JOURNAL OF MATERIALS SCIENCE 20 (1985) 3305 – 3310

A comparison of conductive and crystallographic effects of the phase transition in electrochemical nickel–boron layers

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Experimental data related to the variations with temperature in the film resistivity of amorphous nickel–boron layers (electrochemically deposited) and its temperature coefficient are used for identifying the temperature for the phase transition. Suggestions are presented for interpreting the observed shifts in the resistivity and in the product of resistivity and its temperature coefficient.

1. Introduction

Previous theoretical studies [1] related to the theoretical expression of the product of the metal resistivity, ϱ_f, with its temperature coefficient (t.c.r.), β_f, have shown that this quantity takes the same value as the product of the bulk resistivity, ϱ_0, with its t.c.r., β_0, provided that the film thickness d is larger than 0.1 λ_0, where λ_0 is the electron mean free path in the bulk material. In the case of background, grain-boundary and external surface scatterings the following equation then holds:

$$\beta_f \varrho_f = \beta_0 \varrho_0 \qquad d\lambda_0^{-1} > 0.1 \tag{1}$$

Therefore, in the case where the composition of the conducting material is not modified the product $\beta_f \varrho_f$ remains constant; it then may be used for the characterization of the deposited layer.

Equation 1 has already been used for studying the variations in the Hall coefficient of thin metal films due to impurities [2], and its validity has been confirmed by the experiments of several workers [1]. Since the structure of amorphous layers prepared by a chemical [3–5] or an electrochemical [6–8] procedure exhibits a satisfactory macroscopic homogeneity [9], the extension of Equation 1 to such amorphous layers may be examined. Since the transitions from amorphous to crystalline state of nickel–boron layers have been studied separately by crystallographic procedures [8] we attempt in this paper to check the capability of conduction measurements for analysing the processes of the phase transition.

2. Experimental procedure

The amorphous layers are deposited by using an electrochemical procedure [8] (Table I). The main interest in this procedure is to avoid the use of catalytic components in the bath, whereas these are present in chemical procedures [3–5]; moreover it seems that thick and large homogeneous amorphous layers can be obtained easily [9].

The deposited layers consist of alloys of nickel and boron; the range of the allowed atomic percentages of boron in the deposited layer is more extended than in the case of the chemical procedure, being from 5 to 32% instead of 29 to 34% [5, 8].

The resistivity of as-deposited layers was measured in a vacuum [8] during and after the ageing procedure, which induces the transition of amorphous state to crystallized state.

0022–2461/85 $03.00 + .12

TABLE I Deposition of amorphous layers

Bath composition	25 g $Ni(CH_3COO)_2$ $4H_2O$ 100 cm^3 28% NH_4OH340 cm^3 H_2O < 3.27 g KBH_4 dissolved in 50 cm^3 NH_4OH
Bath temperature	20° C
Constant current intensity	50 mA

The results reported here are related to layers which have been aged at a given temperature θ_{ag}; after the stabilization of electrical parameters at this temperature the values of the resistivity were measured at θ_{ag} and at 0° C, respectively $\varrho_{f\theta}$ and ϱ_{f0}. The average value of the resistivity $\overline{\varrho_f}$ defined by

$$\overline{\varrho_f} = \tfrac{1}{2}(\varrho_{f\theta} + \varrho_{f0}) \tag{2}$$

was used for calculating the average temperature coefficient of resistivity $\overline{\beta_f}$ defined by

$$\overline{\beta_f} = \frac{\varrho_{f\theta} - \varrho_{f0}}{\overline{\varrho_f}\theta_{ag}} \tag{3}$$

Simultaneously crystallographic studies were made [8] in order to check the progressive modifications in the crystallographic state of the layers. It has thus been observed that the amorphous state disappears at a temperature of about 250° C [8].

The thickness of the layer takes such values (more than 20 μm) that no size effect could be observed [1] in the resistivity and its temperature coefficient. We restrict our attention to the case of $Ni_{75}B_{25}$ and $Ni_{83}B_{17}$ layers 76 and 23 μm thick respectively.

3. Experimental results

The variations in the stabilized values [8] of the resistivities $\varrho_{f\theta}$, ϱ_{f0} and $\overline{\varrho_f}$ with ageing temperature θ_{ag} are shown in Figs. 1a and b. The variations in the average temperature coefficient of resistivity $\overline{\beta_f}$ with ageing temperature θ_{ag} are presented in Fig. 2.

