STUDY OF THE DEPOSITION, PROPERTIES AND APPLICATIONS OF ELECTROLESS DEPOSITS CONTAINING PARTICLES

by

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A Thesis submitted for Degree of

DOCTOR OF PHILOSOPHY

June 1981

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Degree: Ph.D. 1981

SUMMARY

The deposition efficiencies of a number of electroless nickel and cobalt plating solutions were studied and in the case of nickel compared with a commercial plating solution Nifoss 80 . At the optimum plating conditions (92°C and pH 4.5) Nifoss 80 produced nickel layers most efficiently, the alkaline cobalt solution operated most efficiently at 90°C and pH 9.

The methodsof producing composite layers containing 2-3 μm carbide particles and chromium powder is described. Nickel and cobalt layers containing approximately 27% carbide particles, or 40% (Ni) and 30% (Co) chromium particles by volume were obtained. This value is independent of the particle concentration in the plating solution within the range (20-200 g/l).

Hardness of the nickel as deposited was 515 Hv, this was increased to a maximum of 1155 Hv by heat treatment at 200°C for 5 hours in vacuum. Incorporation of chromium carbide particles resulted in a maximum hardness of 1225 Hv after heating at 500°C for 5 hours in vacuum and chromium particles resulted in a maximum hardness of 1650 Hv after heat treatment at 400°C for 2 hours in vacuum. Similarly the hardness of cobalt as deposited was 600 Hv, this was increased to a maximum of 1300 Hv after heat treatment at 400°C for 1 hour. Incorporation of chromium carbide particles resulted in a maximum hardness of 1405 Hv after heating at 400°C for 5 hours in vacuum and chromium particles resulted in a maximum hardness of 1440 Hv after heat treating for 2 hours at 400°C in vacuum.

The structure of the deposits was studied by optical and scanning electron microscopy. The wear rate and coefficient of friction was determined by a pin and disc method. Wear rate and coefficient of friction decreased with increase in hardness. The wear resistance of the materials was also determined using a simulated forging test. Dies made of standard die steel were coated and the wear rates of the layers as deposited and after heat treatment were compared with those of uncoated tools. The wear resistance generally increased with hardness, it was 50-75% more than the uncoated die steel.

Acetic acid salt spray test and outdoor exposure for six months was used to study the corrosion behaviour of the deposits and potentiodynamic curves plotted to find their corrosion potential. Nickel deposit exhibited less staining than carbide composite deposit and nickel-chromium deposit had the most noble corrosion potential.

KEY WORDS: ELECTROLESS DEPOSITS; COMPOSITES; WEAR RESISTANCE; HEAT TREATMENT; HARDNESS

DECLARATION

The work described here was carried out at the University of Aston in Birmingham between October 1978 and March 1981. It has been done independently and submitted for no other degree.

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1. INTRODUCTION

Electroless plating is an autocatalytic chemical reduction process in which metallic ions are reduced to metal in an aqueous solution in the presence of a reducing agent without an electric current. The metal deposit has therefore a uniform thickness and any object can be plated regardless of its shape and dimensions.

Electroless plating can be applied to any substrate including non-conductors, such as glass, ceramics, plastics, etc., and thickness can be built up to any reasonable value. The electroless plating solutions in many cases can be continually maintained as with electroplating solutions. Many metals and alloys can now be obtained from electroless plating solutions, for example, nickel, copper, cobalt, gold, nickel-cobalt, nickel-phosphorus, nickel-boron, cobalt-phosphorus.

Electroless nickel was rediscovered by Brenner and Riddel in 1944. The solution most commonly used to obtain electroless nickel coatings contains acid hypophosphite. The overall reaction in an acid solution is

$$Ni^{++} + 3[H_2PO_2]^- \underset{+H(cat)}{+ H_2O} \rightarrow Ni + 2[HPO_3]^{2-} \underset{+4H}{+ H_2} + P + OH^-$$

A solution of phosphorus in nickel is obtained along with the evolution of hydrogen.

Electrodeposited coatings with inclusions have been developed since the beginning of the 1960's. Since then considerable work has been done with a variety of particles both hard and soft with several types of matrices. The idea of co-depositing hard particles with electroless plated metals or alloys was encouraged, by these developments and has led to the development of several electroless composite coatings.

The unique characteristics of electroless coatings such as inherent thickness uniformity, corrosion resistance and hardenability can be further enhanced by co-depositing hard particles with electroless metals or alloys. Many varieties of composite electroless coatings are made possible by using different particles, smooth and abrasive surfaces may be generated simply by choosing appropriate particles.

The main object of this project is to study the deposition, properties and application of electroless coatings, particularly nickel-phosphorus and cobalt-phosphorus containing particles of carbides and chromium.

1.1 Scope of the Project

Electroless acid nickel and alkaline cobalt plating solutions deposit nickel-phosphorus and cobalt-phosphorus alloys which are capable of providing effective wear resistance, particularly when they are heat treated at 400-500°C. This project involves the study of the role of the particles in improving the properties of electroless nickel-phorphorus and cobalt-phosphorus deposits by the addition of hard particles, such as carbides and chromium metal.

The main objectives are to study the following:

i) Effects of the particle volume fraction in the coating on the hardness and wear resistance of the coating.

ii) Determination of properties such as hardness, ductility, and corrosion resistance.

iii) Wear rate and coefficient of friction, determination by pin and disc method.

iv) Performance of the coating on experimental hot forging dies.

The ideal object would be to develop a commercially viable system, that is cheap and easy to operate, capable of being used for a long period before the solution is discarded and capable of giving a versatile deposit useful for many applications.

2. LITERATURE SURVEY

2.1 Introduction

Metallic nickel was first obtained by A. Wurtz (1) in 1844 by reducing a nickel salt solution with sodium hypophosphite. Later many research workers studied this reaction including Breteau (2), Paal and Frederici (3), Scholder and Heckel (4) and Scholder and Haken (5). Paal and Fredereci (3) have also studied the reduction of cobalt ions to cobalt metal. In most of the cases this spontaneous chemical reduction yields a black powder (6). However Breteau (2) succeeded in obtaining a metallic mirror of the nickel on the walls of the reaction vessel. He investigated the influence of the concentration of the reducing agent on the resulting product, which was considered to be the pure nickel. He also stressed the importance of the autocatalytic nature of the reduction reaction.

Roux (7) was the first person who was granted a patent, which describes the deposition of nickel coatings on solid substrates from hot ammoniacal nickel citrate-sodium hypophosphite solutions. This bath however was not good enough to be commercially feasible as it decomposes spontaneously to yield a coating on all objects immersed in it, including the walls of the vessel, and it was neglected. Brenner and Riddell (8) are credited with rediscovering the electroless nickel coating process in 1946. Their work in developing a process for plating the interiors of the tubes with a nickel-tungsten alloy, using an insoluble anode, rediscovered the unusual reducing properties of sodium hypophosphite. This process was eventually covered by patent (9) in 1950. Brenner and Riddell (8,9) also established the possibility of electroless cobalt deposition on various metal substrates by reducing cobalt salt solutions with sodium hypophosphite. General American Transportation Corporation (G.A.T.C.) (10) was the first organisation to have an Industrial plant for the electroless nickel plating in 1955. This process was all automated and is famous under the brand name of Kanigen (R) (10).

Initially, a great deal of interest was shown in electroless cobalt deposits because of their ability to be readily plated upon suitably activated plastics (11). Because of the wide variety of magnetic properties attainable, cobalt deposits obtained from electroless plating solution have been employed for high quality, high density recordings and for computer storage elements in high speed switching devices (12). Now the recent trend in electroless cobalt deposition has been directed towards the high hardness and wear resistance of the deposits attainable with heat-treatment as originally shown by Brenner (8,9).

2.2 Electroless Plating

Electroless plating is an autocatalytic chemical reduction process. It is catalysed by the metals from group eight of the periodic table, e.g. nickel, cobalt. In order for the reaction to proceed, a catalytic surface must first be formed. When using metals less electronegative than nickel or cobalt, such as iron, a catalytic surface is formed as a result of displacement:

$$Fe + Ni^{2+} = Ni + Fe^{2+}$$
$$Co^{2+} + Fe = Co + Fe^{2+}$$

Therefore once an initial coating of nickel or cobalt has been established, the electroless plating process is self perpetuating. Thus it is better described as an autocatalytic process, which theoretically imposes no limit on the thickness of the metal that can be deposited. This differs from those processes which operate by a displacement reaction leading to thin immersion coatings only. In these systems the metal to be coated has a more negative potential than that of the metal ions in solution. Metals which are not spontaneously coated are usually activated by a galvanic process (13).

Electroless plating solutions usually have four components in common. They contain a source of metal ions, a reducing agent, a buffer and accompanying agents. Many baths have additional compounds added in order to improve their plating rate, stability and surface appearance of the electroless deposit.

2.3 Reducing Agents for Chemical Deposition of Nickel and Cobalt

Hypophosphite, boronhydride, amino borane and hydrazine are the reducing agents used, for the chemical deposition of nickel and cobalt on the metal substrates from their aqueous solutions.

(i) Hypophosphites

Sodium hypophosphite is a commonly used reducing agent. It is manufactured by emulsifying white phosphorus with sodium hydroxide at 45-50° (14).

$$P_4 + 4\bar{O}H + 4H_2O \rightarrow 4H_2PO_2^- + 2H_2$$
$$P_4 + 4\bar{O}H + 2H_2O \rightarrow 2H_2PO_3^- + 2PH_3$$

Sodium phosphite formed as a by-product is precipitated by $Ca(OH)_2$ as insoluble $CaHPO_3$, or sodium hypophosphite can also be produced cheaply by the reaction of red phosphorus with an aqueous solution of sodium perchlorate.

The potential of the hypophosphite ion lies between -1.065 v(pH = 7.0) and -0.882 v(pH = 4.5). So it is a powerful reducing agent.

Calcium and nickel hypophosphites are also used to a lesser degree. Nickel hypophosphite has the advantage that the solution does not contain unwanted anions and cations.

(ii) Boron hydrides

Sodium borohydride is mostly used. It is a colourless hygroscopic salt which if ignited burns quietly in air (15). Sodium borohydride is easily soluble in cold water with slow dissociation. It hydrolyses into sodium borate and hydrogen:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$$

The speed of hydrolysis depends on the temperature, pH value and presence of catalyst.

Sodium borohydride is manufactured by substitution of boron silicate with sodium and hydrogen at 450-500°C (16);

$$Na_2B_4O_7 + 7SiO_2 + 16Na + 8H_2 \rightarrow 4NaBH_4 + 7Na_2SiO_3$$

The mixture of boronhydride/silicate is extracted under pressure with liquid ammonia at room temperature and pure sodium borohydride is precipitated as a white powder.

Substituted borohydrides like sodium trimethoxy borohydride can also be used. It is more powerful reducing agent than sodium borohydride.

(iii) Amine borones

The amine boranes are addition compounds of amines with borohydride of the general formula $R_3N\text{-}BH_3$, where R represents the hydrogen or alkyl or aryl group (17). The most commonly used member of the group is dimethylamine-borane. It is very easily soluble in water and reducing properties are retained in a wide pH range.

(iv) Hydrazine

Pure hydrazine is a clear hygroscopic liquid unstable in air. It is miscible with water, alcohol and amines in all proportions. It is a strong reducing agent for many ions of heavy metals (18). During catalytic oxidation water and nitrogen are formed mainly and so it is an ideal reducing agent, unfortunately hydrazine solutions are not very stable and therefore are used rarely.

Another reducing medium is a hydrogen atmosphere. A suspension containing nickel oxide, acid ammonium phosphate and a wetting agent is applied on the substrate. The nickel oxide is reduced in hydrogen atmosphere at 900-1000°C and the nickel deposit contains 2-3% phosphorus (19), but this reducing medium is used seldom.

2.4 Mechanism of Electroless Nickel and Cobalt Plating

Many theories have been advanced to explain how deposition occurs. Salvago and Cavalloti (20) have reviewed the major theories relating to the long established hypophosphite based bath where the mechanism is still uncertain. The deposition mechanism of baths using other reducing agents, is complex and only a representation of the actual reactions can yet be presented.

2.4.1 Theories for the Explanation of the Mechanism of Chemical Nickel and Cobalt Plating with Hyphosphite

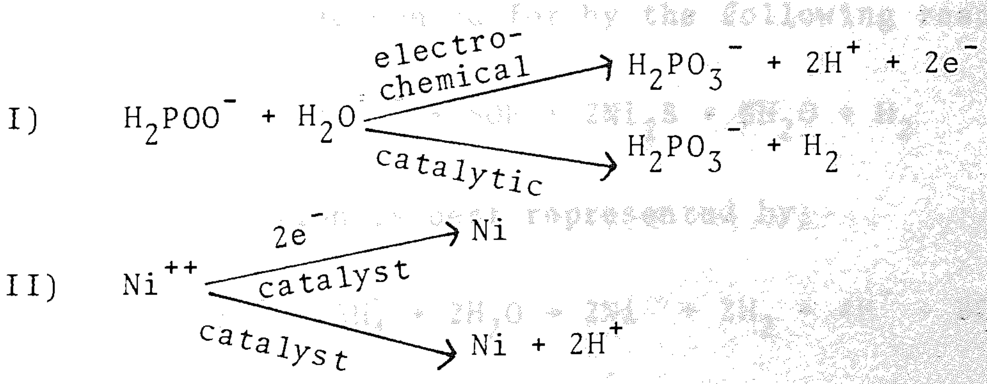
Sodium hypophosphite is used as the reducing agent in this type of bath. Brenner and Riddell (8) proposed the deposition of nickel by a chemical reduction brought about by the adsorption of atomic hydrogen. Gutzeit (21,22), Levy (23) and others supported this hypothesis.

