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# MEASUREMENTS OF ACTIVATION ENERGIES FOR TWO-STEP CRYSTALLIZATION

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АННОТАЦИЯ

Определена энергия активации кристаллизации аморфных пленок NiP по изменениям, измеренным при изотермических термообработках электросопротивления. Сплавы NiP, полученные химическим осаждением, показали двухфазовую кристаллизацию с хорошо разделяемыми энергиями активации.

KIVONAT

Amorf NiP filmek kristályosodásának aktivációs energiáját határoztuk meg az elektromos ellenállás izoterm hőkezelések során mért változásaiból. Az elektroless leválasztással készült NiP ötvözetek két-lépcsős kristályosodást mutattak. Az aktivációs energiák jól megkülönböztethetők.

ABSTRACT

Crystallization activation energies were determined for NiP amorphous films using electrical resistivity changes during isothermal annealings. Crystallization of NiP alloys prepared by electroless deposition showed two distinct stages - with well separated activation energies.

## EXPERIMENTAL

The films were prepared using chemical reduction from bath containing 15-30 mg/cm$^3$ $NiCl_2 \cdot 6H_2O$ salt, 10-20 mg/cm$^3$ $NaH_2PO_4 \cdot H_2O$ reductor and 50 mg/cm$^3$ $CH_3COONa \cdot 3H_2O$ as stabilizer. The phosphorus concentration was determined by spectrophotometric, the other contaminations by atomic absorption analysis. All the samples proved to be amorphous by X-ray diffraction.

Electrical resistivity measurement was carried out in a vacuum furnace. By turning of the furnace around a horizontal shaft, the sample (8x0.2 cm long strip) was shot into the splitted heater. Temperature of the heater was precisely regulated before the shot. Because the mass of the sample was a negligible part of that of the heater the temperature distance after the shot was also negligible. But the temperature of the sample reached very quickly the equilibrium temperature of the heater. So practically the sample was "quenched-up" to temperature regions where the crystallization takes place *(Fig. 1)*. With this method it was possible to pick up resistance decrement curves of rather fast crystallization due to isothermal annealings. Platinum wire contacts for the conventional four probes D.C. resistance measurement were mounted on the inner ceramic surface of the splitted heater.

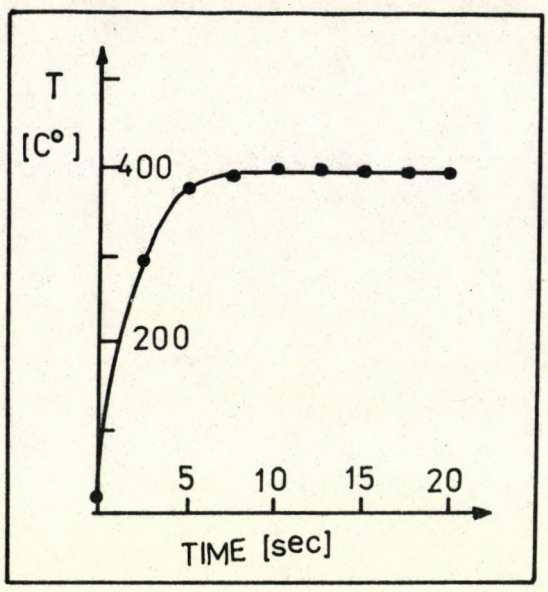


*Fig. 1. The temperature increase of the sample shot into the heater*

## RESULTS, DISCUSSION

Samples with 12.0 a/o and 9.2 a/o phosphorus content showed one or two stages of crystallization, at constant rate heating. At high rate (~ 40 K/min) the resistance decreases smoothly, while at lower rates of heating ( ~ dT/dt < 10 K/min) the resistance change showed two stages *(Fig. 2)*. The same character can be observed using isothermal annealings. In this case at high temperatures (T ~ 600 K) the resistance decrement curve is smooth, while at lower temperatures (T ~ 550 K) there is a definite break in the time dependence of the resistance decrease *(Fig. 3)*. At the break point the samples became already very brittle. It was impossible to take them off without fracture.

According to S.T.Pai et al. [1] amorphous NiP films upon heat treatment transform to f.c.c. Ni and tetragonal $Ni_3P$ phases. But Cziraki et al. [2] showed that these two phases are only the final phases of crystallization. S.P.Pankratov [3] detected not less than six different phases around the end of the first stage. From these measurements it must be concluded that independently of the relatively simple picture of resistivity changes upon isothermal

heat treatment, the crystallization is a rather complicated multi-stage process. The activation energies belonging to the first or the second stage are averaged values for more than one process.

