

SHORT COMMUNICATIONS

COLD WORKING OF NICKEL WIRES AND ITS EFFECT ON ELECTRODE POTENTIALS

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THE usual theory of the electrode potential of a metal dipped in a solution of its own salt is based on thermodynamics and yields the well known formula¹:

$$\epsilon = \epsilon_0 + \frac{RT}{F} \cdot \ln a \quad (1)$$

where a is the activity, T the temperature, R the gas constant and ϵ_0 the standard potential, which is the difference between the respective molar free enthalpies of the metal ions in the metal itself and in solution of unit activity. Targert and Robertson² studied the single crystals of copper and found that ϵ_0 depended on the particular crystal plane exposed to the electrolytic solution. Thus ϵ_0 is related to the solid state properties. However no solid state theory of this phenomena has been formulated.

The object of this note is to point out that such solid state effects exist also in polycrystalline metal wires. Annealing and subsequent cold work affects the electrochemical properties of nickel wires.

Nickel wires, 0.25 mm dia. and 1 m length were vacuum annealed at different temperatures (240°, 290°, 425°, 600° and 750°C) for a period of 24 hr and then furnace cooled. The specimen were then electropolished. Their electrode potentials were measured by dipping them in a saturated solution of nickel sulphate

against a saturated calomel electrode connected by a KCl-agar bridge. Potentials were measured by a Toshniwal model C-106A potentiometer with a least count of 2 mV. The electrode potentials are listed in the second column of table 1 as initial ϵ values and are different for different temperatures of annealing.

Next the specimen wires were cold worked by winding-unwinding method suggested by Wagler and Lorenz³. The samples were hung on a mild steel rod of 0.78 cm dia. Under a 1 kg weight and the winding-unwinding operation was carried out on this rod. After a few cycles the wire broke from the bottom. A piece about 10 cm of wire was cut and its electrode potential measured. The winding-unwinding process was repeated with the remaining wire and this was continued till cold working showed no further increase in ϵ . This value of ϵ is called the saturation value in table 1. Figure 1 shows a typical variation in ϵ with the number of cycles of cold working for 3 samples annealed at 600°C. All the saturation values are higher than the initial values. The order of values in columns 2 and 3 are also different. The electrode potentials of these samples were measured daily. After about four days all the ϵ values became stable and these are listed in column 4 of the table as "recovered values". The order in recovered values is the same as in the saturation values.

We also measured the ϵ values for different planes of single nickel crystals. High purity nickel crystals cut with $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ as surface planes were obtained from M/s Atomergic Chemetals Corporation, Plainview, N.Y. (USA) The different Planes gave the following ϵ values:

Table 1 Electrode potentials of samples annealed at different temperatures
error = ± 5 mV

Annealing temperature	Initial	Saturation after cold working	Recovered value	Crystal planes with value nearest to the recovered
240	302	320	312	2 $\langle 100 \rangle$ + $\langle 111 \rangle$
290	283	303	296	$\langle 100 \rangle$
425	310	350	334	$\langle 111 \rangle$
600	310	363	346	4 $\langle 111 \rangle$ + 1 $\langle 110 \rangle$
750	326	352	342	8 $\langle 111 \rangle$ + 1 $\langle 110 \rangle$
Unannealed	295	Different samples show different behaviour.		