A mechanism proposing hydride ions as a reducing intermediate was suggested by Hersch (24) by an anology with the reduction of nickel salts by borohydride ions and later modified by Lukes (25) who showed it similar to Cannizaro's reaction.

Brenner and Riddell (8) have proposed an electrochemical mechanism in which electrons reduce the nickel intermediates, the deposition of nickel would be an electrolytic process occurring via local cells on a catalytic surface. Hickling and Johnson (26) supported this view though with several modifications. More recently, Donahue and Yu (27) suggested a cathodic process for hydrogen evolution and nickel deposition.

Mechanism involving hydrolysed nickel or cobalt as reducing species were suggested by Salvago and Cavollotti (20), Kovac and Croll (28) and Randin and Hintermann (29).

Gouda et al (30) suggest that there is competition between catalytic and electrochemical decomposition of hypophosphite on the metallic substrate. The electroless deposition of nickel would then depend mainly on the decomposition of hypophosphite. The simplified overall mechanism for the electroless nickel deposition according to Gouda et al (30) is:



2.4.2 Theories for the Explanation of the Mechanism of Chemical Plating of Nickel and Cobalt with Borohydride Based Baths

The exact mechanism of the metal ions with boron hydrides has up to now not been established. Sodium borohydride is mostly used for electroless deposition processes. Some substituted boron hydride, e.g. sodium trimethoxy boron hydride $NaB(OCH_3)_3$ are also used. Sodium boron hydride is hydrolysed in all but strongly alkaline solutions:

$$BH_4^- + 4H_2O \rightarrow B(OH)_4^- + 4H_2$$

or in the presence of an acid:

$$BH_4^- + H_3O^+ + 2H_2O \rightarrow H_3BO_3 + 4H_2$$

For this reason plating baths are usually kept above pH 12 (17). The plating reaction can be represented by the equation below (31,32):

$$BH_4^- + 4Ni^{2+} + 8\bar{O}H \rightarrow 4Ni + BO_2^- + 6H_2O$$

In practice, it is found that 1 to 8% boron is present in the final deposit accounted for by the following reaction:

$$2BH_4^- + 4Ni^{2+} + 6\bar{O}H \rightarrow 2Ni_2B + 6H_2O + H_2$$

The plating reaction is best represented by:

$$2Ni^{2+} + BH_4^- + 2H_2O \rightarrow 2Ni + 2H_2 + 4H^+ + BO_2^-$$

Mochalov and co-workers (33) have investigated the kinetics of the hydrolysis of boron hydrides in an alkaline medium and established that the speed of the process of each elementary reaction follows the first order kinetic laws of reaction.

When substituted amine boranes are used the overall reaction is represented by (17):

$$2(CH_3)_2NHBH_3 + 3Ni^{2+} + 6H_2O = 3Ni + 2(CH_3)_2H_2N + 2H_3BO_3 + 6H^+ + 2H_2$$

Schlesinger and Brown (34) in their investigation have reported that the hydrolysis of boron hydride is accelerated by the presence of Co^-, Ni^-, Cu^-, Fe^- and Mn^- salts in the solution and they suspect that in this case metal salts themselves do not act as the catalyst, but the products of their reduction appear as catalyst. The most active catalysts were the cobalt and nickel ions and the resulting product also contained boron besides cobalt.

Brown and Lyons (35) have also investigated the reduction of cobalt ions by sodium borohydride. From the experimental data obtained, they suggest that the reaction leading to the formation of precipitate can be described by the following equations:

$$2CO^{2+} + BH_4^- + 3H_2O \rightarrow (CO_2B) + 3H_3O^+ + \tfrac{1}{2}H_2$$

The hydronium ions which are formed after this reaction, then react immediately with the boronhydride ions:

$$H_3O^+ + BH_4^- + H_2O \rightarrow HBO_2 + 4H_2$$

The summary reaction is as follows:

$$2CO^{2+} + 4BH_4^- + 6H_2O \rightarrow (CO_2B) + 3HBO_2 + \frac{25}{2}H_2$$

Takezuga and Kazuaki (36) have calculated after a series of experiments that nickel (or cobalt) borohydride is formed during the first stage of the reduction process, afterwards it dissociates into nickel and diborane:

$$Ni^{2+} + 2BH_4^- \rightarrow Ni(BH_4)_2 \rightarrow Ni + B_2H_6 + H_2$$

This scheme rests on the assumption that nickel (or cobalt) borohydride is formed in the beginning and later on this compound is dissociated.

2.5 Acid Nickel Hypophosphite Solution

Electroless nickel acid hypophosphite solution has higher speed of plating than alkaline solution, greater stability, simpler control of solution and better properties of the nickel phosphorus coatings obtained. The following equations illustrate the chemical reactions that take place during the reduction with sodium hypophosphite in acid medium:

$$[H_2PO_2]^- + H_2O \xrightarrow{cat} H^+ + [HPO_3]^{2-} + 2H(cat) \quad \ldots\ldots(1)$$

$$Ni^{++} + 2H(cat) \rightarrow Ni + 2H^+ \quad \ldots\ldots\ldots\ldots\ldots(2)$$

$$[H_2PO_2]^- + H(cat) \rightarrow H_2O + \bar{O}H + P \quad \ldots\ldots\ldots\ldots\ldots(3)$$

$$[H_2PO_2]^- + H_2O \xrightarrow{cat} H^+ + [HPO_3]^{2-} + H_2 \quad \ldots\ldots\ldots\ldots(4)$$

The hypophosphite ions are oxidised to orthophosphite ions in the presence of a catalytic surface, hydrogen atoms given off during this reaction are partly adsorbed on the surface of the substrate. The nickel ions are reduced to metallic nickel by active hydrogen atoms whereby they are oxidised to hydrogen ions. Hypophosphite in small amounts is also reduced to OH$^-$ ions, water and phosphorus by the adsorbed active hydrogen on the catalytically acting surface (substrate), and a part of hypophosphite is oxidised to orthophosphite ions and evolution of hydrogen takes place.

2.5.1 Composition of Acid Nickel Hypophosphite Solution

Electroless nickel acid hypophosphite solutions contain a source of nickel ions in the form of nickel salts, commonly used nickel salts are nickel sulphate, nickel chloride and occasionally nickel acetate, a reducing agent, a buffer and a complexing agent. The buffers are usually organic acids, the most common ones lactic acid, succinic acid, citric acid, malic acid, propionic acid. Sometimes stabilizers are added to prevent solution decomposition by "masking" active nuclei. Typical materials used include thiourea, sodium ethylxanthate, lead or trisulphides.

2.5.2 Factors Influencing the Rate of Plating

Temperature, pH, nickel ion concentration, reducing agent, i.e. sodium hypophosphite concentration, and complexing agent concentration are the important factors which influence the rate of electroless deposition.

(i) Influence of temperature

Reduction of the metallic ion requires energy which is supplied in the form of heat, so bath temperature is the most important factor governing the rate of electroless deposition. Acid nickel hypophosphite solutions need a higher working temperature although the reaction partly starts at $40-50^{\circ}C$. Acid hypophosphite solutions usually work at $90-95^{\circ}C$.

Baldwin and Such (37) have established that coatings from acid hypophosphite solutions become lower in phosphorus content, the higher solution temperature.

(ii) Influence of pH

pH is another important factor in the electroless plating process, the concentration of H^+ ions increases with the reduction of Ni^{2+}, i.e. the pH value decreases. Randin and Hinterman (38) have established the relationship between the phosphorus content of the coating and pH of the solution, they found that with the decrease in H^+ ions, the amount of phosphorus content co-depositing with the nickel decreases. DeMinger and Brenner (39) established that the deposition rate of electroless nickel plating increased with increasing organic acid concentration to a maximum and then decreased. It also depends on the nature of the bonding of the organic additive.

The solubility of nickel phosphide in the plating solution can be increased by reducing pH value of the solution. The reduction in the pH of the solution leads to the prevention of the deposition of basic salts and hydroxides, and reduces the efficiency of the hypophosphite reducing property. Reduction in pH also reduces the effectiveness of the buffers which are present. At pH less than 4 the metallic coating is attacked by the acidic solution and deposition rate is lowered.

(iii) Influence of the nickel concentration

Nickel ion content does not greatly affect the deposition of nickel in the absence of fluoride ions, but in the solutions containing fluoride ions increase in the rate of deposition will occur up to a certain increased concentration of nickel ion (39).

(iv) Influence of hypophosphite concentration

The amount of hypophosphite used is important. Approximately, 3 mol hypophosphite reduces 1 mol nickel ions and a part of the reducing medium is catalytically decomposed on the surface of the nickel. There was no significant influence of hypophosphite concentration on the rate of nickel deposition from glycolate solution (8). With similar solutions containing less glycollic acid, however, Gorbunova and Nikiforova (40) found the maximum rate of deposition is at 10 g/l of sodium hypophosphite. They also established that the increase in the hypophosphite concentration does not influence the speed if the relationship between the hypophosphite and the organic complexing agent lies outside the optimal limits. Gutzeit and Kreig (41) emphasised that the absolute concentration of hypophosphite ions should be in the range of 0.15-0.35 mol/l; the optimal mol ratio of $Ni^{2+}/(H_2PO_2)^-$ is in the range 0.25-0.6. Higher concentration of hypophosphite leads to the spontaneous decomposition of the solution.

(v) <u>Influence of the complexing agent</u>

The organic additives play an important two-fold part. The organic acid acts as a buffer and prevents the pH value of the solution from decreasing too rapidly, also they act as complexing agents for nickel and thus reduces the concentration of free nickel ions. In this way, the solution is stablised and nickel phosphide precipitation is restrained.

Gutzeit and Ramirez (42) patented the use of dicarboxylic acids, e.g. succinic acid and glutonic acid. It was shown that the rate of deposition is a maximum at a certain concentration of acid. Holbrook and Twist (43) have confirmed this hypothesis.

Use of lactic acid (44,45,46) with glycollic acid is very popular, a maximum rate of plating can be achieved with 0.24 mol/l of lactic acid. In these patents it was shown that lactic acid content in the plating solution can be as high as 0.40 mol/l, and under these conditions the concentration of phosphite can also reach up to 2 mol/l without visible deterioration in the quality of the coating. Lactic acid acts as a buffer, a complexing agent and has an accelerating effect.

Combinations of carboxylic and hydroxy carboxylic acids, e.g. propionic acid and lactic acid, are often used. G. Gutzeit (46) has examined the role of many amino acids, e.g. aminoacetic acid (glycine), α-amino propionic acid, aspartic acid, B-alanine, iminodi, triacetic acids as well as EDTE. These acids prevent the separation of unnecessary phosphites, and increase the plating speed. Some inorganic acid salts can also be used to a limited extent, e.g. ammonium salts (45), fluorides, borates (47).

(vi) Influence of the stabilisers and accelerators

Use of ions such as Pb^{++}, Cd^{++}, Zn^{++}, SCN^-, CN^- were described as catalyst poisons for chemical nickel plating. Talmey and Gutzeit (48) established that they act as stabilisers in small concentrations, for example 1 μg/l. Gurdrzynski (49) patented the use of molybidic acid-anhydride, arsenious acid, hydroxyl amino sulphate and hydrazine. Elze (50) while examining the influence of various metal ions and a series of organic substances on the reduction process found strongly inhibiting but also accelerating additives and tried to correlate the effect of the additives on metal deposition with their influence on the separation potential.

Organic additives in the chemical plating solutions act not only as regulators of the pH and complexing agents, but also cause a certain acceleration of the reducing reactions. These substances are called accelerators or stabilisers. When they are at optimum concentrations, they act against the deceleration effect which is exhibited by most complexing agents. These substances are saturated carboxylic acids and their alkali metal salts, ammonium salts, saturated amino carboxylic acids, e.g. glycine and saturated non-substituted dicarboxylic acids with short chains.

(vii) Influence of agitation

Agitation of the solution though not necessary is very useful, as it helps in getting even deposits in recesses and depressions. The movement of the solution increases the pH of the diffusion layer and thereby the speed of the reaction. Brenner and Riddell (51,52) have pointed out that in the case of hot electroless nickel plating baths agitation tends to increase the plating rate. Feldstein and Amodia (53) have established that the maximum deposition rate with acid solution can be obtained at 250-300 cycles/minute of the stirrer in their particular experiment. The degree of lustre and the adhesion of coatings (54) are increased by bubbling of an inert gas with molecular weight under 28 (e.g. hydrogen, helium, methane) or because defects such as roughness, pitting, etc., are eliminated.

