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Electrochemical alloying of nickel with niobium in molten fluorides

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The metalliding of nickel with niobium was carried out by electrolysis in moten fluorides in the temperature range 850 to 1050° C. Several alloy layers were prepared and analysed. The composition of the bulk of the layer corresponds to the $NbNi_3$ compound but it is assumed that during the metalliding process a thin layer of NbNi is formed at the surface of the electrode. Electrochemical measurements were related to the kinetics of layer growth; these allowed the determination of the diffusion coefficient and the Arrhenius linear relationship of this parameter with the temperature.

1. Introduction

The formation of intermetallic compounds and alloys by electrolysis in molten salts is now a well-known and frequently used process [1–12]. In a few cases, where diffusion coefficients in the solid state are sufficiently high, total interdiffusion of the metals brought into contact by the electrodeposition process can be expected [8–12] and the cathodic material is thus completely alloyed with the anodic one. But in most cases, since the diffusion in the solid state is very slow, only an alloy layer of some tenths of a micron at the surface of the cathode may be obtained in a relatively short time and at moderate temperatures [1–7]. This process is often called metalliding [1].

Nevertheless this layer is able to give the initial substrate properties which are useful in various fields [13] such as corrosion resistance, microhardness, superconductivity and catalysis. Niobium is known to give superconducting materials when alloyed with metals such as germanium. For this purpose Cohen [14] obtained intermetallic compounds Nb_xGe by means of codeposition of the two elements in molten fluorides on inert substrates.

Furthermore, niobium–nickel alloys have recently been shown to have the properties required of insoluble anodes [15, 16]. According to the phase diagram [17] a slow interdiffusion of the two metals is possible at relatively low temperatures (above 800° C) and so metalliding appears to be a suitable process for forming these alloys.

2. Experimental details

The electrowinning of niobium–nickel compounds was carried out by electrochemical reduction of niobium IV ions on a nickel cathode in molten fluorides; niobium foils were used as anode and reference electrode. These metals were provided by Alpha Inorganics Laboratory, Danvers, USA (purity 99.9%).

The eutectic mixtures, LiF–NaF–KF (freezing point: 460° C) and LiF–NaF, or NaF–KF (freezing points respectively 650 and 750° C) were chosen as suitable solvents at lower and higher temperatures respectively. Nb IV ions were generated *in situ* by addition of potassium heptafluoroniobiate (V) and metallic niobium to the bath; the following reaction occurs:

$$4\,Nb^{V} + Nb \rightleftharpoons 5\,Nb^{IV} \qquad (1)$$

When an excess of metallic niobium is added to the bath, the equilibrium is shifted towards the right and a valence less than 4.2 of niobium ions may be expected [18].

All the chemicals were reagent grade: the alkaline fluorides and niobium salts were obtained from Merck laboratory (Darmstad, RFA) and Alpha Inorganics respectively.

In order to avoid the deleterious effects of residual moisture, the bath was initially dehydrated by heating under a vacuum (10^{-2}torr) for 30h at 500° C. In the case of solvent containing KF, since this compound is highly hygroscopic, a specific treatment was followed as indicated by Cohen *et al.* [19] KHF_2 was added to the initial mixture and the fusion was carried out under vacuum.

Then excess of moisture and HF were expelled by bubbling argon gas for 16h. After the treatment, the electrolytic bath was always kept under an atmosphere of argon.

The electrochemical set up (cell and measurement device) has been described previously [20, 21].

The micrographic analysis of the layer was performed by means of an X-ray microprobe and an electron microscope.