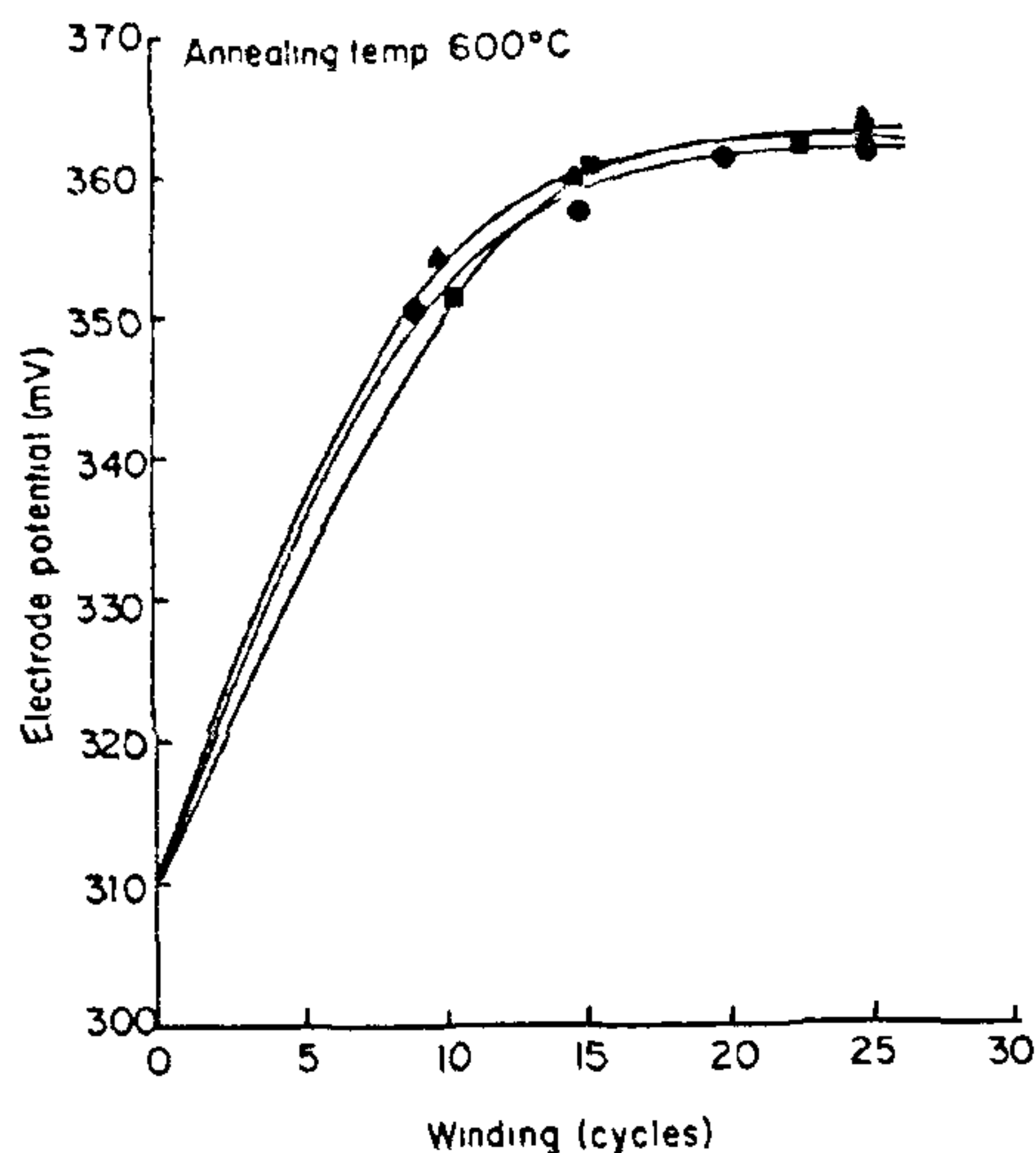


Figure 1. Typical variation in ϵ with the number of cycles of cold working for 3 samples annealed at 600°C.

Plane	in mV
$\langle 100 \rangle$	298
$\langle 110 \rangle$	392
$\langle 111 \rangle$	336

Planes $\langle 100 \rangle$, $\langle 111 \rangle$ have ϵ values nearest to the recovered values for wire samples annealed at 290° and 425°C respectively. These must therefore be the planes dominating the surface for these samples.

For the sample annealed at 240° the value of recovered ϵ lies between the values for $\langle 100 \rangle$ and $\langle 111 \rangle$ planes. An empirical fit gives the fractional contributions from the two surfaces close to 2:1 other contributions shown in the last column of table 1 are calculated likewise. This is only an empirical interpretation of the observed ϵ values.

The data indicate that the annealed polycrystalline wires on cold-working have surfaces with some preferred crystal planes. Which of the planes shall dominate depends sharply on the annealing temperature.

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1. Kortum, G., *Treatise on Electrochemistry*, Elsevier Publishing Co., Amsterdam, 2nd edn, 1965, p. 297.
2. Tragert, W. E. and Robertson, W. D., *J. Electrochem. Soc. (USA)*, 1955, **182**, 86.
3. Wagler, O. and Lorenz, F. R., *Zeit. Tech. Phys.*, 1930, **11**, 242.

CHEMISTRY OF LICHEN PRODUCTS— PART II: SYNTHESIS AND BIOLOGICAL ACTIVITY OF SOME NEW DERIVATIVES OF PULVINIC DILACTONE

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LICHEN metabolites of pulvinic acid group¹ possess the tetronic acid ring system which is also present in a number of important natural products viz vitamin C and the cardenolide, digitoxigenin.

With a view to synthesizing more potent biologically active compounds, various amino acids and differently substituted sulphanilamides are condensed with pulvinic dilactone² by refluxing in acetic acid for 4–5 hr (scheme-I). While the products derived from aminoacids yielded pulvinic dilactone on boiling with acetic anhydride for 3 hr, they gave pulvinic acid on hydrolysis using polyphosphoric acid or acetic acid-sulphuric acid mixture. Further, the enolic hydroxyl of simple sulphonamide condensation product (VIII) got esterified on refluxing in acetic acid for one hour to get its acetate (XVI).

The hydrolysis products were identified by CO TLC, superimposable IR and mixed m.p. measurements. Structures of the products (table 1) were established by the following spectral data. IR ν_{\max} in cm^{-1} (I–VII): 3220–3390 (broad, OH, NH), 1760s (C=O, lactone), 1700–1710s (C=O, carboxylic acid), 1650s (C=O, amide) 1610m (aliphatic C=C).

IR ν_{\max} in cm^{-1} (VIII–XV): 3200–3400 (broad, NH, OH), 1760s (C=O, lactone), 1650s (C=O, amide), 1610m (aliphatic C=C), 1350, 1160s (–SO₂–). (XVI) Acetate of (VIII): 3300 (broad, NH), 1760 (C=O, lactone), 1730 (C=O, ester), 1650 (C=O, amide), 1350 and 1160 (–SO₂–).

PMR of compound (V): In ppm, 1.9 (s, 3H, –CH₃), 2.1 (qua., 2H, –CH₂–) 2.5 (t, 2H, –CH₂–), 4.85 (qua., 1H, –CH–N–), 9.5 (broad, 1H, –CO–NH–), 10.5 (s, 1H, –CO₂H) and 12.8 (s, 1H, –OH).