Blowing of oxygen through the solution (55) during the process has also been patented as well as the addition of typical oxidising media, e.g. hydrogen peroxide or potassium peroxide.

2.6 Alkaline Hypophosphite Solution

The first patent by Roux (7) and the solution investigated by Brenner and Riddell (8) were both based on alkaline hypophosphite solution. The reaction of nickel ions in alkaline solutions takes place in the same manner as in acid solution: It is accompanied by evolution of hydrogen and oxidation of hypophosphite to phosphite. The alkaline plating solutions have a lower rate of metal deposition than acid plating solutions and the coatings obtained are more porous and less resistant to corrosion but often more lustrous.

2.6.1 Composition

The alkaline electroless nickel/cobalt solutions consist of a source of nickel/cobalt ion in the form of a metal salt, a suitable complexing agent, a reducing agent and a buffer. The common metal salts are nickel chloride (8,9), nickel sulphate/cobaltous chloride, complexing agents and buffers are usually organic acids or their ammonium salts, e.g. citric acid, ammonium citrate, tartaric acid, ammonium tartarate. Alkaline solutions also contain special additives (stabilisers, accelerators, brightening agents) to improve the working of the solution.

2.6.2 Factors influencing the rate of reaction

Temperature, pH, concentration of nickel ions, hypophosphite, complexing agents and special additives influence the rate of metal deposition onto the metal substrate.

(i) Influence of temperature and pH

The rate of nickel/cobalt deposition increases exponentially with temperature (8,9). pH is also important for achieving a smooth deposit. As the reaction proceeds, the alkalinity decreases, which has to be counterbalanced by the addition of ammonia. The rate of cobalt deposition increases with increasing pH value of the plating solution and it slows down considerably if the pH goes down below 7. According to Frieze and others (56), this reduction in the deposition rate is due to the inhibiting effect of the increasing phosphorus content in the coatings which are codeposited with the metal in the deposit.

(ii) Influence of nickel/cobalt and hypophosphite concentrations

The rate of deposition is only slightly increased by increasing the nickel/cobalt ions concentration (8,9). At higher concentrations of metal ions, there could be a deterioration in the quality of the deposit and a decrease in the rate of deposition because of the precipitation of nickel/cobalt hydroxides or basic salts. The rate of deposition is proportional to the concentration of hypophosphite. High contents of the hypophosphite increase the deposition rate considerably, but stabilisers need to be added to prevent spontaneous deposition of nickel/cobalt (9). Nickel phosphite does not precipitate when working with ammonia. The phosphite has no influence on the speed of the plating at concentrations up to 60 g/1.

(iii) Influence of complexing agents

Complexing agents are added to prevent the precipitation of hydroxides or basic salts. Ammonia complexes a large part of the metal ions. Citrate is the most common anion used to complex nickel/cobalt in the form of sodium citrate, ammonium citrate, or citric acid. Lipin and Massjutin(57) have established the optimum concentrations of additives for high rate of deposition and to achieve bright coatings. Schwartz (58) suggested the use of pyrophosphate ions ($K_2P_4O_7$,$Na_2P_4O_7$) as the complexing agent. The speed of the reaction is higher than that with ammonical citrate solution. At $80^{o}C$ it is 15 μm/h and according to him it is due to the greater activity of pyrophosphate. It also offers the possiblity to use the solution at high temperature. Barlett (59) and co-workers have recommended the addition of 1 g/l of ferrous ammonium sulphate and 3.5 g/l saccharin for reducing the internal stress in the coating. Lunjazkas (60), while investigating the conditions for the reduction of cobalt in solution of citrates, established that the basic factors are the molar proportions $C_6H_5O_7^{3-}/Co^{2+}$ and $NH_4^+/C_6H_5O_7^{3-}$ in the solution which determine the speed of reaction. The presence of ammonium ions in the citrate solution changes the speed of the reaction and improves the appearance of the coatings. The optimum contents of ammonium ions is in accordance with a molar proportion $NH_4^+/C_6H_5O_7^{3-} = 4.4$. Any further increase in the ammonium ion concentration reduces the speed of the reaction, this can be explained by the formation of permanent ammonium complexes with cobaltous ions and oxidation of cobaltous ions to cobaltic.

(iv) Influence of the stabilisers and additives

Stabilisers and accelerators are not really typical for alkaline nickel/cobalt electroless plating solutions. Machu and Elgendi (61,62) have found that the rate of deposition and appearance of the coating changes after the addition of cobalt, zinc, cadmium, uranium salts to the electroless nickel alkaline solution. Mixture of lustring agents offers no advantage to the appearance of the coating. The lustre of the as deposited nickel-phosphorus layers is in general lower and reaches the value of the most effective lustring agent only when its quantity in the mixture is overwhelming. The rates of deposition are in general more reduced than would be the case according to the algebraic mean of the activity of the separate lustring agent (62). Some of the thio compounds, e.g. thiourea, act as inhibitors in the electroless nickel alkaline plating solutions, this is due to their hydrolysis into HS^{-} ions (63).

Feldstein and Amodia (64) have investigated the inhibiting effect of a series of oxy ions with a solution containing pyrophosphate by measuring the potential of the oxy ions. He divided these ions into two groups on the basis of their inhibiting action:

Group I: AsO_2^-, IO_3^-, NO_2^-, BrO_3^-, NO_3^-

Each of these ions show an inhibiting effect at various concentrations.

Group II: SO_4^{2-}, HPO_3^-, CHO^-, ClO^-, AsO_4^{3-}, PO_4^{3-}, CO_3^{2-} and others.

In a concentration up to 1 mol/l, these ions do not show any inhibiting effect.

2.7 Hydrazine Solution

Levy (65) was the first who investigated the hydrazine based baths. The deposit obtained contained 97-99% nickel with 2-3% nitrogen as impurity. He asserts that the rate of deposition is directly proportional to the concentration of nickel ions, pH and temperature have an exponential effect. The formation of the deposits can be described by the following equation:

$$2Ni^{2+} + N_2H_4 + 4\bar{O}H \xrightarrow{Cat} 2Ni + N_2 + 4H_2O$$

Dini and Coronado (66) have found that some of the physical properties of nickel deposits obtained after reduction with hydrazine are not as good as those of nickel phosphorus coatings. They are for example, brittle, of dark colour, often exhibit internal tensile stresses and their resistance to corrosion is low. The hardness of the as plated deposit is 400 Hv, but after heating the deposit at 450°C for one hour, it becomes softer ($\simeq$ 150 Hv) and much more ductile.

It is possible to deposit cobalt from electroless plating solution by using hydrazine as the reducing agent. Kozlova and Korovin (67) obtained electroless cobalt deposits from a solution containing tartrate, the rate of deposition was 4-5 μm/h, and the deposits were lustrous and relatively pure. Tokana et al (68) have shown that the rate of cobalt deposition can be increased to 6 μm/h if 2-4 mg of thiourea are added as a stabiliser. U.S. Patent (69) protects the use of ethylene diamine as complexing agent in hydrazine solutions for the deposition of cobalt.

2.8 Electroless Nickel/Cobalt Plating Solutions with Boron Compounds as Reducing Agents

The deposition of electroless nickel using borohydride or alkyl amine boranes as reducing agents has commercial applications (15). The solution containing borohydrides as reducing agents are used mainly in hot alkaline solutions for plating onto many alkali-resistant metals(70) while alkali amine boranes are used in cold-weakly acid baths for plating onto light-metals and plastics (71).

Electroless cobalt can also be deposited from plating solutions using borohydride as reducing agents. Valsyunnene and Prokoptchik (72) have recommended an optimum formula for the electroless cobalt plating solution which works at temperature of 60-70°C.

U.S. Patent (73) has the formulations for an electroless cobalt solution using borohydride as reducing agent and works at low temperature of 35-40°C. Formulations for solutions using amine borones as reducing agents have been also given in the technical literature (73).

2.8.1 Composition of Solutions with Borohydride as the Reducing Agent

These solution usually consists of an aqueous alkaline solution of nickel/cobalt salt, containing a complexing agent in the form of organic compounds and sodium borohydride. The addition of stabilisers in the solution is very important.

(i) Influence of pH and temperature

Regulation of pH is important as the hydrolysis of borohydride ions takes place very fast in neutral or acid media, as shown by equation (1) or (2):

$$BH_4^- + 4H_2O \rightarrow B(OH)_4^- + 4H_2 \quad \ldots\ldots\ldots\ldots\ldots(1)$$

$$BH_4^- + H_3O^+ + 2H_2O \rightarrow H_3BO_3 + 4H_2 \quad \ldots\ldots\ldots(2)$$

In the presence of nickel ions in the solution, nickel boride is obtained (15):

$$8BH_4^- + 4Ni^{2+} + 18H_2O \rightarrow 2Ni_2B + 6H_3BO_3 + 25H_2 \quad \ldots(3)$$

If the pH value of the solution is regulated between 12-14, the formation of nickel boride is made more difficult and the main product is pure nickel (15):

$$4Ni^{2+} + BH_4^- + 8\bar{O}H \rightarrow 4Ni + BO_2^- + 6H_2O$$

High temperatures accelerate the unwanted decomposition reactions (1) and (2), while they are suppressed by the addition of alkali. A working temperature of 92-97°C is preferred and the rate of deposition increases exponentially with increase in the temperature of the solution.

(ii) Influence of metallic ion and borohydride concentration

The increase in the concentration of sodium borohydride leads to the decomposition of the solution, so periodic or uninterrupted addition of the reducing agent in small quantities during plating is recommended (74). High concentration of sodium borohydride is only desirable if plating is carried out at low temperature.

2.8.2 Electroless Nickel/Cobalt Plating Solutions with Amine Boranes as Reducing Agents

The amine boranes are weaker reducing agents than borohydrides, being expensive are used only for the deposition of thin metallic layers. Dimethylamine borane is most commonly used and is soluble in water. It is quite stable. The composition of the solution is similar to alkaline and acid hypophosphite solutions in many ways. With amine borane (31,71) solutions deposition can be carried in a broader range of pH and temperature. The concentration of waste products produced is also low. Moreover amine borane solutions have an almost unlimited capacity for regeneration, and therefore long life. The rate of plating is independent of the concentration of metallic ions; at constant pH and controlled temperature, it is a function of the reducing medium. The solution possesses high stability and can be used continuously in automatic plants. The coating obtained is almost pure nickel and possesses a high conductivity.

Stablisers are added to save the solution from spontaneous decomposition, particularly during the addition of the reducing agent and to increase the rate of deposition. The majority of the stabilisers are bivalent compounds of sulphur and selenium; metallic oxides and salts of the elements in Group II and VI of the periodic table and other compounds. Klein and Zimgieble (75,76) have patended many stabilisers and have also explained the stabilising action of these compounds. They remarked that the addition of the compounds of the elements Cd, Tl, Sn, Pb, As, Sb, Se and Te increases the yield of the reducing agent and accelerates the formation of nickel boron precipitates. So it is not important whether these elements are present as cations or anions (eg. $NaAsO_3$) or at the same time as both.

Gorbunova and co-worker (77) also mention some compounds containing selenium as stabilisers, e.g. 2-methyl selenium-s-thiophene carbonic acid, 3-butyl selenium-2-thiophene carbonic acid.

2.9 Properties of Electroless Plated Nickel Cobalt

Chemically deposited nickel/cobalt coatings differ in their physical, chemical and technological properties from electro-deposited nickel/cobalt because phosphorus or boron is co-deposited with the nickel. The contaminants arise from the oxidation of the respective reducing agents used. Generally the properties of the nickel deposits are closely controlled by the solution used. The nature of the substrate and its pretreatment are also factors which influence some properties of the coatings.

2.9.1 Appearance

Electroless nickel-phosphorus coatings are similar in appearance to bright steel with a more matt, metallic silver colour. Nickel-boron coatings have a matt appearance. Cobalt-phosphorus deposits are also bright while cobalt-boron deposits have a matt appearance.

2.9.2 Hardness

The hardness of electroless nickel coating is higher than that of nickel coatings obtained from conventional electroplating solutions and it is also a little higher than the values obtained for hard nickel electro—deposits Heat treatment of electroless deposited nickel coatings increases their hardness while heat treatment softens electrodeposited nickel coatings. The maximum hardness of nickel-phosphorus and nickel-boron coatings is approximately 1100 Hv and 1200 Hv after suitable heat treatment which is comparable with that of hard chromium. The changes in hardness with temperature and time have been investigated and discussed by many authors (21,31,36,37,78,79, 80,81,82,83).

Maximum hardness is dependent on the phosphorus content in the electroless nickel-phosphorus coating. In the early years of development of electroless nickel coatings, two sets of heat treatments were proposed to obtain maximum hardness.

a. 1 hour at 400°C inert conditions

b. 12 hours at 290°C in air.

Under these conditions nickel phosphorus layers do not oxidise.

Lee (78) reported that one hundred hours heat treatment of the nickel-phosphorus coating at 280°C resulted in maximum hardness.

The hardness of cobalt-phosphorus coatings is similar to that of nickel-phosphorus coatings deposited from alkaline solution. After heat treatment, it changes in the same way as electroless deposited nickel-phosphorus coatings.