3. Alloy layer preparation and analysis. Discussion

Several alloy layers were obtained at different temperatures between 850 and 1050° C. In most cases, the technique used was the following: as nickel is more noble than niobium, an electrical connection between the two metals immersed in the bath provides a galvanic cell in which the reaction at the nickel cathode is the formation of the alloy $NbNi_x$. When the electrical circuit is closed, the potential of the cathode versus the niobium reference is slightly positive (5mV). After opening the circuit, the static potential of the cathode increases; a plateau at about 10mV is observed before a further progression occurs towards a stable value of 30mV versus the niobium reference (Fig. 1). The variation of the cell current with time shows a hyperbolic decrease, characteristic of a diffusion controlled process (Fig. 2). Identical curves are observed when the metalliding reaction is produced in potentiostatic conditions with a controlled potential (5mV) of the nickel cathode. The amount of niobium diffused, Δm, is equal to the increase of weight of the cathode and is, in every case, close to the theoretical value:

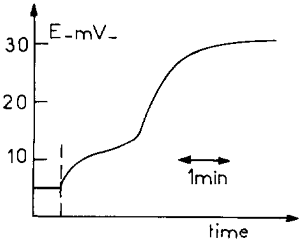

Fig. 1. Evolution of the cathode potential after metalliding (from the dashed line).

$$\frac{\Delta m}{M_{\mathrm{Nb}}} = \frac{Q}{4F} \tag{2}$$

Q is available by means of integration of the current–time curve. In Fig. 3, linearity between $\Delta m/S$ (S is the area of the cathode) and the square root of the diffusion time is observed. In Fig. 4a, a SEM micrograph shows the perfect homogeneity and uniformity of the alloy layer. After etching of the sample, this layer is unattacked (Fig. 4b) and no porosity can be distinguished. According to the X-ray analysis, the composition of the layer is constant and corresponds to the $NbNi_3$ compound, which is termed the β-phase in the phase diagram of the two metals (Fig. 5). A linear relationship, between the square of the thickness, X, of the

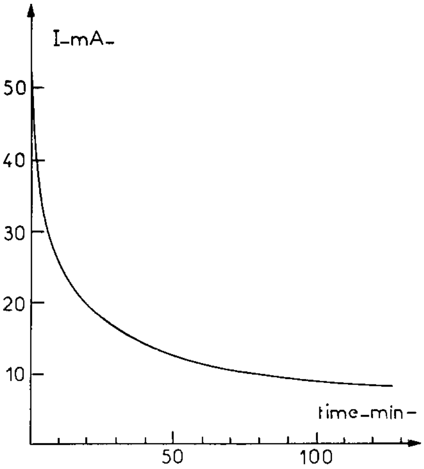

Fig. 2. Typical current time curve observed during the metalliding of nickel with niobium (t = 1050° C; S = 3.6cm^2).

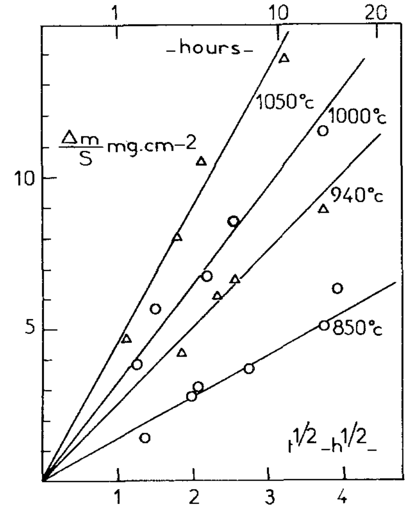

Fig. 3. Linear relationship between $\Delta m/S$ and the square root of time at several temperatures.

layer and the diffusion time is deduced from the slopes of Fig. 3 and the values of the $NbNi_3$ compound density

$$X^2 = Kt \quad (3)$$

It should be remembered that in all diffusion phenomena, the growth of a diffusion layer is described by a parabolic law as in Equation 3 [22].

Table 1 gives the values of the constant K at each temperature of the experimental measurements. Linearity between $\ln K$ and $1/T$ is observed (Fig. 6, straight line 1). K may be expressed as follows;

