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INFLUENCE OF COMPOSITION ON THE THERMAL BEHAVIOUR OF CHEMICALLY DEPOSITED NICKEL–PHOSPHORUS ALLOYS

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The thermal behaviour of a series of Ni–P alloys obtained by electroless plating from chloride–glycollate solutions at different pH values was studied by means of DSC analysis and X-ray diffraction.

Alloys of composition up to $Ni_{78}P_{22}$ are microcrystalline or partially amorphous, depending on the P content; on heating up to 773 K, the amorphous phase is transformed into an equilibrium mixture of Ni and Ni_3P crystals.

Most of the alloys crystallize in two exothermic stages, these occurring ever closer to each other as the P concentration approaches the eutectic value; the alloys with near-eutectic compositions are the only ones crystallizing in one stage.

The first thermal effect in hypo-eutectic alloys is due to the separation of Ni crystallites from the primary amorphous phase and/or to the growth of pre-existing solid-solution crystals; the second one is due to the crystallization of intermediate amorphous phase into Ni_3P plus Ni. The first stage of crystallization in hyper-eutectic alloys corresponds to the formation of randomly-oriented Ni_3P crystals, while in the second one the residual amorphous phase yields the eutectic mixture.

Electroless nickel-plating is an established industrial process used to apply protective and/or decorative metallic coatings to various substrates, including ceramics and plastics. When Ni^{2+} ions are reduced by sodium hypophosphite, the deposited coating consists of Ni–P alloy containing as much as 30 at.% P.

Apart from their peculiar chemical and physico-mechanical properties, one of the more interesting aspects of these alloys is the variation in structure as a function of the composition and heat treatment. Indeed, as deposited, Ni–P electroless alloys appear to be increasingly amorphous to X-ray diffraction as the percentage of P rises, just as in the case of metal-glasses obtained by quenching from the molten state. When annealed, the amorphous structure spontaneously evolved towards its stable state, i.e. a crystalline mixture of nickel and/or nickel phosphides.

The amorphous-to-crystalline transformation of Ni–P alloys has been studied widely from a theoretical point of view, as well as with respect to possible practical applications; the essential aspects of this transformation seem to have been sufficiently

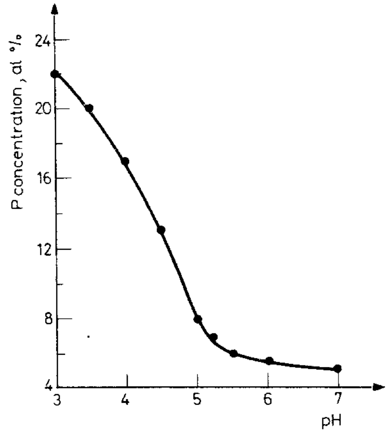

Fig. 1 Influence of solution pH on P concentration in Ni—P alloys chemically deposited from a glycollate—chloride bath

defined already. However, the mechanism of crystallization is less well understood. In this respect, the data so far published in the literature do not permit the unequivocal identification and interpretation of the relevant stages in the process. Of particular significance in this respect is the wide dispersion of the calorimetric data reported by various authors for alloys prepared and treated in apparently analogous ways [1—7].

The most recent studies in this field are those of Cziráky et al. [6] and Allen and Van der Sande [7]. Cziráky et al. observed that, with all other conditions the same, the complexity of the DSC curves depends on the type of bath used for the deposition. Samples obtained from chloride baths seemed to be much less homogeneous and began to crystallize even at around 200°, with the formation of Ni precipitates. Samples ontained from sulphate baths exhibited simpler and more systematic behaviour; in particular, three stages of crystallization were observed, whose importance depends on the P concentration; in the case studied, this varied from 16 to 19.3 at.%. The first stage was associated with the formation of regions rich in Ni, but not yet perfectly crystalline; the second, with the crystallization of phosphides such as Ni_7P_3 and Ni_5P_2; and the third (found only in the alloys with the highest P contents) with the conversion of these phosphides into Ni_3P. When the third stage of crystallization was absent, the only phosphide present at complete crystallization was Ni_7P_3.

