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Surfactant effects on the electrical and thermal properties of $\text{Ni}_{76}\text{P}_{24}$ metallic glass alloy

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Abstract. Samples of $\text{Ni}_{76}\text{P}_{24}$ metallic glass alloy were prepared by the electroplating technique. Two types of surfactant material, namely triton-X 100 (non-ionic) and sodium lauryl sulphate (anionic) were used, each of which was added—at different concentrations—to the preparation bath. The x-ray diffractograms of the samples indicate that the addition of surfactants has changed the disorder in the system. The electrical resistivity, measured by the conventional four-probe technique in a temperature range from 300 K down to 18 K, is reduced. Also the temperature coefficient of resistivity is changed to a positive value instead of remaining nearly zero. Moreover, the thermal expansion coefficient decreases as the concentration of surfactant increases. The results of all the measurements indicate that the anionic surfactant has more influence on the enhancement of the crystalline behaviour of the system than the non-ionic one does.

1. Introduction

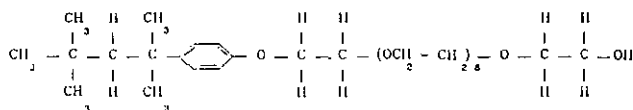
Previous work on Ni–P metallic glasses has shown that at concentrations below 17 at.% P the material is ferromagnetic, while above this concentration it is non-magnetic (Pan and Turnbull 1973). The electrical resistivity of most metallic glasses and Ni–P as well has exhibited a low temperature minimum which depends on the alloy composition (Ziman 1961, Kondo 1967, Tsuei and Hasegawa 1969, Mott 1972, Nagel and Tauc 1975, Cochran *et al* 1975, Imry 1980). By introducing more disorder in the system it is expected to change the behaviour of the resistivity as well as the low temperature minimum. The temperature coefficient of resistivity (TCR) for Ni–P is found to be negative above 23 at.% P and positive below that value (Cote and Meisel 1979). However, Grest and Nagel (1979) showed that the crystalline Ni–P alloys have positive TCR values. The Hall-effect data of this system indicate that the Hall coefficient changes sign from negative to positive at about 23 at.% P (McKnight *et al* 1987).

The study of the thermal expansion of an amorphous system, which depends on temperature via short-range order (Egami 1978), leads to a good understanding of the dynamics of relaxation in these compounds. There are two contributions to the thermal expansion, the first is due to the anharmonicity of the atomic vibrations, while the second originates from the relaxation movements of the atoms. The latter is limited to a relatively high temperature range, which is related to the collective motions of groups of atoms (Fukamichi *et al* 1970). Such processes lead to the crystallization of the amorphous system.

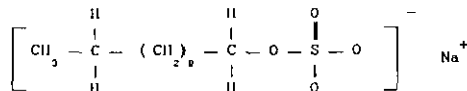
Generally, metals and their alloys are deposited in a rough form when the electrolysis is carried out. Therefore, some organic substances, known as surface active substances or surfactants (Ahmed and Zourab 1988), are added during the electroplating process to improve the quality of the electrodeposits. Although the exact mechanism by which the surfactants improve the quality of the electrodeposits is not known, there are indications that adsorption of these substances on the electrode is involved. Adsorption of these organic compounds on the cathode surface may block a part of the active electrode area and therefore reduces the rate of deposition.

In this work, $\text{Ni}_{76}\text{P}_{24}$ metallic glass alloy, which has a TCR of nearly zero, was chosen to study the behaviour of the amorphous structure, electrical resistivity and thermal expansion after adding surfactant materials to the preparation bath. The surfactants used in this study are triton-X 100 (T-X 100) and sodium loruyil sulphate (SLS), which have the following chemical structures:

(i) Non-ionic T-X 100



(ii) Anionic SLS



2. Experimental details

2.1. Preparation of samples

The electroplating technique was used to prepare samples of $\text{Ni}_{76}\text{P}_{24}$ metallic glass alloy. The composition of the bath used was described by Cargill (1970). The samples were electroplated onto carefully polished copper substrates of about 0.3 mm thickness and plating windows of $1.5 \times 0.3 \text{ cm}^2$ and $2.2 \times 0.3 \text{ cm}^2$. The bath's temperature was retained at about 70°C and the plating current was kept constant at 100 mA cm^2 . During plating, the bath solution was vigorously stirred to prevent gas bubbles from adhering to the cathode.

In addition, two sets of five samples of $\text{Ni}_{76}\text{P}_{24}$ were prepared from baths containing one of each of the surfactant compounds T-X 100 and SLS at different concentrations. These compounds were completely dissolved in the solution of the baths before electroplating was started. After the plating was completed, the substrates were removed by using a chromic acid solution. The resulting samples were smooth thin rectangular plates of about 0.2 mm thickness.