2.9.3 Internal Stress

Relatively little research has been done on Internal Stress measurements, and the results obtained are to a certain degree contradictory. The reasons for this are the use of different measuring methods and on the lack of knowledge of the mathematical relationships between the internal stress and the measured parameters. The causes of the stress have not been fully explained but may be caused by impurities in the plating solution.

Spahn (79) had investigated the mechanical properties of electrodeposited nickel and electroless deposited nickel-phosphorus layers. He reports very low values of internal stresses in nickel-phosphorus layers, viz. tensile stress of 1 to 4 Kg/mm^2.

Baldwin and Such (37) have found that internal stress produced in deposits plated from acid hypophosphite solution with pH range of 4.0-6.0 varies in a linear fashion. The stress was tensile at pH higher than 4.65, zero at 4.65 and compressive at pH lower than 4.65. Bartlett et al (59) showed that the internal stress developed in nickel-phosphorus coatings obtained from an alkaline plating solution containing pyrophosphates was reduced by the addition of 3.5 g/l saccharin and 1 g/l ferric ammonium sulphite.

Shemenski et al (84) found that 10 mμ Kanigen thick electroless nickel coatings on 10 mμ thick beryllium strips had a tensile stress of 1.4 - 3.5 Kg/mm^2 in the as plated condition which increased to 7-14 Kg/mm^2 after heating at 190^{o}C. They attributed the associated contraction of the coating to a solid state reaction with the formation of the stable Ni_3P phase.

Parker and Shah (85) have investigated the internal stresses of electroless nickel plated onto six different substrates. The stress varies from tensile to compressive depending on the thermal expansion coefficient of the substrate and the phosphorus content of the deposit. Due to differential shrinkage upon cooling on substrates with high thermal expansion coefficient (aluminium), compressively stressed coatings were produced, while on low thermal expansion metals (such as titanium) tensile coatings were produced. The phosphorus content in the nickel deposit also influenced the internal stress. Increase in phosphorus reduced tensile stresses to zero and ultimately compressive stress developed.

2.9.4 Wear Behaviour and Coefficient of Friction

The resistance of electroless nickel to wear is quite good. It lies between that of hard-chromium and of electrodeposited nickel. With suitable heat treatment electroless nickel wear rate is similar to that of hard chromium. Campbell(86), in his investigations on heat-treated electroless nickel-phosphorus coatings, has shown that a coating of 25 μm thickness was removed completely in the course of nine hours with an average wear rate of 2.8 μm hour. This was nine times better than the wear rate of low carbon steel which was 25 μm/hour while the speed of carbon steel alloyed with nickel was 3.8 μm/hour.

Gostin, (87), gives information about the resistance to wear of nickel-phosphorus layers obtained by tests using the pin and disc method. The rate of wear of carbon steel alloyed with nickel was 3.8 μm/hour, i.e. higher than that of electroless deposited nickel.

Radin et al (37) examined the influence of phosphorus contents in the coating on the wear rate in dry friction. Wear was highest in the as plated condition when phosphorus content was about 7%. When the layer was heat treated the wear rate decreased. After heat treating the coating at 400°C, wear decreased with increase in phosphorus content, while at lower temperatures wear at first decreased with increasing phosphorus content, and then above 7% it increased again. Weightman and Pearlstein (80) showed wear resistance to be generally related to hardness and not to phosphorus contents or other variables. Wiegand and Heinke (88) have investigated the behaviour of nickel-boron and nickel-phosphorus coatings. They suggested that there was not always a relationship between hardness and resistance to wear.

2.9.5 Corrosion Behaviour

Gutzeit and Mapp (89) claim that electroless nickel deposits are in all cases more resistant than electrodeposited nickel coatings of the same thickness. Gutzeit (89) established that corrosive stains appearing on the surface do not spread, even during continuous immersion of the samples in the corrosive medium.

Minger (39) and Brenner have compared the properties of electroless nickel and electrodeposited nickel deposits. The samples were subjected to salt spray, sea water and an Industrial atmosphere (duration of test about 15 months). From the results obtained, they concluded acid electroless nickel deposits are the more resistant coatings to corrosive attack.

Metzger (90) traced the poor corrosion resistance of alkaline electroless nickel phosphorus coatings to the pores in the coatings and he also suggested that coatings free from pores deposited from alkaline solutions are just as resistant as those obtained from acid solutions.

Spraul (91) asserts that heating the coated components for four hours at 750°C improves the corrosion resistance of the deposit. Corrosion resistance also depends on the nature of the substrate surface. It has been shown that even a thin layer applied on a metallurgically better prepared metal surface produced a better corrosion resistant coating (92). Andrew and Heron (93) have investigated the corrosion resistance of samples of steel and brass plated from an acid electroless solution. The amount of phosphorus in the coating varied from 9.3-12.5%. The corrosion resistance of the coating increased with increase in the thickness upto 50 μm. Further increase in the thickness up to 75 μm gave only moderate improvement. Heat treatment for one hour at 400°C led to an increase in the corrosion resistance in atmospheric testing while it led to a deterioration of the corrosion resistance in salt spray test. Nickel-phosphorus layers on brass (thickness 4 to 30 μm) have shown good protective properties against atmospheric corrosion as well as against corrosion caused by perspiration.

Nickel-boron coatings have good resistance to corrosion, this chemical resistance may be due to their peculiar composition and structure, uniformity and low porosity(15).

The corrosion resistance of the nickel-boron coatings can be increased further by oxidising after-treatment. Klein et al (94) have carried out detailed corrosion resistance testing of electroless nickel-boron coatings on steel. Nickel-boron coatings were resistant against hydroxides, alkali carbonates, and chlorinated hydrocarbons. Nickel-boron coatings were also resistant against aqueous salt solutions, e.g. potassium dichromate, potassium permanganate, potassium chlorate, but they did not have good resistance against strong organic acids (e.g. acetic acid, citric acid),ammonia solution and aqueous ammonium salt solutions. Heat treatment at 350°C for two hours duration increased the rate of corrosion.

Better corrosion resistance has been shown by nickel-boron coatings which had been heat treated at temperatures above 600°C in air for two hours. This may be due to the diffusion of nickel into the base material. Nickel-boron coatings show a significant resistance against oxidation at increased temperature, they are noted in the patent specifications (95) as coatings having lower porosity as compared to electrodeposited nickel coatings.

2.9.6 Composition of Electroless Nickel and Cobalt Deposits

The composition of the coating depends upon the conditions of the plating, viz. pH, temperature, loading of the solution, duration of nickel plating, etc. The amounts of the phosphorus in the deposit can reach up to 15% by weight (96).

Electroless nickel-phosphorus coatings on average contain 7-10% phosphorus as well as hydrogen, nitrogen, oxygen and carbon (90). Cobalt, aluminium, iron, manganese, lead and silicon are present in trace amounts (90).

Nickel-boron coatings from a standard Ni-bodur* solution with sodium borohydride as reducing agent contain on an average 5-7% boron (71). The coatings from the various amine-borane solutions contain between 0.4-5% boron (31,71). Electroless cobalt-boron coatings contain about 3% boron (72).

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* Trade name of P1050 (Bayer, A.G.)

2.9.7 Structure of As Plated Nickel-Phosphorus/Cobalt-Phosphorus and Nickel-Boron/Cobalt-Boron Coatings

The electroless nickel-phosphorus as deposited has a very fine grained structure. This is confirmed by X-ray diffraction which shows line broadening typical of small particle size (66). They also observed no changes in microstructure with heat treatment up to 400°C. Graham et al (97) suggested that there is a morphological difference between the deposits obtained from acid and alkaline solutions. Coatings obtained from alkaline solutions are characterised by more frequent change of Laminae than those obtained from acid solutions. Lee (78) confirmed this by measuring the potential value of nickel-phosphorus layers during their anodic dissolution in nitric acid. The exact nature of the lamellar structure of the coating remains unsolved and is a subject for further discussions.

Goldstein et al (98) also examined the structure of chemically deposited nickel-phosphorus deposits containing 7-10% phosphorus by weight using X-ray analysis and electron diffraction techniques. Freshly prepared nickel-phosphorus layers were found to have an amorphous structure. This structure seemed to be independent of the deposition method and the pretreatment of the substrate. The phosphorus in freshly deposited layers was not present as nickel-phosphide, Ni_3P.

Zienkle et al (99) have accepted the amorphous structure of the coatings deposited from acid solutions and containing above 7% of phosphorus. Metzger (90) also proposed the amorphous structure. Randin and co-workers (29,100, 101) have claimed that the phosphorus is present as Ni_2P in freshly deposited electroless nickel-phosphorus layers. They assume that most of the phosphorus is present as nickel phosphide Ni_2P and only a very little is present in its elementary state. On the basis of data obtained from differential thermal analyses, microanalytic and X-ray examination techniques they showed that during heat treatment Ni_2P becomes Ni_3P.

Pai et al (102) measured the size of the crystals in nickel-phosphorus layers to the between 10-20°A. Rantell (103) carried out measurements in the formation of nuclei and the growth of the layers. He found that the nature of the substrates influences the structure of the metal coating. Schlesinger and Morton's (104) stand is also analogous to that of Rantell.

Khoperia and Kharati (105) using electron microscopy and electron diffraction to study the initial stages of formation and distribution of electroless nickel have shown that sensitization helps to produce a compact coating and reduces the nucleus size. When preliminary sensitization is applied, the ratio of crystallisation to that of crystal growth shifts towards increasing crystallization rate. The microstructure of nickel-boron, cobalt-boron coatings obtained by using borohydride as reducing agent is at present the subject of intensive research.

Berzins (106) assumes that in an amorphous matrix, 5-10% of nickel/cobalt was present in the crystalline form. Klein et al (94) reported that 5% of B was present in the elementary stage after X-ray analyses of nickel-boron layers in the as plated condition and after heat treatment.

Electroless cobalt-phosphorus had a layered structure which may be due to the non-uniform distribution of phosphorus (107). Chow et al (108) have shown that the crystal structure of cobalt deposits can be either FCC or HCP depending on the chemistry of the metallisation solution.

2.9.8 Structure of the Heat Treated Electroless Nickel-Cobalt Coatings

Electroless nickel-phosphorus deposits undergo important structural changes during heat treatment. Goldstein et al (98) have found that heat treatment at 200°C for a duration of twenty hours does not produce changes in the structure of the coating, but the halo observed using back scattering X-ray techniques differs from that produced from as deposited layers. Heating at 400°C even for one minute led to significant changes in the structure and intense rings of spots corresponding to cubic crystalline nickel and the phase Ni_3P showed on the X-ray photograph. By increasing the time of heat treatment to two minutes there was an increase in the intensity of the spots and to the appearance of new ring of spots on the X-ray film.

The speed at which the Ni_3P formed is so high that it is practically impossible to control this change. So Goldstein (98) assumes that the metastable solution first changes during heat treatment into a supersaturated crystalline solid solution which afterwards decomposes under segregation of the intermetallic compound Ni_3P. The result is a balanced mixture of the phases of nickel and nickel phosphide. Further heat treatment at increased temperatures (600-800°C) led to recrystallisation.

Graham and others (97) asserted that the crystallisation of the Ni_3P phase in the solid solution is initiated on the basis of β-nickel on a surface of the crystal lattice of β-nickel in which the position of the atoms is similar to that in the crystal lattices surface of Ni_3P.

By heat treating the Ni-B coating at 600°C for 1 hour the crystalline Ni_3B phase is formed in the coating and in addition crystalline nickel is also formed (106).

2.10 Electrodeposited Composite Coatings

2.10.1 Introduction

Electrodeposited composite coatings can be defined as those coatings which are produced when insoluble materials in fine powder form are added to the conventional electroplating solutions and electrodeposition is carried out in the normal manner. In this way two solid materials are combined together in such a manner that the desirable properties of one are enhanced by those of the other, resulting in the production of a single composite system possessing both extended physical and mechanical properties.

2.10.2 Types of Electrodeposited Composite Coatings

Electrodeposition is used to produce three types of composite coatings. They are as follows:

(i) wear resistant coatings
(ii) dry lubricant coatings
(iii) heat treatable metal alloys of varying compositions.

They are produced by suspending the selected materials in fine powder form in conventional plating electrolytes, the particles being held in suspension throughout the plating period by mechanical agitation. Kedward (109) has suggested two efficient means of agitation to keep the particles in suspension during the plating in order to obtain a homogeneous composite on all sizes and shape of components to be plated. One of these processes is the liquid/air process. This operates by drawing the liquid from the top of the electrolyte through a tube connected to a peristaltic pump and reintroducing it through an inlet point at the base of a specifically manufactured conical shaped vessel. Air is pumped into the system to supplement the agitation. The second method is known as the plate pumper process. In this, suspension of the particles is achieved by the vertical reciprocation of a closely fitting perforated plate in the containing vessel. Movement of the plate in this manner causes liquid jets to be formed which agitate the electrolyte sufficiently to keep the particles in suspension. The particle size and shape is also important in composite production. It is possible to deposit almost any particles up to 100 μm size. Particles larger than this size are difficult to incorporate in the deposit by mechanical means. Particles of 1-3 μm are used generally to give smooth deposits and particles below this size usually coagulate in the electrolyte and prevent uniform dispersion. Materials can also be incorporated in the form of fine fibres (110).