Analyzing samples obtained from commercial sulphate baths at different pH values, Allen et Van der Sande observed that, between 300 and 700 K, each DSC curve displayed one or two exothermic peaks, with intensities depending on the P concentration. Alloys with 5.5 and 17.3 at.% P gave only one peak, at 690 K and 520 K, respectively. Alloys with 2.4 and 9.5 at.% P gave two peaks, at 640 and 690 K, and at 520 and 640 K, respectively. The peak at 520 K was attributed to the precipitation of Ni crystallites in an amorphous matrix. This peak appeared only in the alloys with the highest P contents, i.e. the ones with the most amorphous structures.

From the results reported in these two publications, it would seem that the thermal behaviour of Ni–P alloys differs from case to case for apparently uncontrollable reasons. In order to unravel these reasons and to gain a better understanding of the nature of the phenomena involved, we began a systematic study of Ni–P alloys obtained from different types of baths. Here we report results for samples deposited from a glycollate–chloride bath.

Experimental

The samples examined in this study were obtained from a bath with the following composition:

$NiCl_2 \cdot 6\,H_2O = 30$ g/l, $CH_2(OH)COONa = 40$ g/l,
$CH_3COONa \cdot 3\,H_2O = 50$ g/l, $NaH_2PO_2 \cdot H_2O = 10$ g/l

(C. Erba reagent grade chemicals); HCl additions were made so as to adjust the initial pH to values between 3 and 6. The alloy was deposited on sheets of stainless steel measuring around 9 cm^2, which had been previously activated with $PdCl_2$. The operation was carried-out using 500 ml of solution at 93±2°, with continual renewal of the reagents. With a deposition time of 60 min, the layer thicknesses obtained varied from 5 to 20 μm, depending on the rate of deposition.

Chemical analysis of the coatings mechanically stripped from the substrate was carried out using three different methods in order to ensure the best possible accuracy. The methods used were EDS analysis, impulse polarography (for Ni) and spectrophotometry (for P); the values reported for each alloy are the average values obtained from the three different analytical techniques, taking into account their limits and sensitivities. X-ray diffraction analyses, before and after heat treatment, were carried out using a Philips diffractometer with Cu–K_α radiation. The thermal analysis was performed using a Perkin–Elmer DSC-2C microcalorimeter equipped with a computer and plotter.

Results and discussion

Chemical and structural analysis

Results of chemical analysis of the Ni–P alloys obtained confirm that the P concentration decreases with increasing pH. However, the relationship between the P contents of the alloys and the pH, illustrated in Fig. 1, is specific for the type of bath used and is not valid either for baths of other compositions or for other operating conditions. Indeed, there is no one relationship between the pH of the bath and the P content of the deposit that is valid for all types of baths and operating conditions.

The maximum variation in composition was found between pH 3 and pH 5, in accordance with an analogously rapid variation in the velocity of deposition. Beginning from pH $\sim$ 5.25, the influence of the bath acidity on the quantity of co-deposited P becomes much more modest, probably beacuse of a progressive change in the mechanism of deposition. This change could also be responsible for the gradual change in microstructure which the samples underwent between pH 5 and 5.5; whereas at pH $\leqslant$ 5 the layers grew preferentially along the (111) crystallographic direction, starting from pH 5.5 they began to grow preferentially along the (100) direction. In any case, between pH 6 and pH 3 a homogeneous series of alloys was obtained whose composition, which varies from $Ni_{95}P_5$ to $Ni_{78}P_{22}$, covers a wide range of the binary phase diagram Ni–Ni_3P [8].