2.2. Measurements

X-ray diffraction scans were taken for each sample using an x-ray diffractometer (Shimadzu XD-3) with a copper target tube and nickel filter, $Cu K_{\alpha}$ radiation ($\lambda = 1.54051 \text{ \AA}$). The tube's parameters were kept fixed during the measurements to make sure that all scans were carried out at the same conditions.

The electrical resistivity of the samples was measured by the conventional four-probe technique in a temperature range from 300 K down to 18 K. These temperatures were achieved by means of a closed-cycle cryogenic refrigeration system model Displex CSA-202. The temperature was measured using a Kp-Au 0.07 at.%Fe thermocouple which was calibrated against a silicon diode thermometer.

The samples ($1.5 \times 0.3 \times 0.02 \text{ cm}^3$) were glued to the sample support block with a thin piece of lens paper soaked with GE 7031 varnish between the two, to electrically isolate the sample but retain good thermal contact with the support block. A current source (Keithley 225) was used to provide a constant current of 10 mA. The voltage drop across the samples was measured using a nanovoltmeter model Keithley 181.

A home-made Michelson interferometer set-up was used to detect the length variations of the samples due to a small temperature change. The samples used for thermal expansion measurements were typically 2.2 cm long, 3 mm wide and 0.2 mm thick. A He-Ne laser of wavelength 6328 \AA was used as the interferometer source. One end of the sample was attached to a fixed holder, while the other end was fixed perpendicularly to the back of the movable mirror of the interferometer. The other mirror was placed on a stationary support. An iron core surrounded by two coils of Ni-Cr heater wire was used to heat the sample. The temperature of the sample was measured by using a Cu-Fe thermocouple which was located at a distance of about 1 mm from the sample. The interference fringes were projected on a large screen 3 m from the interferometer. A schematic diagram of the set-up of this apparatus is shown in figure 1.

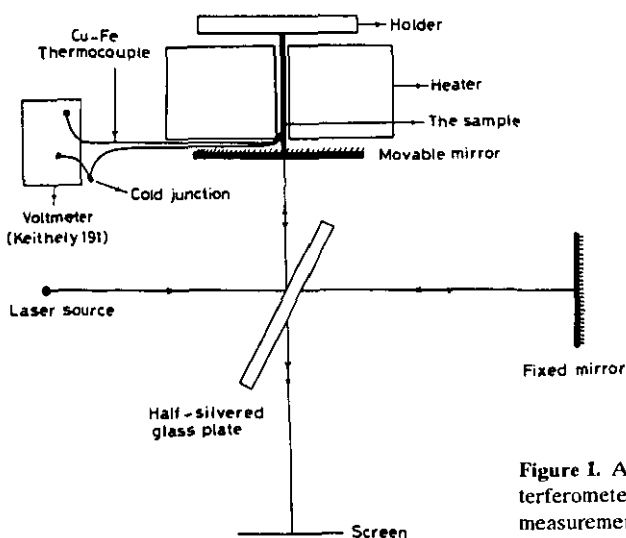


Figure 1. A schematic diagram of the Michelson interferometer set-up used for the thermal expansion measurement.

By proper placement of the heater and the thermocouple, the temperature of the system was controlled and kept uniform. During the experiment the heating rate of

the sample was about $1^{\circ}\text{C min}^{-1}$. By increasing the temperature, the sample expands and pushes the movable mirror. Therefore one can count the change in the number of fringes n , and then the expansion ($\Delta L = n\lambda/2$) can be determined. Thus, the thermal expansion coefficient (α) can be deduced from the relation

$$\Delta L = \alpha L_0 \Delta T$$

where L_0 is the original sample length and ΔT the temperature change corresponding to ΔL expansion. The apparatus was tested and calibrated using standard materials such as copper and steel.

3. Results and discussion

3.1. X-ray diffraction data

In figure 2 the plot labelled 0 M is the x-ray scan of an $\text{Ni}_{76}\text{P}_{24}$ sample prepared from a pure bath. The diffractogram exhibits a broad peak which characterizes the amorphous state. The plots labelled 1.2×10^{-4} M through 12.4×10^{-4} M are the scans of samples prepared from baths containing surfactant T-X 100 dissolved in their solution at different concentrations. In the scans 1.2×10^{-4} M through 12.4×10^{-4} M (figure 2), although the broad peaks which characterize the amorphous state still exist, there are signs of new features which indicate that there is a change in the disorder of the system.