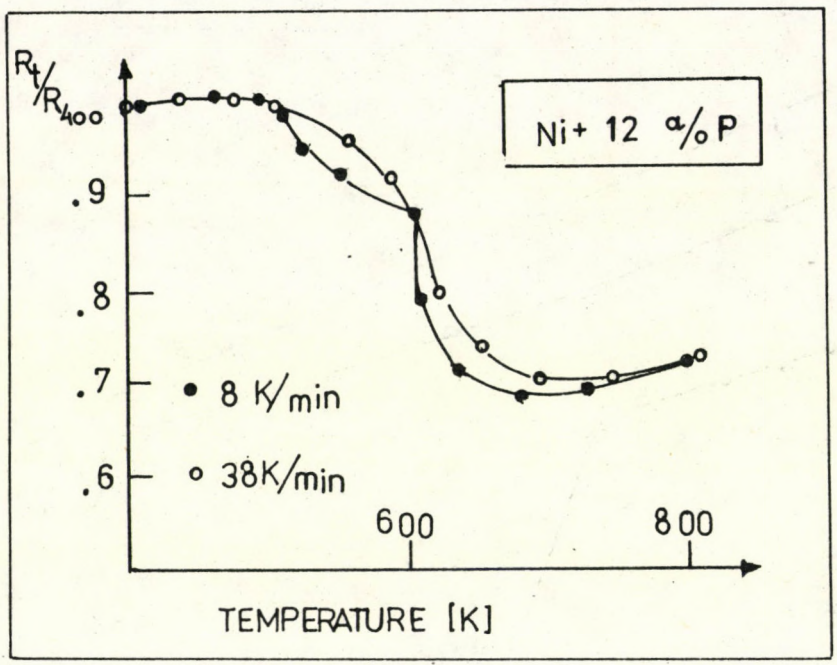


*Fig. 2. Resistance changes at different heating rates*

Time logarithms at 0.9 $R_t/R_o$ values were used for the determination of activation energy of the first stage. $R_t$ denotes the resistance value at moment t of the isothermal annealing. $R_o$ is the value of the constant resistance in the incubation period. For the determination of the second stage activation energy, the samples were uniformly pre-annealed for 5 hours at 492 K. During this time the crystallization belonging to the first stage has completed. Then the temperature of the heater was increased - as quickly as it was allowed by its small thermal inertia - to higher temperatures where the second isothermal anneal started. $R'_o$ is the value of resistance at the beginning of the second anneal. $R'_o$ was determined from the temperature dependence of preannealed samples during the fast unheating. The activation energies were determined similarly as in the first stage.