Pushpavanam et al (111) suggested that agglomeration of the particles can be prevented by blending the particles with a portion of the electrolyte, and then adding this mixture to the bath.

2.10.3 Wear Resistant Coatings

Wear resistant coatings usually consist of hard particles such as oxides, e.g. SiO_2, alumina, titanium dioxide, zirconium, carbides, e.g. chromium carbide, tungsten carbide, silicon carbides, diamond, and other materials, e.g. glass being codeposited with electrodeposits such as Watts nickel, copper, etc.

2.10.4 Nickel Composite Coatings

Particles of hard materials, viz. carbides, oxides, diamond, have been successfully codeposited in nickel matrices both in Watts type (112,113,114,115,116) and sulphamate baths (117).

Nickel-alumina cermets have high hardness, tensile strength, and wear resistance which are maintained at high temperature. Sautter (113) has reported, that temperature, current density and pH show no influence on the codeposition of alumina with nickel. However Sinha et al (112) reported that incorporation is dependent on the above variables. Cationic surface agents give cracked deposits while anionic surface agents give uniform dispersions of particles (114).

Nickel-TiO_2 deposits have hardness values of about 350 Hv dependent on the plating variables (115,116). They are softer than nickel-alumina composites, even though the amount of TiO_2 codeposited is double that of alumina. Nickel-silicon carbide (117) coatings are deposited, at the rate of 25-125 μm/hour from a Watts bath at a current density of 2-5A/dm^2 at 50°C. A revolving sleeve has been used as a cathode in the codeposition of silicon carbide, and tungsten carbide with nickel cermets containing silicon dioxide and zirconium dioxide with a particle size of 2-5 μm have been successfully codeposited (118). Nickel-silicon carbide cermets deposited from a sulphamate nickel solution at pH 5, and at a powder concentration of 150 g/l in the electrolyte have a hardness of 600Hv with a high abrasion resistance. The internal stress in nickel-silicon carbide and nickel-alumina composites has been determined (119).

The nickel-boron carbide (116), nickel-tantalum carbide (120), nickel-titanium carbide cermets have been reported to be oxidation resistant, corrosion and wear resistant with high tensile strength. Other materials such as uranium oxide, iron oxide, boron nitride (120) and zirconium boride have been successfully incorporated into the metal matrix (121). In electroforming fibres of insoluble inert materials have been employed to give enhanced engineering properties to the formed materials (122,123,124).

Additions of insoluble particles such as oxides, sulphate, carbides, etc., to semi bright or bright nickel plating gives a pattern of fine porosity in the final chromium plate which gives excellent corrosion protection (124,125). In the Nickel Seal* process a maximum addition of 20-30 g/l of insoluble particles is possible, otherwise the deposited nickel is dulled, whereas in the composite coating since the decorative process is not the main criterion, much greater amounts of the insoluble particles is possible.

Diamond particles incorporated in a nickel matrix (126) are used in saws for jewellery and grinding wheels. The life of a diamond grinding stone produced by electrodeposition in the Watts type bath was nearly twenty times greater than that of a conventional stone.

* Trade name OXY product

Nickel cermet coatings are heat resistant up to 800°C. Nickel-boron carbide coatings, even after heat treatment at 375°C, show no change in the surface structure of the deposit. Heat treatment of nickel-alumina composites produced no change in the microstructure up to 750°C(117), but at 1110°C the oxide particles get dissolved and large crystals of nickel aluminate were formed. Nickel-titanium dioxide composites when heat treated in a hydrogen atmosphere showed no change up to 800°C, but at 1000°C there was some change in the structure of the deposit which is attributed to the partial reduction of TiO_2 to Ti_2O_3 or to the redistribution of the particles(114).

2.10.5 Copper Composite Coatings

Generally, it is more difficult to codeposit particles with copper than with nickel. However using copper cyanide solution silica, alumina (115), silicon carbide (117) and boron carbide, all could be codeposited with copper relatively easily. But conducting particles are co-deposited only from acid solutions. Alumina is difficult to codeposit with copper from acid copper sulphate (116) solution, but when a suspension of tungsten carbide was added more alumina was incorporated. Sautter (112) failed to codeposit silicon carbide and alumina from copper sulphate electrolyte and he compared this with the poor behaviour of alumina in nickel deposits below pH 2. Saifullin (128) has reported that the codeposition of alumina in acid copper baths is possible, even in the absence of metallic ions such as thallium, rubidium and cesium as reported by Tomaszewski (129).

Foster and Kariapper (130), have indicated that this behaviour is due to the difference in the adsorption of charge by the inert particles. In an acid fluorborate bath (129), unlike copper sulphate bath, many of the insoluble powders could be codeposited. This indicates that anions have an effect on codeposition as well as the monovalent cations. Aliphatic amines, thallium, cesium and rubidium ions help to maintain codeposition. With other copper baths such as ethylene diamine and pyrophosphate baths (127), those particles which are not codeposited with acid copper bath can be deposited easily. Silicon carbide and chromium diboride and tungsten carbide have been codeposited from a copper sulphate bath on a strip cathode with paddle wheel agitation (131).

2.10.6 Chromium Composite Coatings

Chromium takes a new form when it combines with certain ceramics. When zirconium diboride particles are included in chromium plating baths there is an exothermic reaction and this produces a permanent and unknown change in the solution, so that this composite has better corrosion and oxidation resistance than conventionally plated chromium. Zirconium diboride and chromium tantalum boride cermets show the most promising results (132).

Greco (133) has reported that a codeposit of Cr-TiO_2 gives a hardness of 1500-2300 Hv. Generally, codeposition of oxides with chromium is very difficult to achieve and alumina and SiO_2 in a hexavalent chromium bath gave no deposition (116).

Addison and Kedward (134) showed that composites were produced with trivalent chromium dimethyl formanide solution (DMF). These had inclusions up to 25% by volume but were microcracked and it could only be deposited as a thin layer which made them unsuitable for meaningful evaluations.

2.10.7 Cobalt Composite Coatings

Cobalt-chromium carbide composites have been produced by liquid/air and plate pumper processes by Kedwards and Wright (135). They investigated the application of cobalt-chromium carbide composite for wear control of aircraft engine parts. They obtained a composite coating, consisting of a matrix of cobalt and containing approximately 30% by volume chromium carbide, which is capable of controlling wear on aircraft engine components up to 800°C. They suggested that the carbide additive grows to twice its original volume when heat treated for four hours in vacuum at 1000°C by the diffusion of cobalt into the carbide to produce a M_3C_7 type compound. The wear resistance (135) of the coating probably stems from the formation of a "cobalt oxide" on the load bearing areas of the cobalt components. At high temperatures, due to frictional heating, the oxide develops and rapidly becomes compacted on the surface and finally glazes on the load bearing regions. When the glaze has formed, the wear rate falls dramatically. The formation of the glaze is time temperature dependent; 300°C is the lowest ambient temperature at which glaze forms rapidly. It develops more rapidly at higher temperatures with reduction of the initial metallic wear phase, so with increase in temperature wear resistance improves.

Foster et al (136) have investigated the effect of carbide content and pre-heat treatment on the oxidation characteristics of cobalt-chromium electrodeposits in air at 1000°C. They found that chromium carbide is unstable at elevated temperatures in the electrodeposited cobalt composite coatings, the rate of carbide breakdown being directly proportional to the temperature and is very rapid at 1000°C. The carbide breakdown is controlled by the loss of carbon to the substrate, if it contains strong carbide forming elements and to the atmosphere. The supply of chromium to the oxide scale improves the oxidation resistance of the cobalt.

Chisholm (137) has reviewed cobalt-chromium electrodeposition, and described results for composite electrodeposits from a fluoborate and dimethyl formamide water bath. The rate controlling factor was the inability to sustain codeposition, and thus achieve the requisite thickness for coatings and electroforms.

2.10.8 Lubricant Coatings

Dry lubricant coatings are produced by the inclusion of certain laminar solids like molybdenum disulphide in a metal matrix. Such coatings exhibit both low coefficient of friction and low wear rate. The codeposition of a laminar solid is more difficult than the codeposition of ceramic particles. Nickel-molybdenum disulphide systems have a low inclusion content, but which is sufficient to generate a low shear strength surface film under conditions of low load (125,126,127). Lowering pH and current density raises the volume percent (138) of molybdenumdisulphide in the coating. The same behaviour is observed in the codeposition of graphite mica and polytetra-fluoroethylene. This effect can be attributed to the adsorption of hydrogen ions on the particles (127). Nickel-boron nitride composites have similar properties to nickel-molybdenum disulphide but possess high oxidation resistance and are used to overcome the problems of fretting corrosion. Five micron size mica particles are codeposited with a metal to produce a surface which reduces wear (139).

Graphite is included in nickel or copper matrices either as fibres (140) or powder (141) to produce a dry lubricating surface. Extensive studies are being carried out on the codeposition of barium sulphate in nickel or copper baths since they are useful in sliding contacts because of their antistick properties (130).

2.10.9 Metal Alloys

Another object of composite coatings is the production of heat treatable metal alloys. Chromium powder has been codeposited with nickel and heat treated above 1000°C to produce nickel-chromium alloys (141). By this technique cupro-nickel stellite and ball bearing steels have also been produced. Metal powders and ceramics codeposited simultaneously with chromium (133) and Co-Mo alloys are being developed as high temperature corrosion and oxidation resistant coatings.

Bazzard et al (142) have used a sponge covered roller along with usual mechanical stirring to control dendritic like growths and porous deposits to produce nickel-chromium alloys. Saifullin et al (128) have obtained relatively compact copper deposits containing 8-12% nickel powder, with 25 g/l of nickel powder in a copper sulphate bath. The use of nickel matrix layers produced by the codeposition of nickel powder in nickel matrix in electron tubes has been studied by Varadi et al (143). Such a nickel matrix improves heat or electrical conductivity, adherence to the base metal, decreases the interfacial resistance and minimises the electrical effect of high voltage sparking.

Nuclear materials such as UO_2 or ThO_2 can be codeposited with nickel to be used as fuel elements or as radiation detectors. Neutron absorbing materials like boron and its compounds have been codeposited with nickel to produce reactor coating materials. Efforts have been made to include luminescent phosphorus in the metal plating which can be used in the decorative field in the name plates and traffic signals (117).

2.11 Mechanism of Codeposition with Electrodeposited Coatings

Williams (118) has attributed codeposition to the cataphoretic movements of the particles to the cathodes and subsequent entrapment into the growing metal films. pH plays an important role in the successful codeposition of particles, but there are two extreme views on the mechanism of powder transport involved in this process. Electrophoresis is said to be taking part and on the other hand the particles are carried to the cathode simply by mechanical agitation of the electrolyte and are trapped by the deposited metal. Most of the theories postulated rely on an attractive force holding the particles at the cathode while the metal film grows around it.

Brandes (116) states the importance of surface charge to particle size and the microthrowing power. Electrophoresis may be an important effect, once the particle has entered the diffusion layer surrounding the cathode. Kedwards (109) suggests that high current density areas will be produced when large numbers of particles are entrapped, causing an increase in the thickness of the double layers. The voltage drop will then increase and this is sufficient to cause the codeposition of other particles in the neighbourhood of the double layer. So electrophoresis plays an important part as concluded by Kedward (109).

Foster et al (130) proposed that the adsorption charge which is manifested by the Zeta potential is the principal factor determining codeposition. From the study of codeposition from copper sulphate and nickel baths they conclude that deposition occurs readily in a nickel bath due to strong adsorption of nickel ions on the particle surface, thereby producing a surface charge which causes the particles to be attracted to the cathode surface and cling to it. Since the cation adsorption in copper sulphate is very small, the attractive force towards the cathode surface is not strong and additions of thallous or rubidium ions produce a large positive charge on the particle surface thereby promoting codeposition.

In the case of metal powders like chromium, once the incorporation has occurred, the metal particle becomes an integral part of the cathode surface contributing to an increase in current density on the cathode, which would ensure rapid incorporation and because of this dendritic growth of the cathode surface is avoidable. Bazzard et al (142) have concluded that inclusions in the cathode must depend on the residence time, microthrowing power, and thickness of the deposit. Sykes et al (144) have found that the zeta potential of alumina in Watts nickel or acid copper sulphate plating bath is very small and negative. There will therefore be no electrophoretic transport of the particles to the cathode in either solution. In addition plating tests with alumina dispersed in nickel sulphamate or copper fluoborate solution, in which the zeta potential would be positive gave similar results to the sulphate baths, thus deposition was obtained with nickel but not with copper. The only way in which electrical effects would assist codeposition of alumina particles is if they are held at the cathode by the electrostatic forces between the positive charge on the cathode surface and the negative charge on the cathode. Snaith et al (145) have suggested the importance of solution pH on the ease of deposition of solid particles. Kedward (109) and Brandes (116) suggested that pH of a solution was important in the codeposition of certain materials, particularly lubricant such as graphite and molybdenum disulphide. They suggested that particles of these materials could absorb hydrogen ions from solutions of low pH (below 4) thus becoming positively charged. The findings on silicon carbide show no sudden change in zeta potential as the pH of the solution is lowered. The change of the zeta potential with electrolyte concentration is dependent on the total specific conductance of the solution, that it is an ionic strength effect rather than depending on the particular electrolyte or combination of electrolytes present. Consequently pH has little effect on the zeta potential in the case of silicon carbide. Particles may be mechanically trapped on those parts of the cathode surface which are rough or irregular, so the bond between the metal and the ceramic particle appears to be mechanical. The hydrodynamic transport of the particles to the vicinity of the cathode, followed by the possible electrophoretic transport of the particles within the cathode are the most significant factors in the electrodeposition of cermets.