Since the product of the resistivity with its temperature coefficient usually gives an insight on the composition of the conducting medium [1] the variations in $\overline{\beta_f}\varrho_{f0}$ with ageing temperature θ_{ag} have been drawn in Fig. 3. We consider separately the results related to $Ni_{83}B_{17}$ and $Ni_{75}B_{25}$ layers.

3.1. $Ni_{83}B_{17}$ films

The X-ray diffraction patterns obtained after the action of a given ageing temperature (acting as a parameter) are drawn in Fig. 4. The temperature threshold for the amorphous–crystalline transition (≈ 250° C) is in good agreement with the markedly correlated variations in the resistivity and its temperature coefficient, as shown above.

In the amorphous state, i.e. for $\theta_{ag} < 200°$ C, no evolution is observed in the X-ray diffraction pattern [8] whereas the resistivity slightly decreases (Fig. 1b); no clear conclusion can be derived from the variations in $\overline{\beta_f}$ because of the experimental inaccuracies (Fig. 2); however the variations in the product $\overline{\beta_f}\varrho_{f0}$ (Fig. 3) also sustain the assumption of a negligible evolution in the composition of the conducting material.

Since no modification is observed in the diffraction pattern we assume that the structural evolution that occurs only concerns the inside of the clusters which build the structure [4, 10, 11]; a similar phenomenon has been observed in amorphous layers of nickel–boron, chemically deposited [5, 12]. Experimental evidence has been presented [10] for an evolution within the clusters, as previously suggested [12, 13].

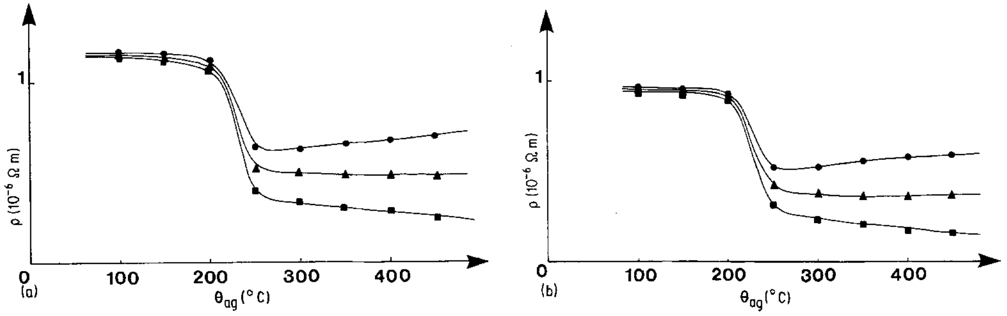

Figure 1 Variations in the stabilized values of the electrical resistivity of layers: ● ϱ_{f0} at θ_{ag} ° C; ■ ϱ_{f0} at 0° C; ▲ $\overline{\varrho_f}$ with average resistivity as defined by Equation 2. (a) $Ni_{75}B_{25}$, (b) $Ni_{83}B_{17}$.

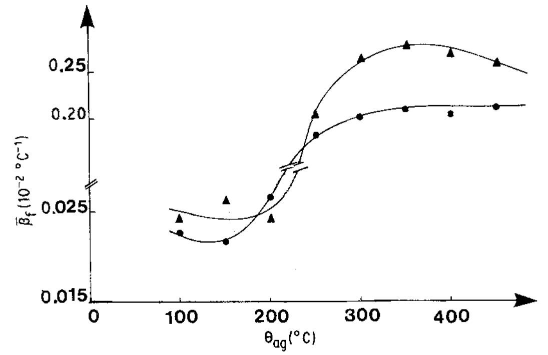

Figure 2 Variations in the stabilized average temperature coefficient of resistivity $\bar{\beta}_f$ (Equation 3) with ageing temperature θ_{ag}: ● $Ni_{75}B_{25}$, ▲ $Ni_{83}B_{17}$.

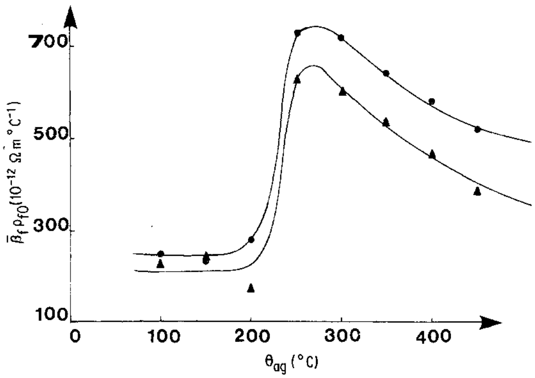

Figure 3 Variations in the product of the average t.c.r., $\bar{\beta}_f$, and the stabilized film resistivity at 0° C, ϱ_{f0}, with ageing temperature θ_{ag}: ● $Ni_{75}B_{25}$, ▲ $Ni_{83}B_{17}$.

