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To cite this version:
E. Bonetti, E. Lanzoni, G. Paparo. ANELASTIC BEHAVIOUR OF Ni100- xPx AMORPHOUS ELECTROLESS DEPOSITED ALLOYS DURING STRUCTURAL RELAXATION AND CRYSTALLIZATION. Journal de Physique Colloques, 1985, 46 (C10), pp.C10-481-C10-484. <10.1051/jphyscol:198510107>. <jpa-00225307>

HAL Id: jpa-00225307
https://hal.archives-ouvertes.fr/jpa-00225307
Submitted on 1 Jan 1985

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ANNELASTIC BEHAVIOUR OF Ni$_{100-x}$P AMORPHOUS ELECTROLESS DEPOSITED ALLOYS DURING STRUCTURAL RELAXATION AND CRYSTALLIZATION

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Resumé - Le comportement anélastique d'une série d'alliages Ni-P obtenus par voie Chimique a été étudié pendant la relaxation structurale et la cristallisation.

Abstract - The anelastic behaviour of a series of Ni-P alloys obtained by electroless plating, during structural relaxation and crystallization, has been investigated as a function of the metalloid content.

I - INTRODUCTION

Detailed studies have recently been made on the mechanical and transport properties /1-3/ of amorphous Ni-P alloys, as well as on their anelastic behaviour /4/. In particular, in the electroless deposited alloys the metalloid content can be varied on a wide range, making thus possible to obtain a series of alloys ranging from amorphous to microcrystalline only as a function of bath composition /2/.

On the other hand it is well known that the mechanical behaviour of these alloys is strongly influenced by the metalloid concentration which, during structural relaxation, may determine or not embrittlement effects /5/. Moreover, the metalloid content can strongly influence the mechanisms and kinetics of amorphous to crystalline transition /2,6/.

Aim of this work is to extend previous internal friction and dynamic modulus measurements to Ni-P alloys covering a wider P content range, to study the influence of the chemical composition on the anelastic parameters during structural relaxation and crystallization.

II - EXPERIMENTAL

The measurements were carried out on Ni-P sheets, 3 to 5 cm long with a(0.03x0.5) cm$^2$ cross section, obtained by electroless deposition from a chloride glycollate bath on a stainless steel substrate.

Specimens with different phosphor contents X$_p$ were obtained by stepwise varying the pH content in the bath (Table I).

<table>
<thead>
<tr>
<th>pH</th>
<th>3.0</th>
<th>3.5</th>
<th>4.0</th>
<th>4.25</th>
<th>4.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>X$_p$(at%)</td>
<td>22</td>
<td>20</td>
<td>18</td>
<td>16</td>
<td>14</td>
</tr>
</tbody>
</table>

Internal friction Q$^{-1}$ and dynamic Young modulus M$_d$ were measured from the flexural vibration decay of specimens cantilever mounted in the frequency range 20-2000 Hz under a 10$^{-2}$ Pa vaccum. Strain amplitude was of the order of 10$^{-6}$.

All the Q$^{-1}$ and M$_d$ measurements vs. T were performed at a constant heating rate of 2 deg/min.

Some measurements were made in isothermal conditions: typical times for thermal...
stabilization, at the measurement temperature, were of the order of 3 - 4 mins.

III - RESULTS AND DISCUSSION

Figure 1a-b) show characteristic $Q^{-1}(T)$ and $M_d(T)$ trends for different $X_p$ values. The curves refer to temperatures $T > 500$ K above which, in measurements carried out at a constant heating rate, as in the present case, irreversible variations of the anelastic parameters are observed: these are brought into evidence by $Q^{-1}$ maxima and $M_d$ steps.

Two distinct processes are noticed for $X_p < 20$ at%.

As shown in Fig. 1 the first dynamic modulus increase occurs in parallel with that of internal friction leading to the first $Q^{-1}$ maximum. The behaviour can be attributed to a short range order increase or to some type of atomic clustering in the amorphous matrix. The temperature of the maximum shifts to higher values with increasing $X_p$, whereas the height of the maximum decreases in the same way.

The X-ray diffraction patterns of the alloys quenched after heating up to the first $Q^{-1}$ maximum /7/ do not differ substantially from those of the same alloys as prepared, apart from a definite sharpening of the (111) Ni reflex on an otherwise diffused background. Our TEM observations (Fig. 2a-b) show that a clear black-white contrast which could be correlated to a local enrichment in the amorphous matrix of the metal atoms /7,8/, appears in the alloys with $X_p \leq 18$ at%, quenched after a run up to the temperature of the first $Q^{-1}$ maxima.