The X-ray diffraction patterns show that the degree of crystallinity is much less at higher P contents. In fact, while the most dilute alloys show all the reflections typical of fcc-Ni, the only important reflection for alloys with a P concentration over *ca.* 10 at.% is that corresponding to $d = 2.03$–2.04; moreover, this reflection becomes increasingly weaker and broader as the percentage of P in the alloy increases. This tendency is illustrated clearly by the variation in average size of the coherent domains as a function of the P percentage, determined by Warrern–Averbach analysis of the layers in the composition range up to $Ni_{83}P_{17}$ (reliable results can not be obtained from this type of analysis for alloys with higher P contents, because their diffraction patterns are not sufficiently well defined). The curve in Fig. 2 shows that between 5 and 8 at.% P, the size of the coherent domains decreases very rapidly; conversely, starting from around 8 at.% P, considerable increases in the quantity of P correspond to relatively modest variations in the size of the domains. This discontinuity in behaviour, which has already been pointed out by other authors for electroless Ni–P alloys deposited from either alkaline or acid baths [9], can be explained if one accepts that in the mode dilute alloys the P atoms enter into supersaturated solid solution in

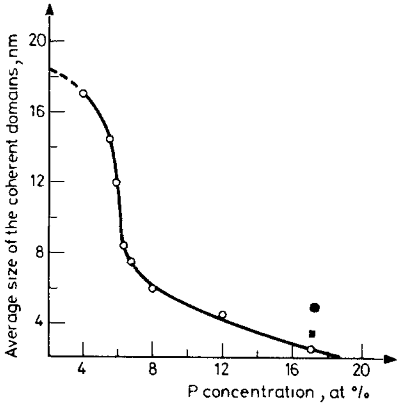

Fig. 2 Average size of coherent domains in Ni–P alloys as a function of P concentration. ● as deposited; ■ after 15 min annealing at 550 K; ▲ after 15 min annealing at 570 K; ○ after heating at 20 degree/min up to 590 K

the Ni matrix, interfering with the growth of the crystallites and consequently rapidly reducing their size; in the more concentrated alloys, the P atoms are partly separated out from the solid solution, generating clusters of a new amorphous phase. As the P content increases, these amorphous clusters expand at the expense of the surrounding crystalline matrix; by around 18 to 20 at.% P, the size of the crystalline domains has become so small that the alloy appears to be completely amorphous, even though the degree of residual order is probably greater than that typical of liquids or that of many metal-glasses obtained via quenching. On the other hand, such a short-range ordering in Ni—P alloys was previously postulated on the basis of optical and electrical measurements [10], and recently confirmed by Exafs [11] and Sxes [12] studies on co-evaporated and electroless deposited layers.

Calorimetric analysis

Figure 2 presents DSC curves for samples of various composition heated from 323 to 773 K at a constant rate of 40 deg/min in a N_2 atmosphere. All the phenomena associated with the amorphous-to-crystalline transformation are exothermic; for each of the samples there are a maximum of two transformation peaks, both of which are simple and well defined, except when they are partially superimposed.

The appearance of more than two thermal effects may well be caused by large differences in P concentration throughout the thickness of the layer or by some other structural inhomogeneity. As regards the influence of composition, we found that:

– The alloys with a P content lower than 6 at.% do not show any definite thermal effect, except a broad and weak endothermic band between 450 and 700 K. We have not yet investigated the nature of this effect; however, it seems to be very similar to that attributed by Fléchon et al. to the release of the hydrogen absorbed during deposition [2]. In spite of the absence of exothermic phenomena, the X-ray patterns of these alloys annealed up to 773 K proves Ni_3P formation and some Ni recrystallization.

– The alloys $Ni_{94}P_6$ and $Ni_{93.5}P_{6.5}$ show only one relatively weak exothermic peak, denoted Tx_2 in Fig. 3, due to the crystallization of Ni_3P.

– The alloys with compositions between $Ni_{93}P_7$ and $Ni_{83}P_{17}$ show a more well-defined exothermic peak preceded by a broad exothermic band; the relative intensity of the two effects, Tx_2 and Tx_1, respectively, depends on the P concentration. The curves reported in Fig. 4 show that Tx_1 and Tx_2 are situated more closely together as the percentage of P increases. The X-ray diffraction patterns of the alloys quenched after completion of the first exothermic effect are not substantially different from those of the same alloys before heating, but for a definite sharpening of the Ni(III) reflection on a still diffuse background. The Ni_3P reflections appear only in correspondence to the second exothermic peak.