Snaith et al (145) in their study of the mechanism concluded that in electrolyte solutions positive ions were contact adsorbed on the materials, i.e. quartz, silicon carbide and chromium diboride powders, the degree of adsorption increasing with concentration and decreasing with temperature. As the concentration was increased the amount of positive charge adsorbed became equivalent to and finally greater than the negative charge on the ceramic material, resulting in a reversal in the polarity of the charge on the ceramic material. The conditions required for maximum positive charge on the materials studied were low temperature and high electrolyte concentration. Measurements of heats of adsorption suggest that this adsorption is physical in nature.

2.12 Electroless Composite Coatings

Encouraged by the successful development and application of electrodeposited composites, work on codepositing hard particles in electroless deposit was initiated. The further potential advantages of electroless layers inherent uniformity, corrosion resistance and hardenability added further impetus to the development of electroless composites.

Metzger et al (146,147) in their patents have described their invention for electroless deposition incorporating particles. The particles were insoluble in aqueous solutions and were non catalytic and inert with respect to the electroless reducing agents for the electroless metals. The particle size ranged from 0.1 μm to about 100 μm and constituted 1% to 30% of the coating volume. The particles were maintained in suspension in the bath by streams of minute bubbles of gas passing through the bath or by agitation within the bath.

Besides electroless nickel composites, electroless cobalt and electroless copper formulations have also been published. The hardness values and Taber wear index of the deposits produced and effects of heat treatment have also been discussed.

Epifanov et al (148) used titanium dioxide powder to obtain high quality coatings of nickel-phosphorus titanium-dioxide composites. The composite coating possesses less porosity than electrodeposited composite coatings, with a similar quantity of nickel applied per unit of the surface. The addition of titanium dioxide increased the deposition rate and had no effect on the phosphorus content.

The microhardness of the coatings increased strongly and passed through a maximum at a titanium dioxide content of 2-4% and changed little with a further increase in titanium dioxide content. Ammonium fluoride in the electrolyte enabled the composite coatings to be applied onto aluminium components without preliminary zincate treatment.

Saifullin et al (149) have obtained nickel composite coatings containing amorphous boron or silicon carbide, particle size 1-8 μm. The rate of deposition was lower from the suspension than from the pure solution. The microhardness of the composite coating without heat treatment was approximately the same as obtained by electrodeposited composite coatings, but the wear resistance was higher by a factor of 1.2-1.5.

Metzger et al (150) have discussed the parameters affecting the deposition of electroless composite coating. The factors studied were pH, agitation and the amount of solid matter in suspension. They concluded that electroless nickel composite coatings could be used in applications, e.g. die-cast moulds used for the manufacture of glass fibre reinforced thermosetting plastics. The mould lasted for 10,000 mouldings without any treatment, 30,000 mouldings with an electroless nickel coating and some 150,000 moulds with a dispersion hardened heat treated 50 μm electroless nickel composite coating.

Lukschandel (151) produced electroless nickel composite coatings containing diamond particles. The coating had high wear resistance. These coatings meet the stringent requirements for machining and finishing tools. The diamond particles used in this application were of 6-12 μm in diameter.

Hubbell (152) discussed the use of chemically deposited composites for commercial applications. In metal forming pick-up and galling is overcome by the use of dies plated with a composite coating (152). An electroless nickel matrix, coupled with the wear resistance of codeposited silicon carbide, resists abrasion and helps release unbroken sand cores from core boxes. In Germany composite coatings have been successfully applied to epoxy plastic patterns. Usually 2,000 moulds were made before applying any coating, but after coating them with electroless nickel composites 25,000 impressions were made prior to damage. Hubbell (152) claims that more than 2% by weight of particles in the bath contributes to bath instability without adding significantly to the volume percent of particles in the deposit. Different particle, sizes and specific gravity have an effect on particle codeposition in the composite.

Borodin (153) has obtained a variety of electroless nickel composites coatings with several types of particle sizes ranging from 1-10 μm. The particles were kept in suspension in the plating bath with a stirrer. The hardness of the nickel deposits is increased significantly by oxides and carbides regardless of the crystal structure of the particles, but crystal structure has a marked effect on the wear resistance of the coating, with cubic titanium carbide having minimum specific wear. Carbides have a relatively low friction coefficient in the absence of a lubricant.

Parker (154) in his patent has described a process for the codeposition of inert, inactive, non catalytic metallic particles with electroless nickel/cobalt using hypophosphite based baths. The size of the particles which can be codeposited ranges from 0.1-50 microns and the volume percentage of the metallic particles codepositing with the metal ranges from 25-60% depending on the plating variables. The hardness of the coating obtained can be increased up to 1300 Hv by suitable heat treatment.

3. EXPERIMENTAL PROCEDURE

3.1 Introduction

The method involved in obtaining the optimum plating solutions and conditions for deposition are described for electroless nickel and cobalt deposits with and without particles. The metallography and topography of the deposits were studied by scanning electron microscope and optical microscopy and the percentage of particles by volume in the composite deposit was determined.

Microhardness of the deposits were determined in the as plated condition, and after heat treatments in vacuum and air for different temperatures and times. The wear rate and coefficient of friction of the deposits in two different conditions were measured with a pin and disc machine and the wear resistance in forging was determined by coating flat dies and then subjecting them to a standard test. The corrosion resistance of the deposits were compared in the salt spray test and by exposure to atmosphere. Potentiodynamic curves of the deposits were also obtained to find the corrosion potentials. The mechanical ductility of the deposits was measured using a hard beam tensile machine.

3.2 Plating Solution Compositions

Four acid electroless nickel and two alkaline electroless cobalt solution formulations given in the literature were investigated. A commercial electroless nickel plating solution, Nifoss 80*, was also used in the work.

* Trademark, W. Canning & Company Limited

The materials used to make up the plating solutions were of reagent grade and they were dissolved in deionised water. The formulations of the solutions selected and their operating conditions were as follows:

1.	Nickel chloride	30 g/1
	Sodium hypophosphite	10 g/1
	Glycollic acid	35 g/1
	pH range	4-6
	Temperature	87-90°C
2.	Nickel chloride	17 g/1
	Sodium hypophosphite	14 g/1
	Acetic acid	12 g/1
	pH range	5.2-5.5
	Temperature	85-90°C
3.	Nickel chloride	26 g/1
	Sodium hypophosphite	24 g/1
	Lactic acid	27 g/1
	Propionic acid	2.25 g/1
	pH range	4-5
	Temperature	92-94°C
4.	Nickel sulphate	20 g/1
	Sodium hypophosphite	27 g/1
	Sodium succinate	16 g/1
	pH range	4.5-5.5
	Temperature	92-94°C

5.

Cobalt chloride	63 g/l
Sodium hypophosphite	58 g/l
Trisodium citrate	58 g/l
Ammonium chloride	42 g/l
pH range	8-9
Temperature	90°C

6.

Cobalt chloride	30 g/l
Sodium hypophosphite	30 g/l
Sodium metaborate	40 g/l
Trisodium citrate	50 g/l
pH range	7-9.5
Temperature	80-84°C

7.

"Nifoss 80"

Nifoss Base solution N2131	100 ml/l
Nifoss initial solution N2132	250 ml/l
pH	4.2-5.5
Temperature	80-97°C

Particles used

2-3 µm chromium carbide

10-12 µm chromium metal

3.3 Method of Solution Preparation

The preparation of the solutions need extra care as they may decompose spontaneously unless special precautions are taken. All the components are dissolved separately in deionised water with gentle heating and stirring, taking care that the temperature does not exceed 70°C. Then the required organic acid is added to the nickel salt solution, so that a stable nickel ion complex is produced. The sodium hypophosphite is added to the stabilised nickel solution and pH of the bath is adjusted by the gradual addition of 5% NaOH or nickel carbonate solution until the required pH is obtained. This is checked with a Universal Indicator paper. In the case of "Nifoss 80" solution, the bath is half filled with deionised water, and the required volumes of "Nifoss 80" base and "Nifoss 80" initial solutions are added. The volume is adjusted with deionised water and the pH is checked with Universal Indicator and adjusted with either 5% HCl or 5% NaOH as necessary.

3.4 Pretreatment of the Substrate Prior to Plating

Electroless nickel and electroless cobalt were deposited on mild steel panels 7.5 cm x 10.00 cm. The panels were given the following cleaning cycle before plating.

1. Polish on soft mop with a proprietory polishing compound

2. Degrease with acetone

3. Anodic cleaning in an alkaline cleaner at a current density of 4 amps/dm^2 for 4 minutes at 70°C

4. Rinse in water

5. Dip in 50% v/v hydrochloric acid for 15-30 seconds

6. Acid swill

7. Alkaline swill

8. Anodic cleaning in a cyanide cleaner at a current density of 4 amps/dm^2 for two minutes

9. Alkaline swill

10. Dip in 20% v/v sulphuric acid for 10-15 seconds

11. Acid swill

12. Immediate transfer to the plating solution.

3.4.1 Selection of Plating Solution

For selecting the optimum plating solution the following procedure was used. The plating solution was contained in a two litre beaker. The cleaned mild steel panel was suspended in the solution by a copper wire attached to a perspex rod at its upper end. Solution lost due to the evaporation of water was made up by the continual addition of nearly boiling deionised water to the plating bath. To avoid streaking and to obtain uniform deposits on the panels, the solution was stirred with a mechanical stirrer. Plating was carried out for one, two and three hours, a new solution being used each time in order to have reproducibility. After plating, specimens were cut from the panel using a guillotine to minimise distortion. They were then mounted in bakelite, ground and polished. The rate of deposition was determined by measuring the thickness of the coatings by examining with a projection microscope. For electroless nickel it was found that the rates of deposition of solution No. 3 and "Nifoss 80" were 14 μm and 20 μm per hour respectively at 92°C while the rates of deposition from solutions 1, 2 and 4 were very low being 2-5 μm per hour. The latter solution also decomposed very rapidly. For electroless cobalt, the rate of deposition of solution number 5 was 12 μm/hour, while that of number 6 was 4 μm/hour.

Acid electroless nickel plating solution number 3 has a good rate of deposition, but it has to to replenished to maintain the rate of deposition, which is a time consuming and expensive process. Therefore the commercial solution "Nifoss 80" was selected to be used for the subsequent work.

For electroless cobalt deposits, solution number 5 was selected for further investigation, as it has a high rate of deposition, is easy to operate and has a long plating life.

3.5 Method of Agitation

For the deposition of electroless nickel and electroless cobalt composite coatings, 10 g/l of chromium carbide or chromium powder was added to the plating solutions.

Mild steel panels 10.0 cm x 7.5 cm were cleaned as described in section 3.3 and then immersed in the plating baths containing the inert particles. As the particles are denser than the plating solution they settle to the bottom of the bath, and so it is essential to agitate the solution to keep the particles in suspension throughout the plating period.

The following methods were investigated to keep the particles in suspension:

i) Air agitation
ii) Bath circulation
iii) Liquid Air process
iv) Plate-pumper process
v) Ultrasonics
vi) Mechanical stirrer

(i) <u>Air agitation</u>

Clean compressed air is pumped into the plating solution contained in a conical shaped vessel either from the top, through glass tubing which forces the compressed air to the bottom of the bath, or the air is supplied from the bottom of a conical vessel. The pressure of the air supplied is controlled to prevent spillage.

(ii) <u>Bath circulation</u>

A peristaltic pump is used to transfer the suspension from the bottom of a conical shaped vessel and to reintroduce it at the top of the bath.