Moreover, the $Q^{-1}$ and $M_d$ isotherms performed in the same $T$ range (Fig. 3) are in agreement with the isochronal spectra of Fig. 1; in particular the $Q^{-1}(t)$ curve shows a maximum which may be correlated to the appearance of black-white zones in the TEM micrographs and with the sharpening of the (111) Ni reflex in XRD.

Ni precipitation around 600 K has also been postulated by other authors to explain resistivity changes in Ni-P alloys of the same nominal composition /9/.

The large $Q^{-1}$ and $M_d$ variation observed in the 600-700 K range are connected with the alloy crystallization, in agreement with DSC and XRD measurements/6,8/. At the crystallization temperature the $Q^{-1}$ behaviour is characterized by a strong maximum followed by a drop, as noticed in general during structural irreversible transitions, diffusion controlled /10/ and the dynamic modulus increases up to 30%.

The $M_d$ minimum preceding the fast increase at crystallization may correspond to the softening of the phonon mode related to the co-operative diffusion processes associated to crystallization.

The temperature of the maximum depends on the heating rate but not on the measurement frequency. In Fig. 4 the temperatures corresponding to the first and second $Q^{-1}$ maximum $T_1$, $T_2$ are plotted as a function of $X_p$ for a constant heating rate of 2K/min. This plot compares well with the results of the DSC analyses in Fe-B alloys /11/. A two branch plot of $T_{\text{cryst}}$ vs. $X_p$ was observed also in that case: the first one attributed to Fe precipitation (primary crystallization), the second starting from $X_p \sim 15$ at% due to an eutectic type crystallization.

XRD observations on specimens quenched at the onset of the second $Q^{-1}$ maximum /6/ show the appearance of the Ni$_3$P reflection. Thus the amorphous to crystalline transition of the Ni-P electroless alloys with P content up to 22 at% occurs in one or more stages depending on the composition. The stage $T_2$ observed in all the alloys (Fig. 4) corresponds to Ni$_3$P crystallization. This stage, in the hypo-eutectic alloys ($X_p \leq 18$ at %) is preceded by a second one $T_1$ corresponding to the appearance of Ni microcrystals.

Finally we consider the reversible part of the $Q^{-1}(T)$ and $M_d(T)$ spectra for $T \leq 500$K. Typical trends for a Ni$_{34}$P$_{16}$ alloy are shown in Fig. 5. Here, as previously noticed in NiB and Ni-P alloys of near eutectic composition /4,12/, a relaxation peak is sometimes present. Even though in this case texts have been carried out on a wide P content range no significant further insight into the very nature of this peak has been obtained. In particular, a systematic dependence of the peak parameters (height and temperature) on $X_p$ has not been noticed even if in some cases ($X_p \sim 20$ at%) a higher peak temperature is observed. Moreover, these peaks anneal out after a run up
to Q-1 max. temperature, i.e. to the formation of the first Ni clusters, whereas heating at lower temperatures leads to a relaxation strength increase (Fig. 5). Further work is in progress to clarify the origin of these peaks.

IV - CONCLUSIONS
The Q-1 and Md measurements confirm that the amorphous to crystalline transformation of Ni-P alloys in the Xp range 14 to 22 at% occurs in one or two stages. The single stage process is limited to Xp values near to the eutectic. In the hypo-eutectic alloys the hypothesis of a separation in the amorphous phase with Ni rich cluster and subsequent microcrystal formation is in agreement with Q-1 and TEM observations. An anelastic relaxation peak has been observed before the onset of the irreversible transformation whose nature has not yet been clarified.

V - ACKNOWLEDGEMENTS
This work was carried out with M.P.I. funds. The authors wish to thank Miss. I. Zucchi and Mr. R. Berti for their collaboration.

VI - REFERENCES
/7/ Bonetti, E., Lanzoni, E. and Poli, G., to be published.
Fig. 2
TEM images of Ni86P14 as prepared (a) and after heating at 2K/min up to 510 K and quenching (b). X 40,000

Fig. 3
Q-1(t) and M_d(t) spectra during annealing at 490 K for a Ni84P16 alloy. Frequency ~ 3x10^2 Hz. M_0: modulus at the beginning of the isotherm.

Fig. 4
Shift of the temperature of the Q^-1 maxima vs X_p (see Fig. 1).

Fig. 5
Low temperature cycling effect on the Q^-1(T) M_d(T) spectra of a Ni84P16 alloy. First run (--), second run (---).