Table 1. Values of K for different temperatures

T(°K)	1123	1213	1273	1323
$K \times 10^{11}(\mathrm{cm^2 s^{-1}})$	5.85	19.32	34.59	69.17

$$K = 2.6 \times 10^{-4} \exp\left(-\frac{17200}{T}\right) \quad (4)$$

The growth of intermetallic niobium–nickel compounds has been previously investigated by Muramatsu *et al.* [23, 24] by diffusion welding of the two metals. In this technique, the samples are submitted to pressures between 0.6 and 2.0 kg mm^{-2}. At low temperatures (750 to 850° C) only the β-phase is observed with growth kinetics comparable to those observed here (Fig. 6 straight line 2). Above 850° C, the γ-phase NbNi forms at the niobium interface and at the same time, the growth rate of the β-phase is significantly slowed down (Fig. 6, straight line 3). According to Muramatsu this development is due to the pressure applied to the sample. Under our experimental conditions, no significant layer of the γ-phase was detected since the thermodynamic stability of $NbNi_3$ is greater than that of NbNi [25]. Nevertheless, the possibility of formation of this compound as a thin layer at the outer surface of the cathode during the metalliding process should not be excluded: the plateau in potential at 10 mV observed in Fig. 1 is characteristic of a change of phase occurring at the surface of the electrode [26], after the opening of the electrical circuit. For a better

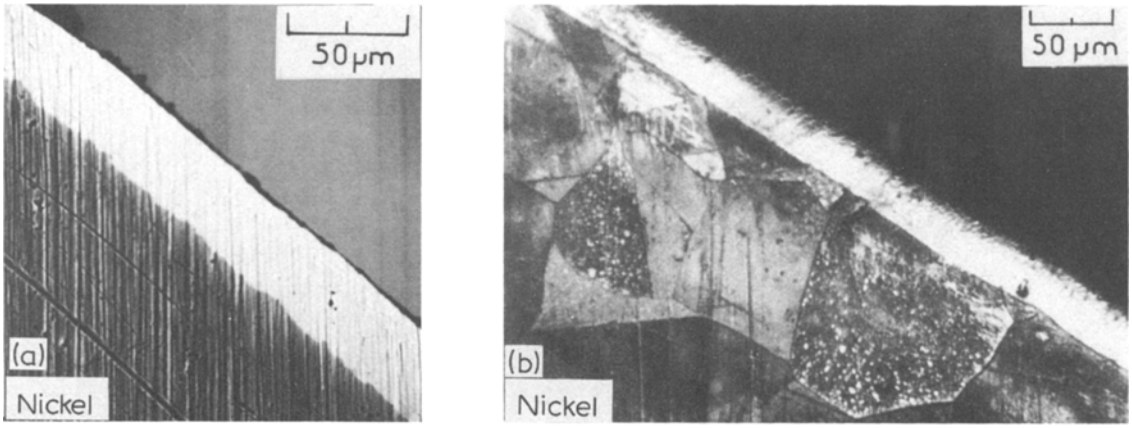

Fig. 4. Microscopic slides of the diffusion layer (a) SEM micrograph of the cross-section of the metallided nickel. (b) Microscopic slide of the section after etching the sample.

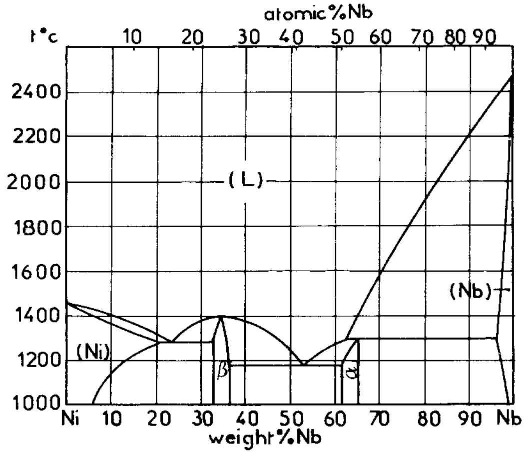

Fig. 5. Phase diagram of the niobium–nickel system reproduced from Metals Handbook 8th edition, American Society for Metals, Metals Park (1973).

understanding, the following experiment was performed: a thin sheet of nickel (thickness 12.5 μm) was metallided with niobium. Initially, only $NbNi_3$ was formed and the corresponding equilibrium potential was 30 mV versus the niobium reference. After complete saturation of the nickel substrate, the niobium content was raised by means of galvanostatic pulses. A rapid shift of the equilibrium potential (measured at each off-time) to a value of about 10 mV was noted. Afterwards, the formation of the γ-phase on the edges of the sample was observed by X-ray analysis. Therefore, the plateau of Fig. 1 may be related to the transformation of NbNi compound into $NbNi_3$ and, thus, it is concluded that the composition of the layer at the surface of the cathode during the metalliding process is close to that of the γ-phase.