(iii) <u>Plate-pumper process</u>

In this process the suspension of particles was maintained by the vertical reciprocation of a perforated plate (A),

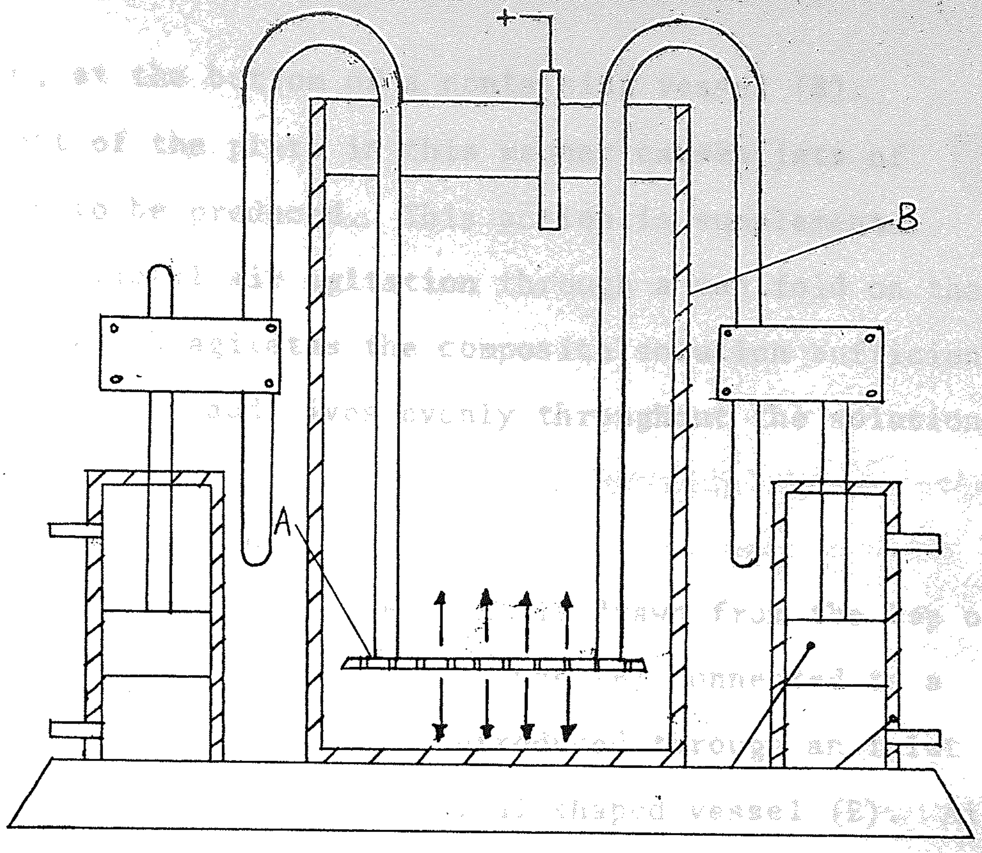


FIGURE 1 PLATE PUMPING UNIT

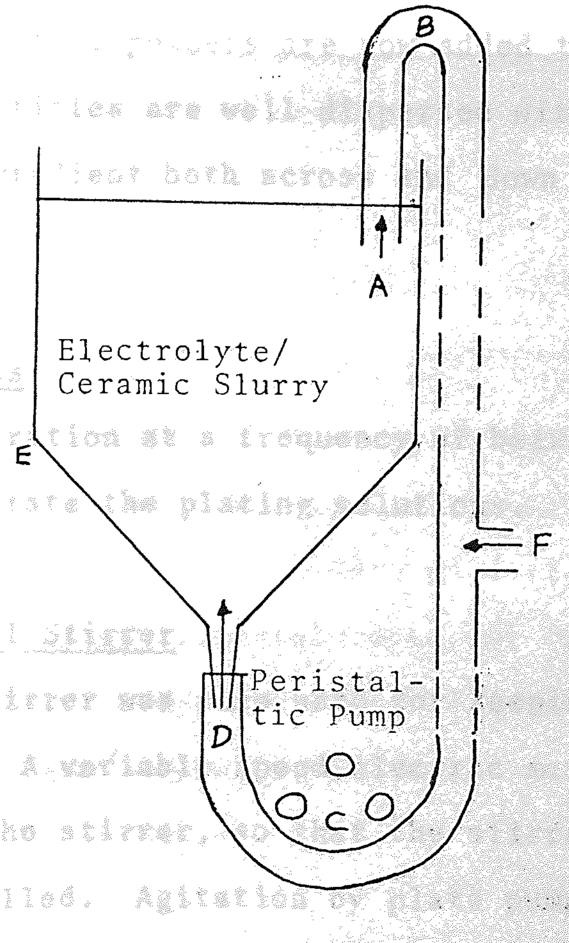


FIGURE 2 LIQUID/AIR PROCESS

Fig. 1 , at the bottom of a containing vessel (B). Movement of the plate in this manner causes jets of liquids to be produced. This action is supplemented by conventional air agitation through a manifold on the vessel, which agitates the composite solution sufficiently to suspend the additives evenly throughout the solution.

(iv) Liquid-Air process

In this process liquid (Fig. 2) is drawn from the top of the electrolyte (A) through a tube (B) connected to a peristaltic pump (C) and reintroduced through an inlet point (D) at the base of conical shaped vessel (E). Air is blown into the system at point (F) by suitable adjustment of the pumping rate, causing violent agitation of the solution. When fine powders are now added to this dynamic system, the particles are well dispersed with minimal concentration gradient both across and down through the electrolyte.

(v) Ultrasonics

Ultrasonics vibration at a frequency of between 12-26 kHz was used to agitate the plating solutions.

(vi) Mechanical Stirrer

A mechanical stirrer was also used for keeping the particles in suspension. A variable speed electric motor provided the power for the stirrer, so that the stirrer movement could be controlled. Agitation by plate pumper, liquid-air process, air agitation (especially if the air is supplied at the bottom of the conical plating vessel) result in homogeneous composite deposits. With agitation by ultrasonics the deposits were more porous and were not uniform and there were few particles in the deposit. Since the composite deposits produced by air agitation with compressed air supplied at the bottom of the conical shaped vessel were as good as those produced by the other methods, it was used throughout the subsequent work on nickel.

Unfortunately, due to the presence of ammonia in the cobalt plating solution any form of agitation employing air could not be considered as this would increase the rate of ammonia evaporation. Thus, although not wholly satisfactory with respect to particle dispersion in the plating solution, mechanical agitation was employed using a glass impellor.

3.6 Plating Conditions

(i) Temperature

To determine the optimum plating temperature for the electroless plating solutions containing particles, the rate of deposition onto the standard mild steel panels was measured at various temperatures. For "Nifoss 80" solution the optimum temperature was 92°C and for electroless cobalt solution was 90°C. At temperatures above these optima the solution decomposes.

(ii) pH value

The electroless solutions containing the required particles were operated at different pH ranges to find the optimum pH for maximum rate of deposition. The optimum pH for "Nifoss 80" solution was 4.5 and for electroless cobalt solution 9.

3.7 Determination of the Optimum Concentration of the Particles for Electroless Composite Deposits

Different concentrations of particles ranging from 10 g/1 to 200 g/1 of chromium carbide and chromium were added to the electroless plating solutions and deposition was carried out on mild steel panels which had been throughly precleaned. Transverse sections were then cut from the coated panels using a guillotine to minimise distortion and cracking of the deposit. These sections were then mounted in conducting bakelite, ground and polished with 0.25 µm diamond paste in a vibratory polisher to ensure that the surface was as flat as possible. The polished specimenswere then examined,using a Quantimet microscope, to determine the volume fraction of carbide particles in the deposit. The equipment was operated at the limit of its magnification range (x 1600) using an oil immersion lens.

3.8 Electron Microprobe Analysis of the Deposits

Transverse sections were cut from the coated mild steel panels. The sections were then mounted in conducting bakelite, ground and polished with 0.25 µm diamond paste in a vibratory polisher to ensure that the surfaces were as flat as possible.

Nickel, cobalt, chromium and phosphorus were quantitatively determined using the electron-probe microanalyser. This was operated at 20 Kv using a 50 nano-ampere beam current. Standard crystals of nickel, cobalt and chromium were used for analysing nickel, cobalt and chromium, but a copper phosphide (Cu_3P) crystal was used for the analysis of phosphorus. Corrections were made for background count, dead time, fluorescence, and adsorption effects to precisely determine the percentages of the above mentioned elements present. The amount of chromium carbide was calculated from the chromium analysis.

3.9 Optical Examination

Mild steel panels after precleaning were plated with electroless and electroless composite deposits for time periods of $\frac{1}{4}$, $\frac{1}{2}$, 1, 2, 4, 6 and 7 hours respectively. Cross sections were prepared from each of the panels using the same method as that employed prior to electron-probe microanalysis. The cross sections were examined with an optical projection microscope and micrographs of the sections were taken with a 35 mm camera.

3.10 Scanning Electron Microscope Examination

The scanning electron microscope was used to examine the surface of the samples cut from the centre of the panels coated for different times. 2 cm x 1 cm samples were cut from the panels using a guillotine, mounted on the stubs and viewed directly.

Polished cross sections prepared for optical examination were etched and examined by the scanning electron microscope to study the distribution of the particles in the composite deposits.

To study the structure of electroless (nickel and cobalt) deposits, cross sections cut from the plated panels were polished in the same way as for electron probe analysis. Electroless nickel deposits were etched electrolytically in 10% chromic acid solution at 2 volts for 10-15 seconds. Electroless cobalt was etched electrolytically in an electrolyte containing 10 g/l of chromium anhydride and 3 g/l of sulphuric acid at a current density of 0.5-1 A/dm^2 or etched anodically in ortho-phosphoric acid solution.

3.11 Microhardness Measurements

Hardness measurements were made on the deposits plated on mild steel panels, the minimum thickness of the deposits being 30 μm. Sections were cut from the plated panels using a guillotine and were heat treated in the temperature range 200-800°C. Half of them were heat treated in vacuum (better than 10^{-4} torr) for times up to 24 hours and half in air for up to 100 hours. The hardness was determined using a Vickers microhardness tester with a load of 20 gms. Every value reported is an average of at least six hardness measurements taken from indentations that were free from cracks and distortions.

FIGURE 3 PIN AND DISC WEAR TESTING EQUIPMENT

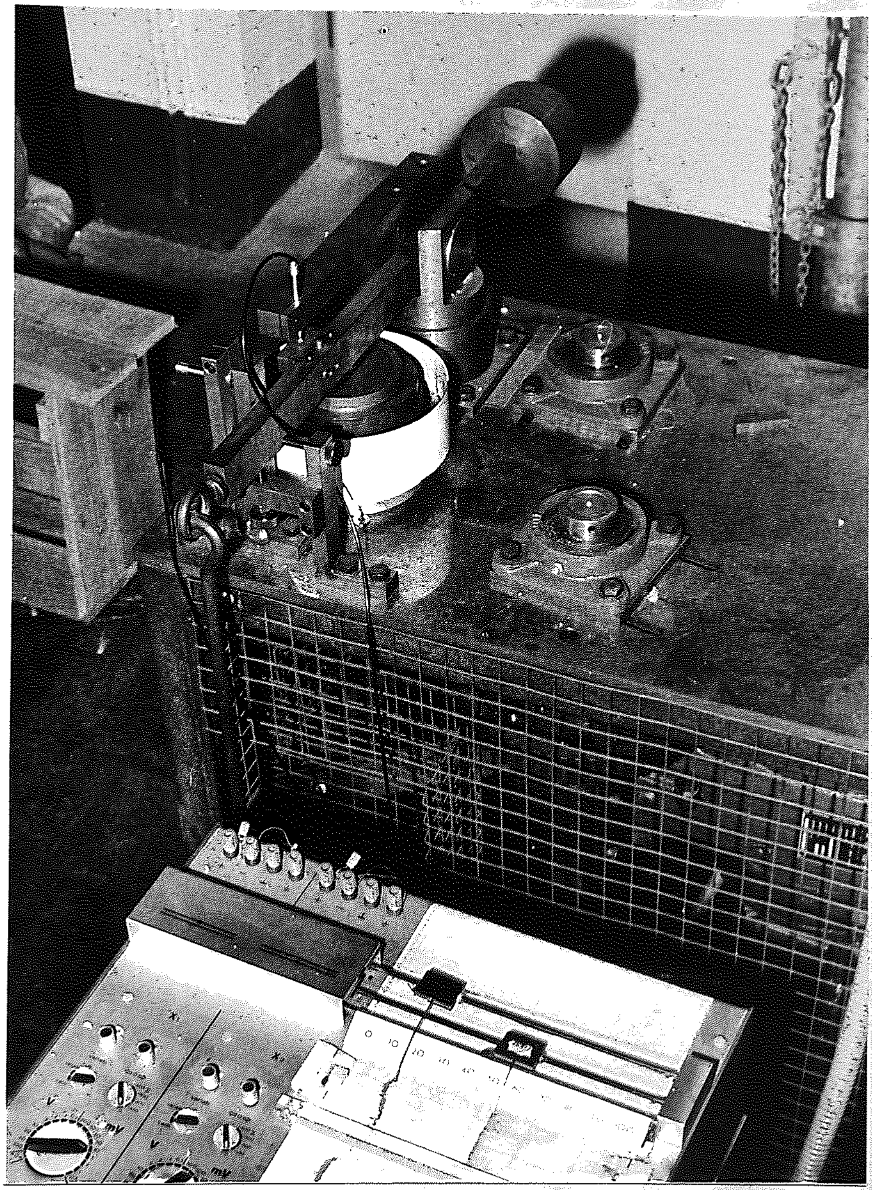
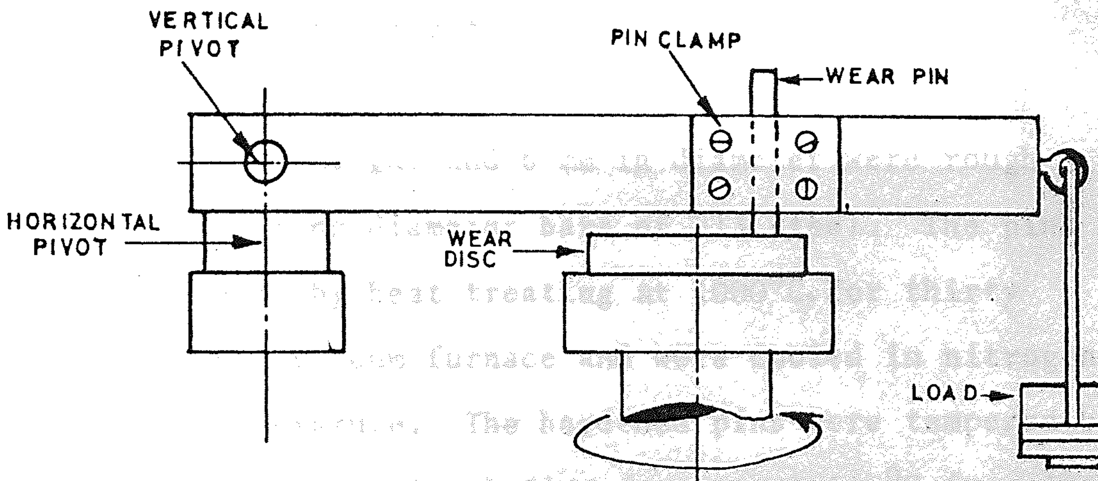