Figure 3 shows the x-ray diffraction patterns of samples prepared from baths containing the anionic surfactant SLS at different concentrations. The scans did not exhibit dramatic changes from those of figure 2 (for samples prepared with neutral surfactant). Therefore, the chemical interaction between the surfactant and the constituents of the baths is excluded as a possible cause of the structural changes in the system.

The adhesion and adsorption of the surfactant molecules to the cathode are expected to control the rate of deposition of the alloy, which is considered as a possible cause of the structural changes in the system. A fast rate of deposition would not give enough time for the atoms to relax in their lower energy states, whereas a slow rate of deposition would allow a longer period of time for the deposited atoms to relax and thus a more ordered phase would be formed in this case. The small and narrow peaks which appear in the x-ray diffractograms indicate that the system contains clusters of microcrystals and thus one would expect the system to possess some characteristics of a crystalline phase. Moreover, one would observe on the scans in figures 2 and 3 that the broad peaks appear at lower diffraction angles (θ) after adding the surfactants. This indicates that the local structure in the amorphous phase is changed, i.e. a different short-range order exists. The presence of small clusters in the system is expected to increase the interplanar spacing (d) between the scattering centres and therefore the value of θ becomes lower ($1.22\lambda = 2d \sin \theta$).

3.2. Resistivity data

Resistivity ratios (normalized to the room temperature value) for the samples as a function of temperature are shown in figures 4 and 5. The data of an $\text{Ni}_{76}\text{P}_{24}$ sample prepared without surfactant is in good agreement with that reported by Cote (1976).

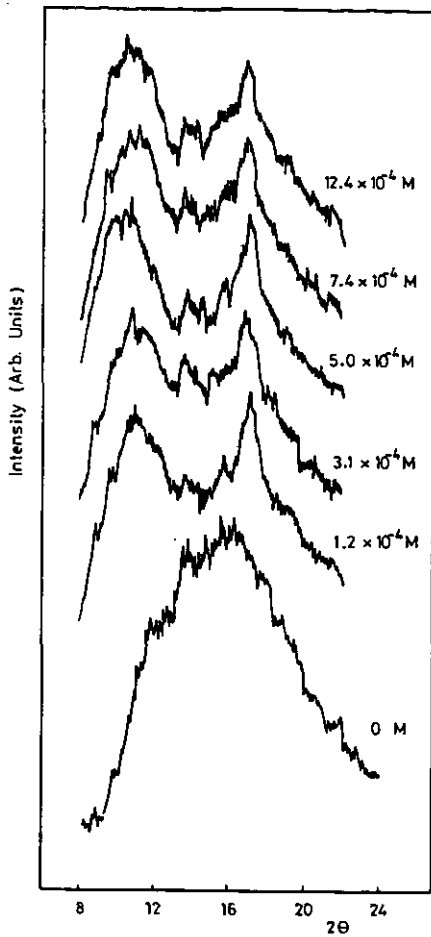


Figure 2. X-ray scans of $Ni_{76}P_{24}$ prepared without and with different surfactant T-X 100 concentrations.

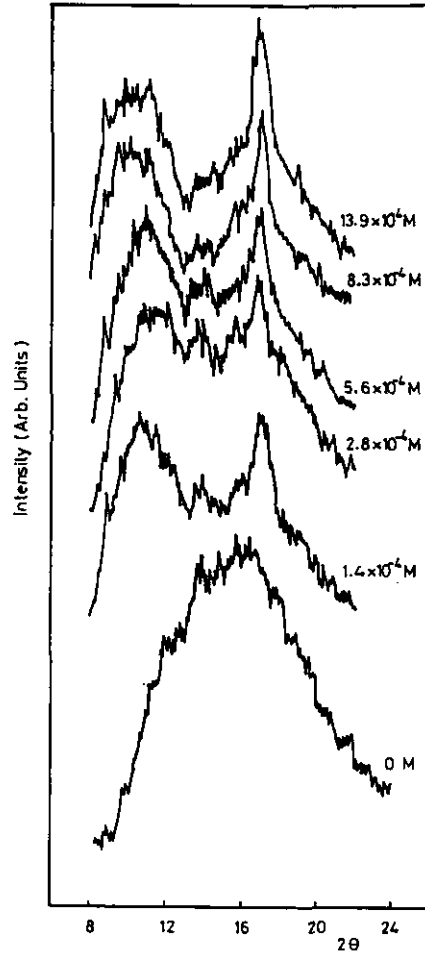


Figure 3. X-ray scans of $Ni_{76}P_{24}$ prepared without and with different surfactant SLS concentrations.