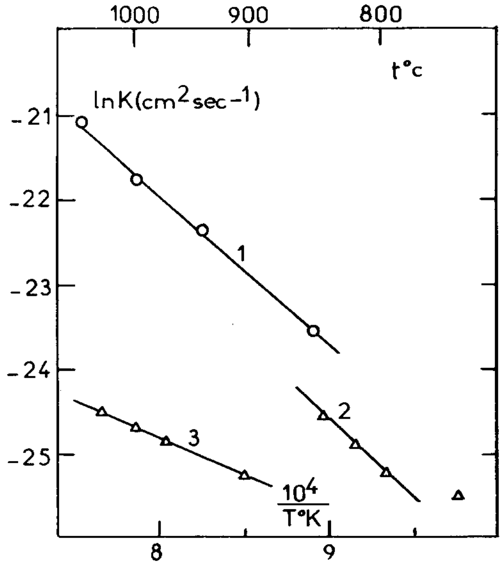

Fig. 6. Variation of $\ln K = f(1/T)$. Comparison with work of Muramatsu *et al.* [24] (1) Growth of the β-phase: present work. (2) and (3) Growth of the β-phase following Muramatsu *et al.*

4. Electrochemical analysis of the intermetallic diffusion

In order to describe the metalliding process theoretically, we assume that the chemical diffusion within the layer is the rate determining step and that the mass transfer is controlled by the flux of the diffusing species at the nickel interface. The chemical diffusion coefficient in the layer, D, corresponds to only $NbNi_3$ since only this phase is present in the bulk of the layer; diffusion phenomena are possibly induced by the variation of stoichiometry within this phase which is approximately 2% according to Muramatsu's measurements [24]. Then, it is clear that D can be considered as invariant. So, this mechanism of layer growth is comparable to the one of oxide formation on metals, theoretically investigaged by Danckwerts [27]. As in this case, the process is described by Fick's second law:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (5)$$

where x is the distance into the solid from the electrolyte and c the niobium content in the solid phase. It is clear that c is related to the concentration of crystal gaps in the binary compound and that the moving rate of metal atoms depends on the gradient of c within the layer.

The appropriate boundary conditions are:

$$c = 0 \quad x = 0 \quad t = 0 \qquad (6)$$

$$c = C_0 \quad x = 0 \quad t > 0 \qquad (7)$$

$$c = 0 \quad x = \infty \quad t > 0 \qquad (8)$$

the solution is:

$$c = C_0 \operatorname{erfc}\frac{x}{2(Dt)^{1/2}} \qquad (9)$$

Then, the flux of diffusing species (niobium) across the nickel interface and the resulting current density are given by the following equations:

$$J = -D\left(\frac{\partial c}{\partial x}\right)_{x=X}$$

$$= \frac{C_0 D^{1/2}}{(\pi t)^{1/2}} \exp\left\{-\left[\frac{X}{2(Dt)^{\frac{1}{2}}}\right]^2\right\} \quad (10)$$

$$i = \frac{nFD^{1/2}C_0}{(\pi t)^{1/2}} \exp\left\{-\left[\frac{X}{2(Dt)^{\frac{1}{2}}}\right]^2\right\} \quad (11)$$

with $n = 4$.

According to Equation 3 and assuming that K and D are proportional [22], Equation 11 becomes:

$$i = \frac{4FD^{1/2}C_0}{(\pi t)^{1/2}} \exp(-\alpha^2) \quad (12)$$

$$\text{with } \alpha = \tfrac{1}{2}\left(\frac{K}{D}\right)^{\frac{1}{2}} \quad (13)$$

As in the Cottrell equation [28], a linear relationship of the metalliding current density to the reciprocal of $t^{1/2}$ is expected; this relationship is verified in Fig. 7 for all the temperature used in the experimental work. The slope of the straight lines $i = f(t^{-1/2})$ is called p.

