, determining the rate of reaction, proceeded simultaneously in different ways. A suitable coordinate system enabled linearization of the obtained $\alpha(t)$ functions and calculation of the slopes and $\ln k$. The values of n, found for all the prepared $Ni_{100-x}P_x$ samples did not significantly differ from 1, which was confirmed by non-parametric statistical tests. This indicates clearly that the oxidation kinetics of the investigated alloys is consistent with Ginstling–Brounstein model. Moreover, the fact that no temperature dependence of parameter n was observed allows for the conclusion that the same diffusion process controls the oxidation rate independently of the reaction progress.

The parabolic rate constants obtained through simple linear regression on Eq. (3) are summarized in Fig. 5. From Arrhenius dependence activation energy of $Ni_{100-x}P_x$ powders oxidation was determined and was found to be 127.8 kJ mol^{-1} for x=7.3 at% to 157.7 kJ mol^{-1} for x=25.0 at% (Fig. 6).

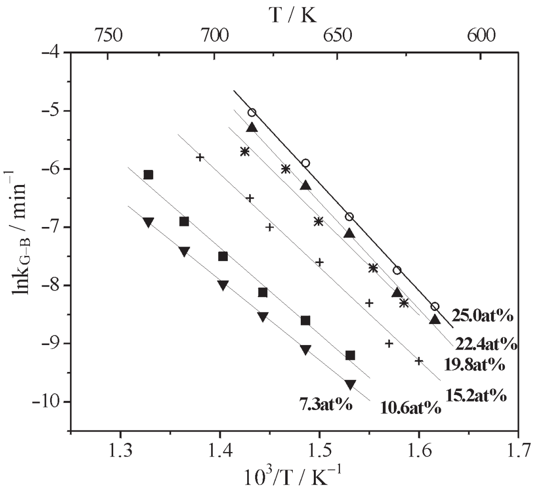

Fig. 5 Parabolic rate constants for the oxidation of $Ni_{100-x}P_x$ powders

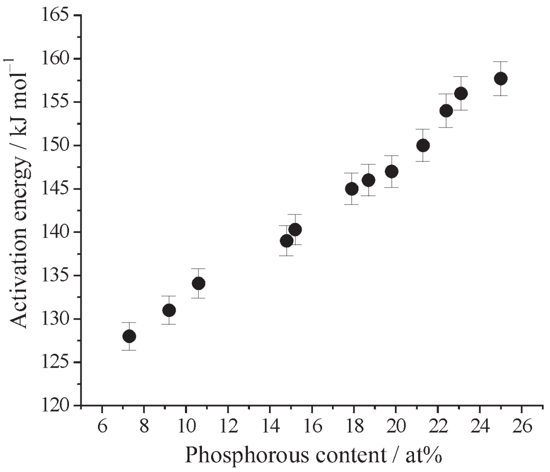

Fig. 6 Activation energy for the oxidation $Ni_{100-x}P_x$ powders

Conclusions

The present study has given the following results:

- the obtained results allow to propose an equation for the oxidation reaction,
- below 600°C the oxidation products are crystalline Ni_2P and NiO; no gaseous or amorphous phases are formed,
- high phosphorus samples oxidize about 100 times faster than low phosphorus ones,
- diffusion-rate-limited Ginstling–Brounstein model satisfactorily describes the oxidation kinetics.

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