Figures 4 and 5 show that the addition of the surfactants to the preparation bath has reduced the resistivity ratios. It is well known that the crystalline phase has a relatively small resistivity as compared with that of the amorphous phase. The lack of periodicity in amorphous structure introduces fictitious scattering centres which enhance the resistivity of the system. Therefore the decrease of the resistivity ratios of $Ni_{76}P_{24}$ samples prepared after adding surfactant materials in the plating bath, as shown in figures 4 and 5, is caused by the existence of a crystalline phase.

Moreover, figures 4 and 5 show that the addition of the surfactants has changed the TCR to a positive value instead of remaining nearly zero as for the $Ni_{76}P_{24}$ sample prepared without surfactant. The TCR value obtained is proportional to the concentration of surfactant, the proportionality factor depending highly on the type of surfactant, and in the case of SLS is higher than that in the case of T-X 100. This means that the crystallinity induced in the SLS case is more than that induced in the T-X 100 case, which may be attributed to the different nature in their head SO_4^{2-}

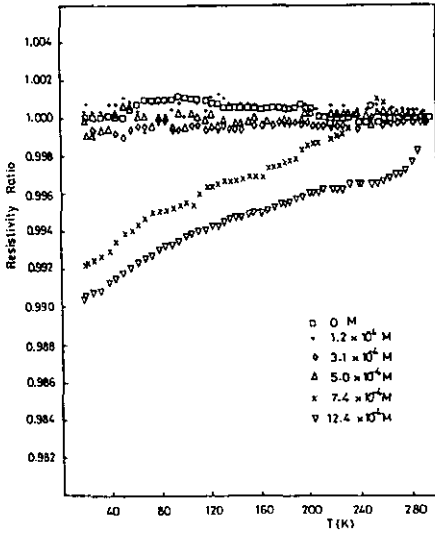


Figure 4. Resistivity ratio versus temperature for $\text{Ni}_{76}\text{P}_{24}$ without and with different surfactant T-X 100 concentrations.

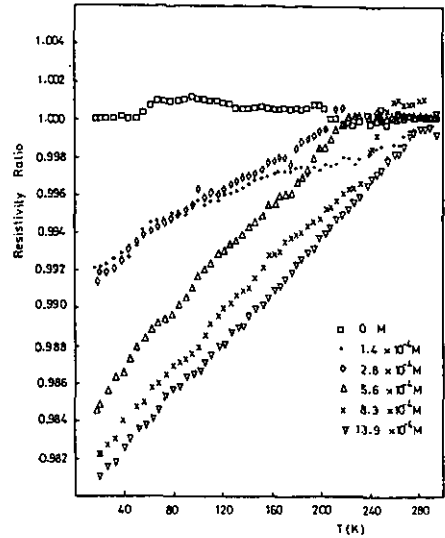


Figure 5. Resistivity ratio versus temperature for $\text{Ni}_{76}\text{P}_{24}$ without and with different surfactant SLS concentrations.

and OH groups, where the SO_4^{2-} group (SLS) has a larger steric hindrance than that of the OH group (T-X 100). These results are in agreement with those of Patrick *et al* (1988).

3.3. Thermal expansion data

Figure 6 shows the relative elongation of $\text{Ni}_{76}\text{P}_{24}$ samples prepared without and with different concentrations of T-X 100 as a function of temperature difference. To avoid a deviation of the data from linearity and to be well below the crystallization point, the temperature was kept below 100°C . Therefore the expansion of the samples is mainly caused by the anharmonicity of the thermal vibration. This explains the positive slopes of all graphs in the temperature range of these measurements. The thermal expansion coefficient is determined for each T-X 100 concentration by calculating the slopes of the straight lines in figure 6. Figure 7 represents the thermal expansion coefficients α versus T-X 100 concentrations. As shown in this figure, the value of α decreases with increasing concentration of T-X 100. These results are consistent with the obtained x-ray and resistivity data, which indicate enhanced crystalline behaviour with increasing T-X 100 concentration.

The data reported by Freeman and Shimizu (1979) indicate that nickel-based amorphous alloys exhibit a drastic shrinkage at the crystallization temperature, and the thermal expansion coefficient of their crystalline phase is less than that of the amorphous one. This due to the enhancement of quasi-elastic forces in the nickel matrix and the decrease, with crystallization, in the anharmonicity coefficient which leads to a decrease of the average distance between the atoms.