The values of p are also available in galvanostatic conditions: if a low cathodic current is imposed at the nickel electrode the potential versus the niobium reference stays at positive values for a time τ, before decreasing more quickly towards negative values (Fig. 8) where it was previously stated that nucleation occurs [21]. τ is assumed to be the time required to reach the saturation concentration C_0 of niobium at the surface of the electrode. Thus, we have:

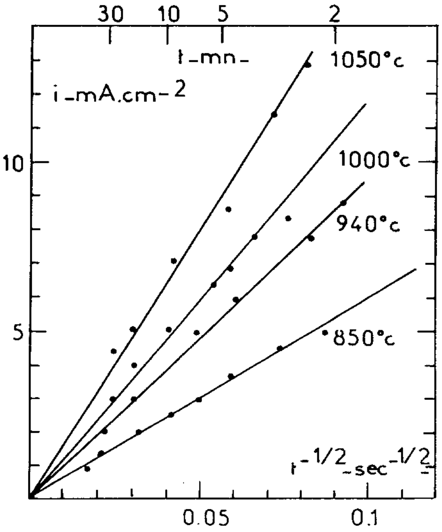

Fig. 7. Linear relationship between the metalliding current density and the reciprocal square root of time.

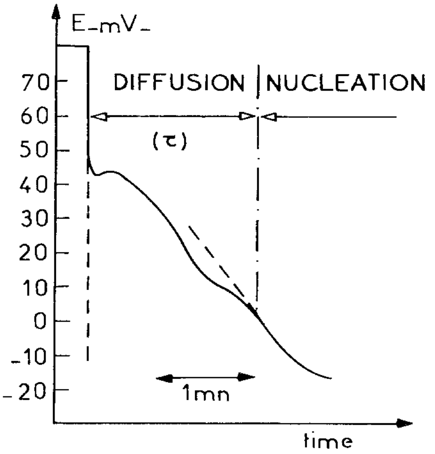

Fig. 8. Typical potential–time transient related to solid state diffusion when a cathodic galvanostatic pulse is applied at a nickel electrode (here $t = 900°$ C; $S = 0.7\,\text{cm}^2$; $I = 10\,\text{mA}$).

$$i\tau^{1/2} = \frac{4FC_0D^{1/2}}{\pi^{1/2}} \exp(-\alpha^2) = p \quad (12a)$$

Average values of p are given in Table 2:

The variation of $\ln p$ versus $1/T$(°K) gives a linear plot, the slope of which is approximately half the slope of $\ln K = f(1/T)$ as expected from Equations 4, 12 and 13. Thus, it is confirmed that α is a constant. The combination of Equations 12 and 13 gives:

$$\frac{\exp(-\alpha^2)}{\alpha} = \frac{\pi^{1/2}p}{2FC_0K^{1/2}} = f(\alpha) \quad (14)$$

As stated in the preceding paragraph, C_0 is close to the value of niobium content in the γ-phase ($C_0 \simeq 0.051$ at g cm^{-3}) and the average value of α is found to be 0.64 from Equation 14. So the

Table 2. Values for p at different temperatures

T(°K)	1123	1173	1213	1273	1323
p(A cm^{-2} s$^{-1/2}$)	0.061	0.068	0.098	0.115	0.164

intermetallic diffusion coefficient is given by the following expression, derived from Equation 4,

$$D = 1.6 \times 10^{-4} \exp\left(-\frac{17200}{T}\right) \mathrm{cm}^2\,\mathrm{s}^{-1} \quad (15)$$

5. Conclusion

The electrochemical investigation of the metalliding transients seems to be in agreement with the analysis of the layers obtained since the value of α is confirmed to be constant; α is known to be an important parameter, often introduced elsewhere into various mathematical diffusion models [29]. From a practical point of view, metalliding with niobium gives interesting properties to relatively cheap substrates such as nickel. The improvement in corrosion resistance conferred to this metal by a thin layer of $NbNi_3$ at the surface is so effective that further use of this new material for insoluble anodes in electrolysis of aqueous solutions is to be expected. Among the advantages of this process over more classical metallurgical techniques, the possibility of control of the layer thickness by the measurement of the metalliding current should be noted.

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