– The alloys $Ni_{82}P_{18}$ and $Ni_{80}P_{20}$ crystallize in a single sharp stage, Tx_2, at around 645 K; after this stage the amorphous-to-crystalline transformation is complete and a mixture of Ni and Ni_3P crystals is formed.

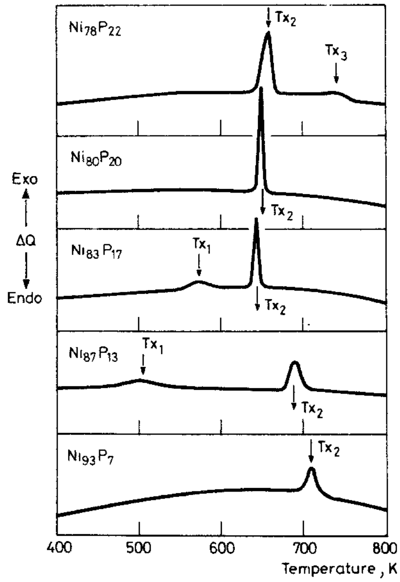

Fig. 3 DSC curves of some representative Ni–P alloys heated at a constant rate of 40 degree/min

– The alloys with P concentrations between 20.5 and 22 at.% give rise to two exothermic effects: the first sharp and intense at around 650 K, and the second much weaker and broader, at increasing temperatures starting from about 675 K. The X-ray pattern of the alloy annealed up to 660 K and air-quenched shows that the crystallization is nearly complete, but the only identifiable phase is Ni_3P. Other weaker reflections corresponding to Ni (especially the (200) reflection) appear only after the alloy has been heated above 675 K.

Figure 5 reports the values of the heat developed during the different transformation stages as a function of the P content. The total heat of crystallization, i.e. the sum of all the thermal effects measured (dashed curve), increases rapidly with increasing P content up to around 12 at.% P, reaches a maximum between 12 and 16 at.% P, and then decreases slightly between 16 and 22 at.%. The heat Q_1 developed during the first stage of crystallization increases with increasing P concentration until around 15 at.% P, and decreases rapidly between 16 and 18 at.%, becoming zero when the first stage of crystallization merges into the second.

The heat Q_3 released during the third stage probably follows a bell-shaped curve, in the same way as Q_1.

Thus, the amorphous-to-crystalline transformation of Ni–P alloys with P contents, up to 22 at.% takes place in one or two stages, depending on the composition. The Tx_2 stage, common to all alloys, is that associated with the crystallization of Ni_3P. It may be preceded (in many hypo-eutectic alloys) or followed (in some hyper-eutectic alloys) by another stage, corresponding to the appearance of Ni crystals.

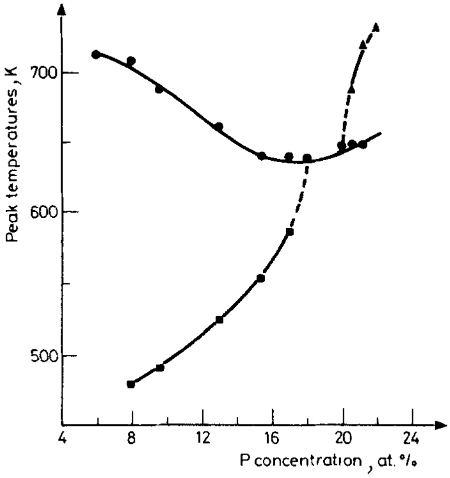

Fig. 4 Variation of peak temperatures as a function of composition for Ni–P alloys ranging from $Ni_{94}P_6$ to $Ni_{78}P_{22}$; heating rate = 40 degree/min. ■ Tx_1; ● Tx_2; ▲ Tx_3