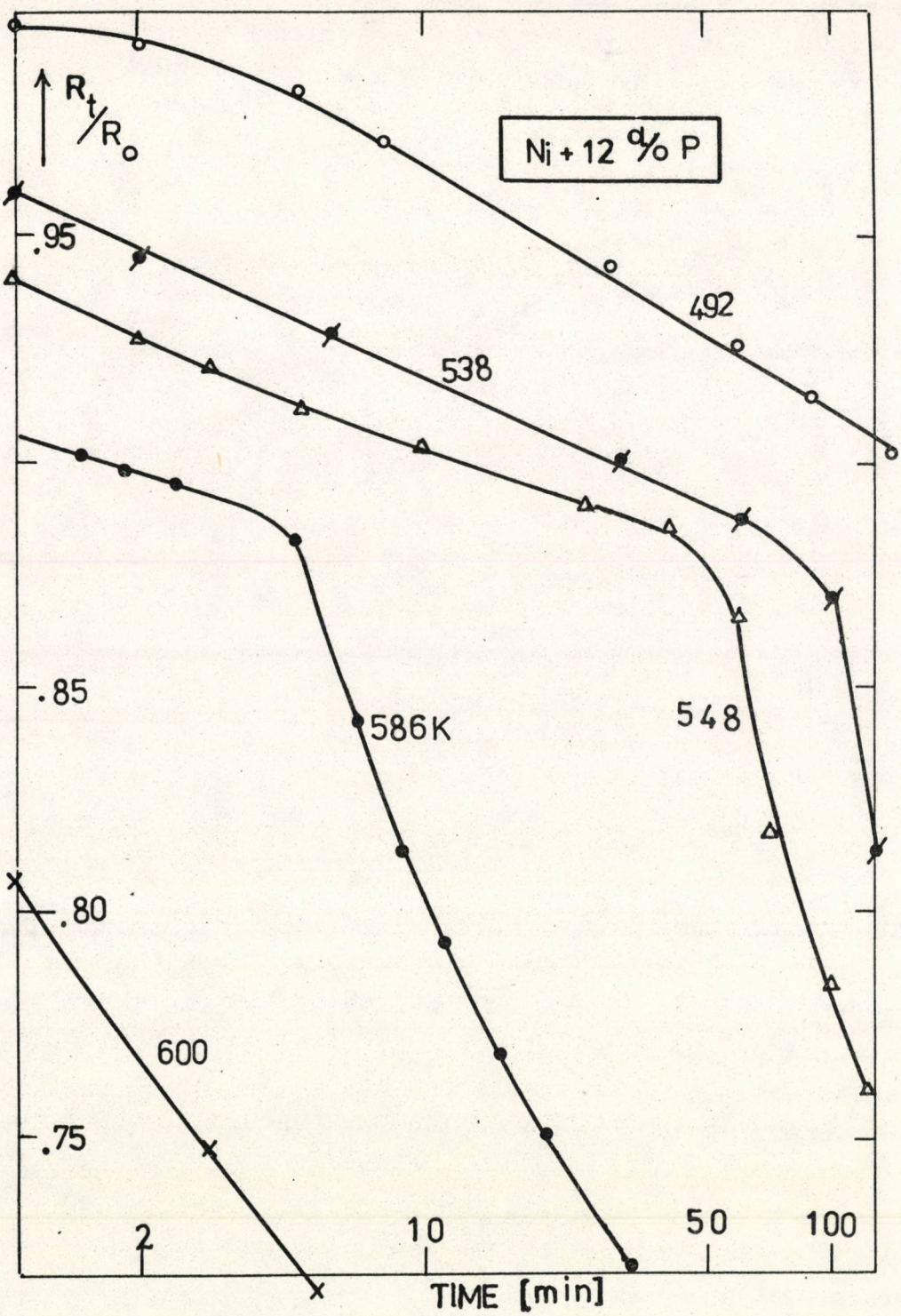


*Fig. 3. Time dependence of the resistance at different annealing temperatures*

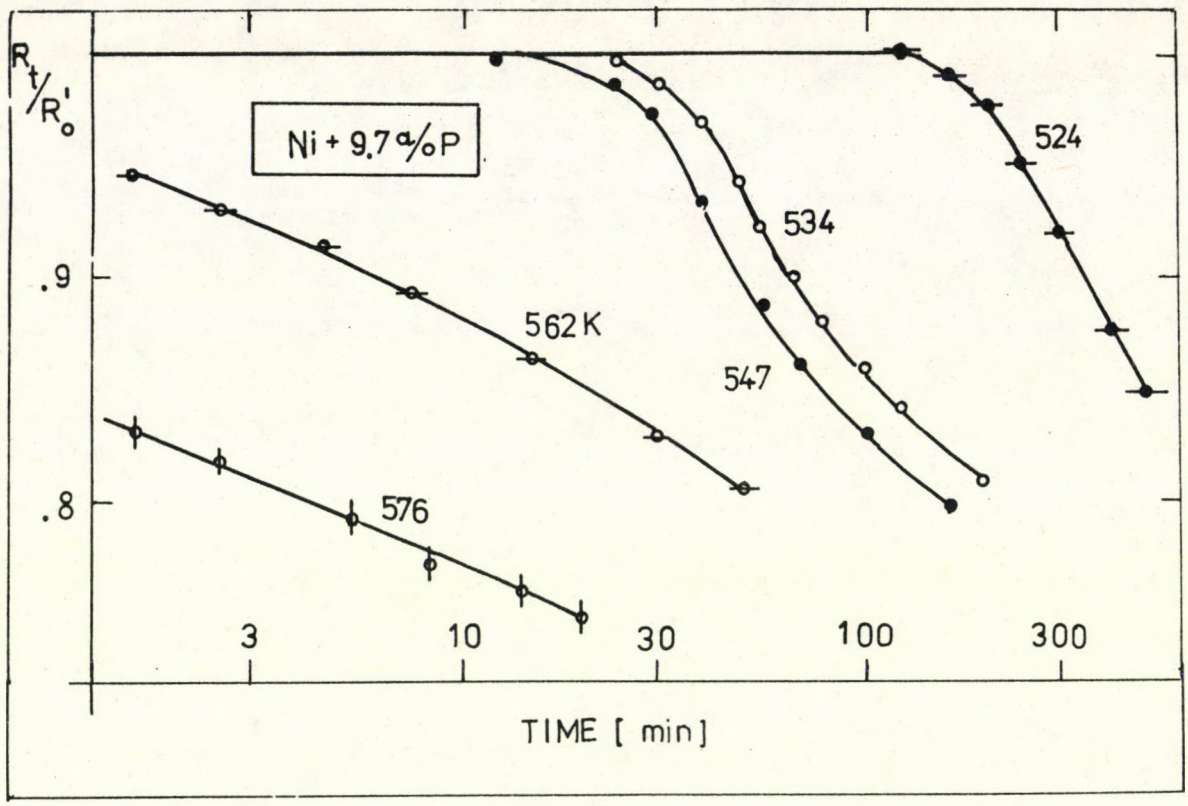


*Fig. 4. Time dependence of the resistance of preannealed samples at different temperatures*

For Ni + 9.7 a/o P alloy the activation energy of the first stage was: $E_1 = 0.5 \pm 0.1$ eV and for the second stage $E_2 = 2.5 \pm 0.2$ eV. The same energies for the Ni + 12.0 a/o P alloy are the following values: $E_1 = 1.1 \pm 0.2$ eV and $E_2 = 2.3 \pm 0.2$ eV. Because the final phases are the same for the two alloys, the activation energies of the second stage are approximately equal. But