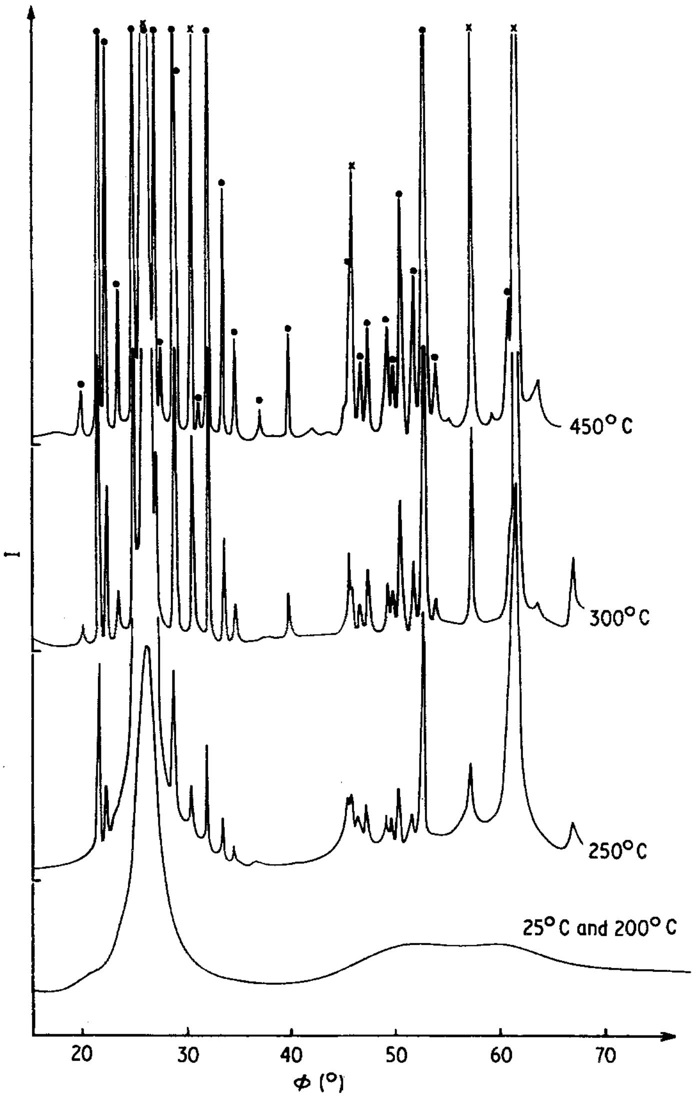

Figure 4 Variations in the X-ray diffraction pattern of $Ni_{83}B_{17}$ layers with ageing temperature: ● Ni_3B, x Ni.