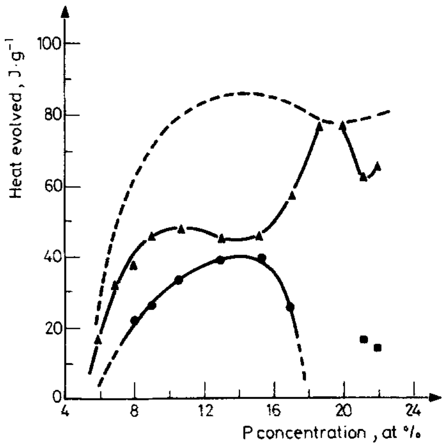

Fig. 5 Heats of crystallization as a function of Ni–P alloy composition. ● Q_1; ▲ Q_2; ■ Q_3

Crystallization mechanism

In order to gain a better understanding of the mechanism of the crystallization, two alloys, $Ni_{80}P_{20}$ (representative of a single-stage transformation) and $Ni_{83}P_{17}$ (representative of a two-stage transformation), were submitted to DSC isothermal analysis.

1) $Ni_{80}P_{20}$ alloy: the crystallized fraction α grows with time according to an equation of the type: $\alpha = 1 - \exp(-kt)^n$, like most of the transformations proceeding via a mechanism of nucleation and growth [11]. The Avrami exponent n, de-

termined graphically from a plot of log [– log (1 – α)] *vs.* log *t*, remains nearly constant (coefficient of linear correlation better than 0.98) during the course of the crystallization, but varies from about 4 to 3 with decreasing temperature. This range of values is characteristic of spherulitic crystallization processes; the X-ray diffraction data indicate that the initial amorphous phase is transformed completely into a eutectic mixture of randomly-oriented Ni and Ni_3P fine crystals.

The sigmoidal trend of the curves on a log *t* scale shows some dependence of the temperature, as predicted by theory for a decreasing nucleation rate [13].

2) $Ni_{83}P_{17}$ alloy: the Tx_2 stage behaves kinetically much like the stage corresponding to the crystallization of the eutectic mixture in the $Ni_{80}P_{20}$ alloy. Even so, in this case the Avrami exponent *n* varies from 3.5 (at 603 K) to 2.5 (at 583 K). The difference may be attributed to an increasing influence of the pre-crystallized Ni-rich phase on the growth symmetry. In this case also there is evidence of a decreasing nucleation rate.

The more significant calorimetric data concerning the first stage of the transformation are as follows:

a) For the same composition, the heat of transformation decreases with decreasing temperature of isothermal treatment. Further, the extent of reduction is proportional to the time of preventive annealing at temperatures 20 to 30° below onset of the temperature of transformation. Such pre-annealing, however, has no influence on the intensity and position of the second stage of transformation.

b) For all temperatures within the peak, there is no incubation time and the transformation proceeds at a rate almost immediately decreasing. The Avrami exponent *n* determined by measuring the area beneath the DSC isothermal peaks beginning 10 s after the isothermal start, varies from 1.03 (at 574 K) to 1.56 (at 560 K), that is it increases with decreasing temperatures.

c) Isothermal heating causes an increase in the average size of the coherent domains proportional (at the same temperature) to the annealing time and (at the same time) to the temperature chosen. For alloy heated at a rate of 20 deg/min up to 590 K, i.e. until completion of the first stage of transformation, the average size of the coherent domains increases from 2.5 to 4.6 nm (see Fig. 2).

These data lead one to believe that the first stage of transformation of the alloys with P concentrations between 6 and 17 at.% is an intermediate step of crystallization of the amorphous P-rich phase, leading both to the separation of iso-oriented Ni crystallites and to growth of the pre-existing solid-solution grains, either process being favoured by changing the annealing temperature.

Likewise, the crystallization of the alloys containing more than 20 at.% P passes through an intermediate stage, Tx_2 in this case, during which the original amorphous phase separates Ni_3P crystals; the residual Ni-rich, but still disordered phase crystallizes then at a higher temperature, say Tx_3.

In this respect, the thermal behaviour of these Ni–P alloys seems to fit very closely the general pattern recently proposed by Hornbogen to systematize the crystallization reactions in solid solutions [14]. In fact, on the basis of a reasonable free energy *vs.*

concentration diagram for the binary system Ni—Ni_3P, the composition range from 6 to 17 at.% seems to be the most kinetically favourable for a two-stage mechanism of the type:

$$a \xrightarrow[Tx_1]{1st} Ni' + a' \xrightarrow[Tx_2]{2nd} Ni + Ni_3P$$

where a = original amorphous phase, a' = intermediate amorphous phase.