Figure 8 shows the relative elongation as a function of temperature difference for $\text{Ni}_{76}\text{P}_{24}$ samples prepared with and without SLS. Figure 9, meanwhile, represents the thermal expansion coefficients for the same samples as a function of SLS concentration. These plots show the same behaviour as in the case of T-X 100. The thermal

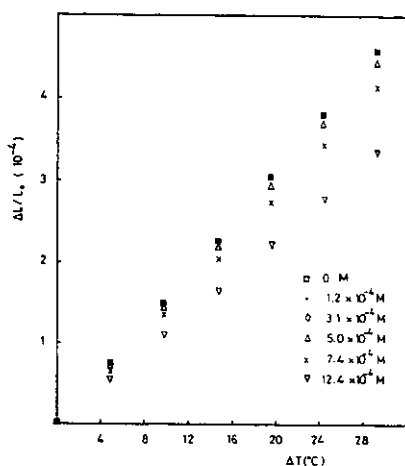


Figure 6. Relative elongation versus the temperature differences for $Ni_{76}P_{24}$ without and with different surfactant T-X 100 concentrations.

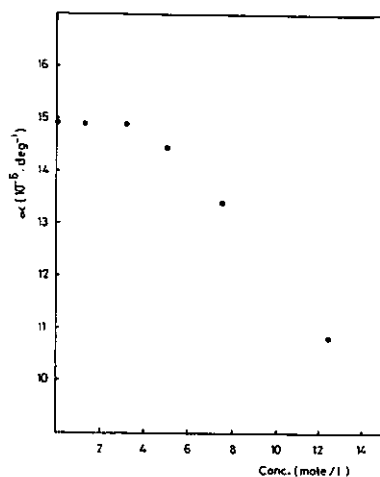


Figure 7. Thermal expansion coefficient α versus T-X 100 concentration.

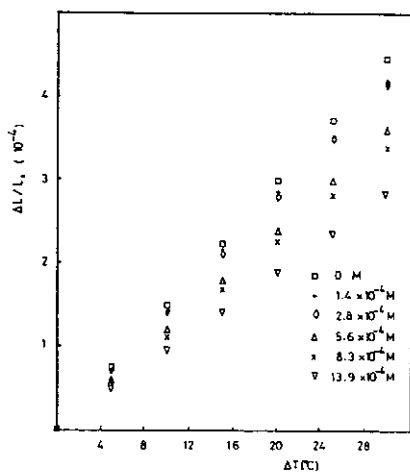


Figure 8. Relative elongation versus the temperature differences for $Ni_{76}P_{24}$ without and with different surfactant SLS concentrations.

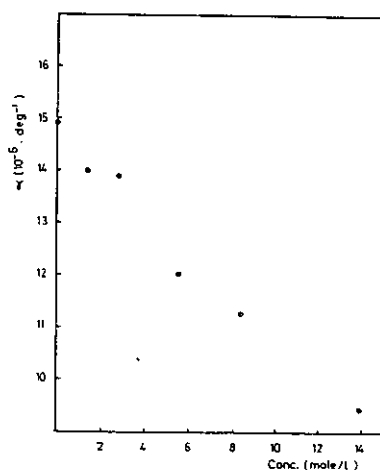


Figure 9. Thermal expansion coefficient α versus SLS concentration.

expansion coefficients of all samples are listed in table 1. The coefficients α are close to those reported for other metallic glasses ($8-14 \times 10^{-6} \text{ deg}^{-1}$, see Fukamichi *et al* 1978). The difference between the effect of adding SLS or T-X 100 on the thermal expansion coefficient is that the former has more influence than the latter, i.e. SLS induces more crystallinity in the system than T-X 100. Accordingly, the suggestion of microcrystal formation is a reasonable argument for understanding the decrease in the thermal expansion coefficient with increasing surfactant concentration.

Table 1. Thermal expansion coefficient α for $\text{Ni}_{76}\text{P}_{24}$ samples prepared without and with different surfactant concentrations.

T-X 100 concentration (10^{-4} mole l^{-1})	α (10^{-6} deg $^{-1}$)	SLS concentration (10^{-4} mole l^{-1})	α (10^{-6} deg $^{-1}$)
0.0	14.9	0.0	14.9
1.2	14.9	1.4	14.0
3.1	14.9	2.8	13.9
5.0	14.5	5.6	12.1
7.4	13.4	8.3	11.3
12.4	10.8	13.9	9.4

4. Conclusion

In conclusion, all the results of the x-ray diffraction, electrical resistivity and thermal expansion measurements for $\text{Ni}_{76}\text{P}_{24}$ metallic glass alloy are consistent and indicate that the system has suffered structural changes which are more pronounced for samples prepared in the presence of the anionic surfactant SLS than in the case of the non-ionic surfactant T-X 100.

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