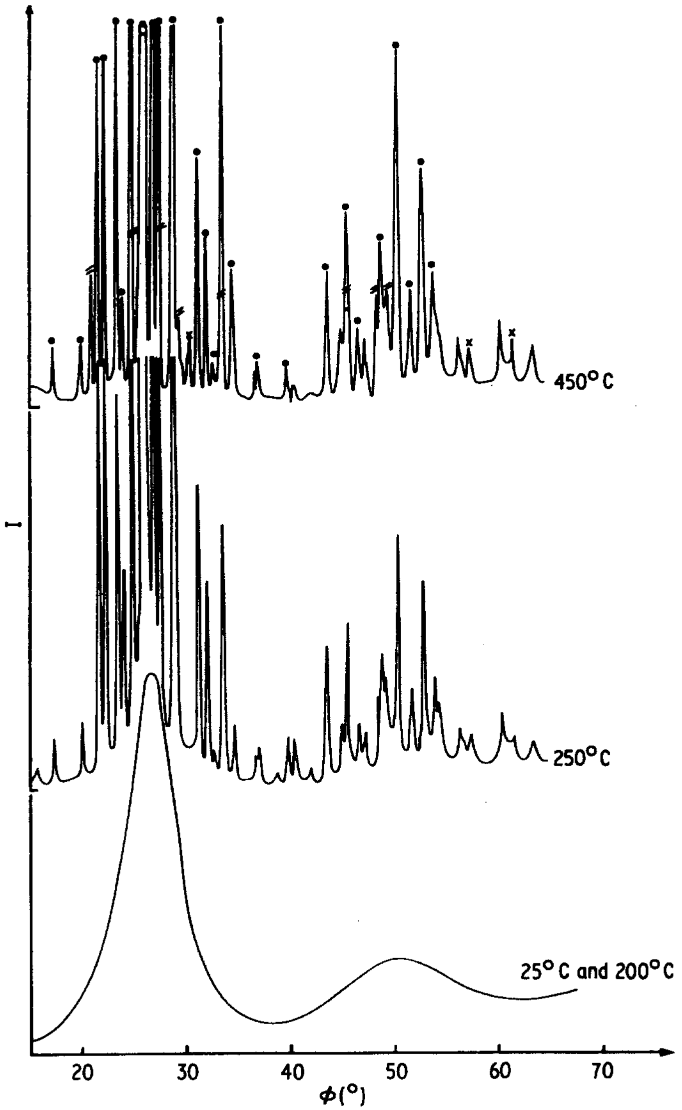

Figure 5 Variations in the X-ray diffraction pattern of $Ni_{75}B_{25}$ layers with ageing temperature: ● Ni_3B, x Ni, ≠ Ni_2B.

In the non-amorphous state, the diffraction patterns (Fig. 4) show an increasing importance of nickel and Ni_3P phases; therefore the decrease in ϱ_{f0} with θ_{ag} (Fig. 1b) can be attributed to new conducting paths in the material, whose composition varies with ageing temperature, as shown from Fig. 2. It may be noted that the evolution is not finished at the ageing temperature of 450° C; nevertheless, the limit value for $\overline{\beta_f}\varrho_{f0}$ cannot be accurately determined from experiments, because of the inaccuracies in the measurements of $\overline{\beta_f}$.

3.2. $Ni_{75}B_{25}$ layers

The X-ray diffraction patterns are not modified up to θ_{ag} = 200° C (Fig. 5) as in the case of $Ni_{83}B_{17}$ layers. In the amorphous state (i.e. for θ_{ag} < 200° C) the variations in the product $\varrho_{f0}\overline{\beta_f}$ are of slight magnitude, and it may be considered that the composition of the conducting material is not altered; this is in good agreement with the absence of the variations in the diffraction pattern, as in the case of $Ni_{83}B_{17}$ films.

The aspect of the pattern changes for $\theta_{ag} \geqslant$ 250° C; for 250 to 350° C only the presence of Ni_3B phase may be detected. Above 350° C Ni_2B and Ni phases exist [8], since rays (of low magnitude) appear in the diffraction pattern (Fig. 5); it seems that the nickel and Ni_2B phases play a minor role in the conduction process since the decrease of the resistivity is not clearly modified (as shown from Fig. 1a).

In the non-amorphous state, for θ_{ag} > 250° C, $\overline{\varrho_f}$ decreases while the Ni_3B rays of the diffraction

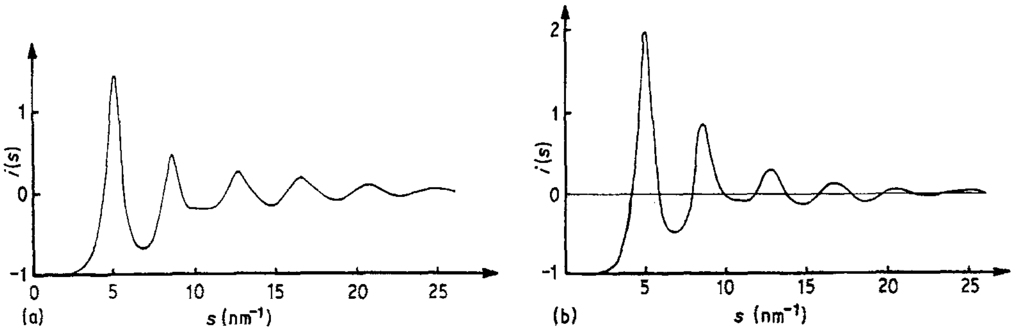

Figure 6 Interference functions of amorphous layers: (a) $Ni_{75}B_{25}$ layers, electrochemically deposited; (b) $Ni_{66}B_{34}$ layers chemically deposited.