the activation energy of the first more complex process has significantly increased with the small change in the phosphorous content. Further measurements on alloys with higher phosphorus concentration are going on.

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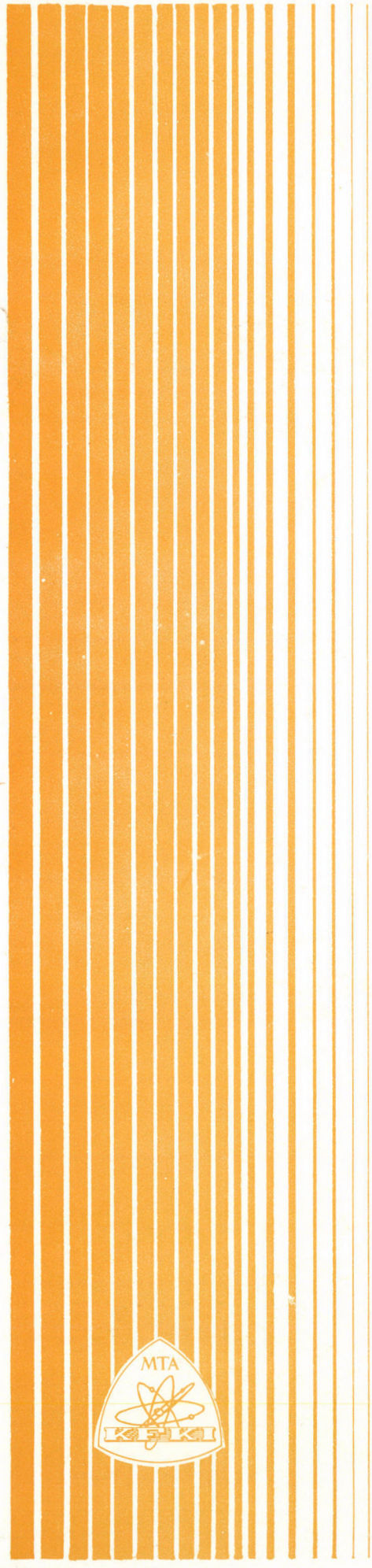
REFERENCES

[1] S.T.Pai, J.P.Marton and J.D.Brown, J.Appl.Phys 43 (1972) 282

[2] Á.Cziráki, B.Fogarassy, I.Bakonyi, K.Tompa, T.Bagi and Z.Hegedüs, Presented at the Fourth International Conference on Liquid and Amorphous Metals, Grenoble, 1980

[3] S.P.Pankratov, (private communication)

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