Conversely, for composition with more than 21 at.% P, the phase kinetically favoured for pre-crystallization is Ni_3P or a phosphide of composition very near to Ni_3P, so that the overall reaction can be represented schematically as follows:

$$a \xrightarrow[Tx_2]{1st} Ni_3P' + a' \xrightarrow[Tx_3]{2nd} Ni_3P + Ni$$

where the symbols have the same meaning as above.

Conclusions

The amorphous-to-crystalline transformation of Ni—P alloys, in the composition range from $Ni_{94}P_6$ to $Ni_{78}P_{22}$, obtained by electroless plating from a well buffered glycollate—chloride bath, takes place in one of two stages, depending on the P content. The single-stage mechanism is limited to those alloys whose compositions are near the eutectic point and whose P concentrations are about 6—7 at.%. For most of the hypo-eutectic and hyper-eutectic alloys, the initial amorphous phase is not transformed directly into a mixture of the equilibrium crystalline phases, but rather passes through an intermediate stage characterized by the separation of Ni and Ni_3P crystallites, respectively.

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Zusammenfassung — Das thermische Verhalten einer Reihe von durch stromlose Platierung mit Chlorid-Clykollat-Lösungen bei verschiedenen pH-Werten erhaltenen Ni—P—Legierungen wurde mittels DSC und Röntgendiffraktion untersucht. Legierungen mit einer Zusammensetzung bis $Ni_{78}P_{22}$ sind, abhängig vom P-Gehalt, kristallin oder teilweise amorph. Beim Erhitzen auf 773 K wird die amorphe Phase in ein Gleichgewichtsgemisch von Ni- und Ni_3P-Kristallen überführt. Die meisten Legierungen kristallisieren in zwei exothermen Schritten, die sich einander umso mehr nähern, je mehr sich die P-Konzentration dem eutektischen Wert nähert. Als einzige kristallisieren die in der Zusammensetzung dem Eutektikum nahekommenden Legierungen in einem Schritt. Bei hypoeutektischen Legierungen ist der erste thermische Effekt der Ausscheidung von Ni-Kristallen aus der primären amorphen Phase und/oder dem Wachstum von bereits in der festen Lösung vorliegenden Kristallen, der zweite der Kristallization von Ni_3P und Ni aus der intermediären amorphen Phase zuzuschreiben. Bei hypereutektischen Legierungen entspricht der erste Schritt der Kristallisation der Bildung von random-orientierten Ni_3P-Kristallen, während des zweiten wird dagegen die verbleibende amorphe Phase in das eutektische Gemisch überführt.

Резюме — С помощью ДСК и диффракции рентгеновских лучей изучено термическое поведение ряда Ni—P сплавов, полученных беззлектродным никелированием из растворов хлорид-гликолята при различных значениях pH. Сплавы с составом до $Ni_{78}P_{22}$ являются, в зависимости от содержания фосфора, микрокристаллическими или частично аморфными. При нагревании до 773 К аморфная фаза превращается в равновесную смесь Ni и Ni_3P кристаллов. Большинство сплавов кристаллизуется в две экзотермические стадии, которые сближаются по мере приближения концентрации фосфора к эвтектическому значению. Сплавы с почти эвтектическим составом кристаллизуются в одну стадию. Первый термический еффект и гипо-эвтектических сплавах обусловлен разделением кристаллитов никеля от первичной аморфной фазы или же ростом кристаллитов ранее существующего твердого раствора. Второй эффект обусловлен кристаллизацией промежуточной аморфной фазы с образованием Ni_3P и никеля. Первая стадия кристаллизации в гипер-эвтектических сплавах соответствует образованию произвольно ориентированных кристаллов Ni_3P, тогда как на второй стадии оставшаяся аморфная фаза дает эвтектическую смесь.