pattern take higher magnitude; moreover extrapolating the variations in the product $\varrho_{f0}\overline{\beta_f}$ above 450° C gives a saturated value of about $5 \times 10^{-10}\,\Omega\,\mathrm{m\,deg}^{-1}$ [8] which is not far from the corresponding value for the nickel bulk material ($4.69 \times 10^{-10}\,\Omega\,\mathrm{m\,deg}^{-1}$ [14]). A similar feature has been observed in chemically deposited $Ni_{66}B_{34}$ layers [15] and attributed to conduction through nickel fibres. Since the interference functions related to chemically deposited $Ni_{66}B_{34}$ layers [5] and electrochemically deposited $Ni_{75}B_{25}$ layers [8] are quite close (Fig. 6), the same assumption can be proposed; moreover it suggests that the structures are built in similar clusters. This fact is not surprising since crystallographic analyses suggest a bi-dimensional array of clusters in the case of a chemical deposition procedure [4] and a three-dimensional array in the case of an electrochemical procedure [6, 8, 11]. In fact, electron micrographs reveal a deficit of matter in chemically deposited layers [5, 10, 13], and require the introduction of a filling coefficient for modelling the electrical conduction [15], whereas it is not the case for electrochemically deposited layers [9].

The fact that the resistivity of electrochemical layers takes values much lower (about three times) than that of chemical layers agrees with the above structure model [11].

4. Discussion

Early theoretical work related to liquid and amorphous transitions in metals and alloys was made by Mott in 1935 [16]; it was based on the assumption of an s-like and a p-like part of the Fermi surface. Under the assumption of a narrow d-band hybridized with an s-band, the success of this model for crystalline metal is clear [17]. Adaptations [18–20] of Ziman theory [21] for conduction in liquid metals are now generally retained for amorphous films [22–24]; the main interest of the Ziman-like expression of the electronic transport properties is to use separately the interference functions of the conducting material and the Fourier transform of the potential function in the material.

The interference functions must be estimated in the framework of a structural model; in agreement with the pioneering assumptions of Machizaud [4] it is now considered [24] that the structure of metal–metalloid alloys must be described by a model of clusters array [11, 23, 25], rejecting the DRPHS model [24].

The definition of the potential function requires a potential model; in the case of liquid metals the potential model of Abarenkov and Heine [26] can be used, and modified, for this purpose [27] but no clear basis for extending this type of calculation to amorphous material exists. Furthermore, in the case of tin–lead and zinc–lead liquid alloys, a relative deviation of 40% is usually observed from experimental values of electrical resistivity to theoretical ones based on the DRPHS assumption [27].

Similarly, the quasi-chemical model of binary alloys [28–31] in the way suggested by Guggenheim [32] has never been compared with experimental results for the electrical conductivity of amorphous layers, to our knowledge, whereas good agreement was found for the thermoelectric power of liquid metal and alloys [31].

Moreover, it is not obvious that a Ziman-like expression is suitable for calculating the transport properties in a bi-dimensional or three-dimensional array of clusters [23, 25], and we prefer to give an empirical description [12, 33] of the electrical conduction in which an electron statistically passes through the conducting material of the cluster and the poorly-conducting embedding medium of the clusters [11, 12]. In this way the observed variations in resistivity have recently been interpreted [12] and can be correlated to non-electric phenomena, as shown above.

The fact that an Ni_3B ray appears in the non-amorphous state is not surprising since it is established by several teams [3, 4, 13, 34, 35] that the local order of nickel–phosphorus layers around the metalloid atom tends to be like that of the closest crystalline compound, with a tendency to a greater compactness of the environment; this feature has been established experimentally [6–8, 34] from measurements of extended X-ray absorption fine structure [35].

All these experimental results show that there is a good qualitative agreement between the properties of amorphous layers built in metal—metalloid alloys whatever be the preparation procedure; quantitative data differ, between chemical and electrochemical procedures, and our attention is now focused on this point.

5. Conclusion

Simultaneous variations in the resistivity of nickel–boron layers, its temperature coefficient, its thermal derivative and the X-ray diffraction pattern with ageing temperature show that the structure evolution in the amorphous state is not detectable from X-ray diffraction, whereas the resistivity is modified; in the non-amorphous state the composition of the conducting material is modified by the action of the ageing temperature and can be correlated with the existence of Ni_3B rays in the diffraction pattern, in good qualitative agreement with experimental data of other workers.

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Received 19 March
and accepted 2 November 1984