FIGURE 4 DIAGRAMMATIC REPRESENTATION OF PIN AND DISC WEAR EQUIPMENT



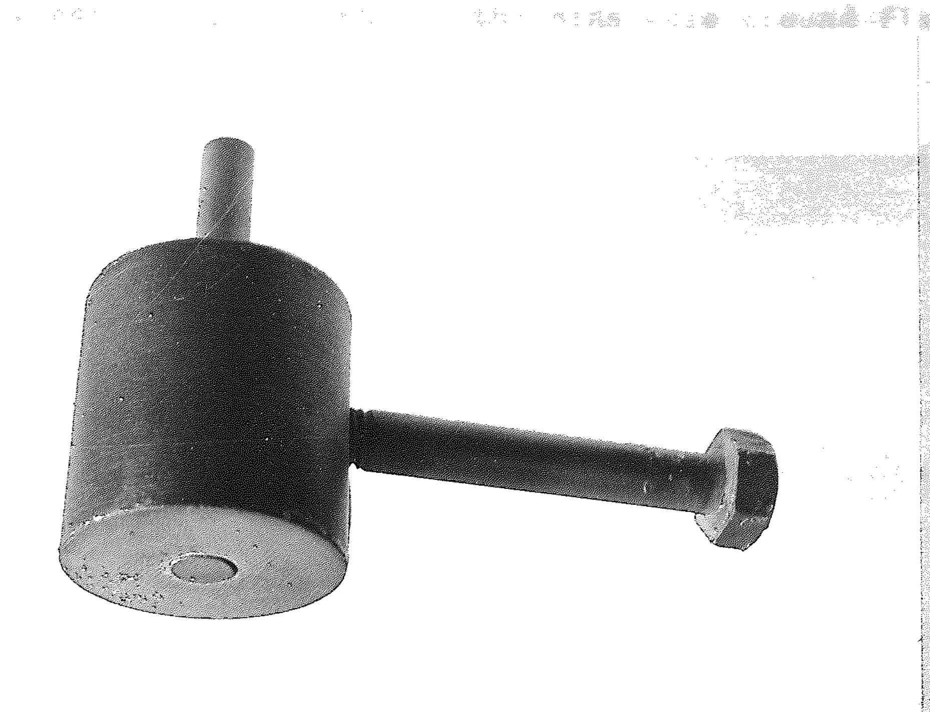
3.12 Wear Rate and Coefficient of Friction Measurements

The pin and disc method was used for determining the wear rate and coefficient of friction of electroless and electroless composite deposits. The pin and disc wear test equipment is shown in Fig. 3 and a diagrammatic representation is also given in Fig. 4. The pin under test is clamped in a rigid arm which is free to move in the vertical and horizontal planes. Appropriately positioned transducers measure the wear of the pin and the frictional force produced at the pin and the disc interface. The load is applied at the end of the arm, the actual load at the pin being calculated by taking moments about the pivot.

Pins 60 mm in height and 6 mm in diameter were rough turned from 8 mm diameter bars of B13 steel. The pins were hardened by heat treating at 1000°C, for thirty minutes, in a vacuum furnace and were cooled in nitrogen to room temperature. The hardened pins were tempered by heating in an air circulating furnace at 550°C for ninety minutes and cooled to room temperature. After repeating the tempering process the hardness of the pins was 520 Hv.

Discs 12.5 cm in diameter and 1.5 cm thick were rough turned from suitably sized stocks of EN31 steel. They were hardened by heating in a salt bath at 820°C, for 30 minutes, and quenched in a water soluble mineral oil. The discs were heated before being put into the salt bath to prevent thermal shock. They were then rinsed with hot water and tempered by heating in an air circulatory

FIGURE 5 JIG FOR FLATTENING PIN TIPS



furnace at 150°C for one hour and cooled to room temperature. The hardness of the disc was 720-724 Hv.

The choice of the materials was based on experience gained from earlier work (155).

To measure the wear rate of the electroless and electroless composite deposits, it was decided to coat pins rather than discs, because more time was required to coat a disc and the weight loss in the case of the disc would be small compared to its mass.

After descaling, the end of the pins were ground flat and made perpendicular to their axis using the jig shown in Fig. 5. The heights of the pins were measured and were lacquered all over except for one end. They were then dried in an oven and repainted.

The unlacquered end of the pin was degreased with acetone and the following preplating operations were carried out before introduction into the plating bath.

1. Anodic cleaning in hot alkaline solution at 70°C for 4 minutes at 4 A/dm^2.
2. Rinse in water
3. Anodic treatment in commercial cyanide solution for 2 minutes at 4 A/dm^2 at room temperature
4. Rinse in water

5. Dip in 20% sulphuric acid for 15-20 seconds
6. Rinse in water
7. Anodic etch in sulphuric acid solution, 50% v/v concentrated acid at 6.5 volts (approximately 60 A/dm^2) until the surface attained a light grey appearance
8. Rinse in water
9. Anodic treatment in commercial cyanide solution, 4 A/dm^2 at room temperature
10. Rinse in water
11. Dip in 2% sulphuric acid, for 10-15 seconds
12. Rinse in water

Then the pins were immersed in the plating solution and deposition was allowed to take place for three hours, in order to build up a thick deposit. The lacquer was then removed with acetone and the plated face ground flat, removing the minimum amount of deposit. The new height of the pin was measured to determine the thickness of the deposit.

Some pins were heated to 400°C in vacuum for one hour, so that the deposits attain hardness of more than 1000 Hv. To carry out a test, the pin was clamped in the arm taking utmost precaution that the arm remained in a horizontal position whilst the clamps were tightened such that the entire face of the pin was in contact with the disc.The disc face was

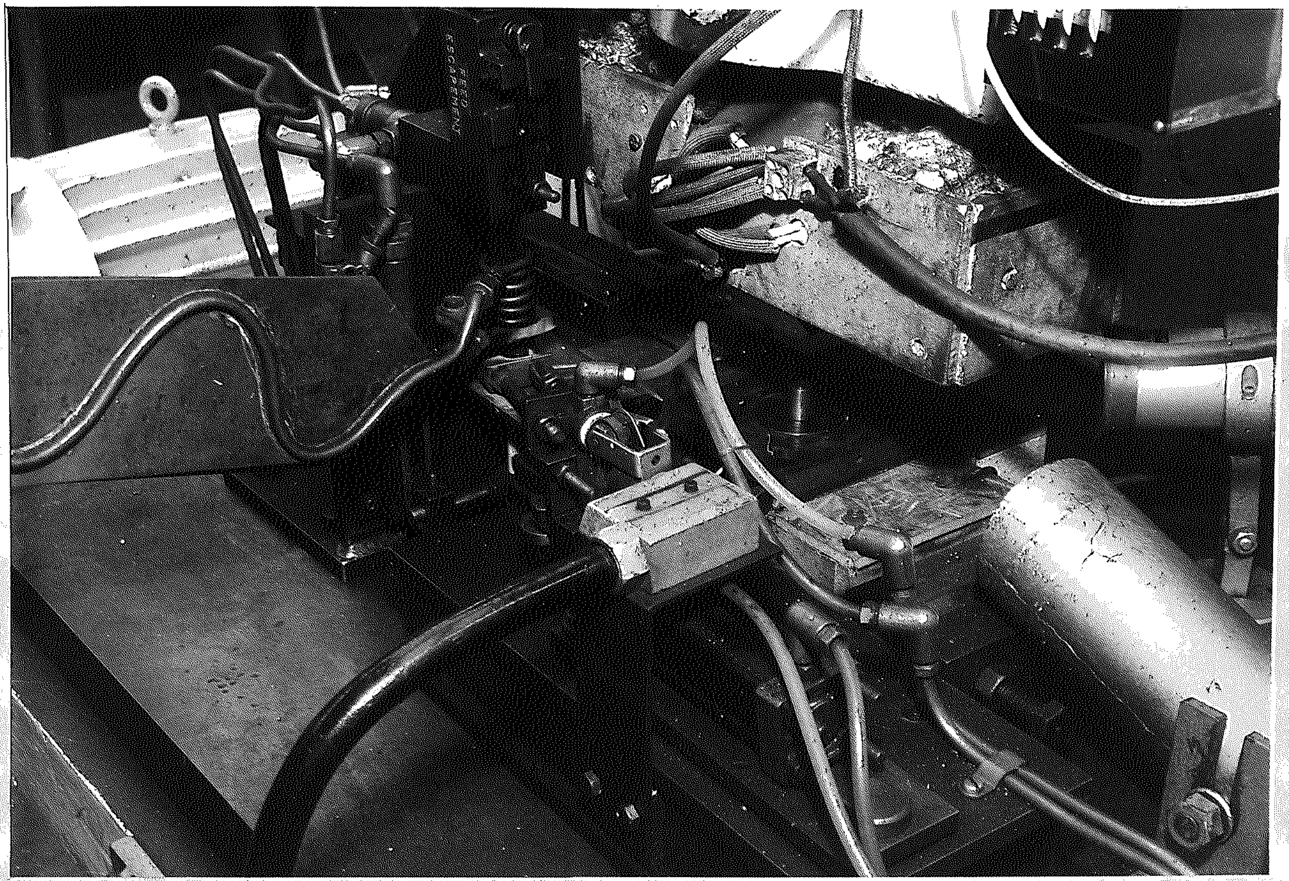


FIGURE 6 FORGING EQUIPMENT SHOWING BILLET IN POSITION ON DIE PRIOR TO FORGING

degreased carefully before the start of the test to prevent contamination. The time was recorded and the disc set in motion with the load applied to the pin. In the initial tests the load applied was 2 Kg, but later 10 Kg load was applied. Changes in the length of the pin and the frictional force were recorded on a chart recorder. The transducers recording the changes in the wear were calibrated as 1 mm = 1.028 mv and the transducer recording the changes in frictional force was 1 Kg = 3 mv.

After a suitable time (usually 2-3 hours) the test was stopped and the pin removed and remeasured. The pin wear relative to the distance the disc surface travelled in contact with it, is a convenient method of quoting wear results for easy comparison. The distance travelled by the disc = πDRT where D = wear track diameter (cm), R = speed of rotation (r.p.m.) and T = time of the test (minutes).

The coefficient of friction between the pin and disc was calculated by dividing the frictional force produced by the disc rotation, by the normal applied force to the pin. Each of these forces need corrections by taking moments about the pivot (see Fig. 4).

3.13 Die Forge Test

The forging equipment constructed in the department (156) was employed to evaluate the wear resistance of electroless and electroless composites deposited onto standard flat dies. The forging equipment was used previously for die wear studies (157), thus it is possible to use the previous results for comparing the wear of the deposits under test in this work.

The wear test was essentially an upset forging operation carried out on a mechanical forge which has automatic feeding of hot billets and ejection of forgings. The essential features of the equipment are shown in Fig. 6. The complete forging cycle occupied only ten seconds, thus enabling a large number of forging operations to be carried out in a relatively short time.

A billet of EN3B steel 1.2 cm diameter x 1.8 cm long was fed into a H.F. coil and heated to approximately 1200°C. It was transferred to the forging dies by tongs. An optical pyrometer determined the billet temperature and activated the forging stoke, but only if the billet temperature was within the range 1110-1140°C. The billet was upset forged from 1.8 cm to 0.6 cm in height and ejected. A counter mechanism operated by the forging stoke determined the number of forging operations. A standard test of a thousand forging operations was employed since this was the same as in the earlier work. The dies were held in the bolsters in the press, which were electrically heated to 130°C. Heating of the die bolsters was necessary, as without auxillary heating the bulk die temperature only rose to about 60°C due to small billet/die mass ratio.

The dies were hardened as follows. They were first soaked for fifty minutes in a salt bath maintained at 840°C. This was followed by oil quenching to room temperature and tempering for twenty minutes at 600°C. This heat treatment produces a tempered martensite structure having a hardness of between 388-411 Hv. A hole was drilled and tapped to enable the dies to be jigged for plating.

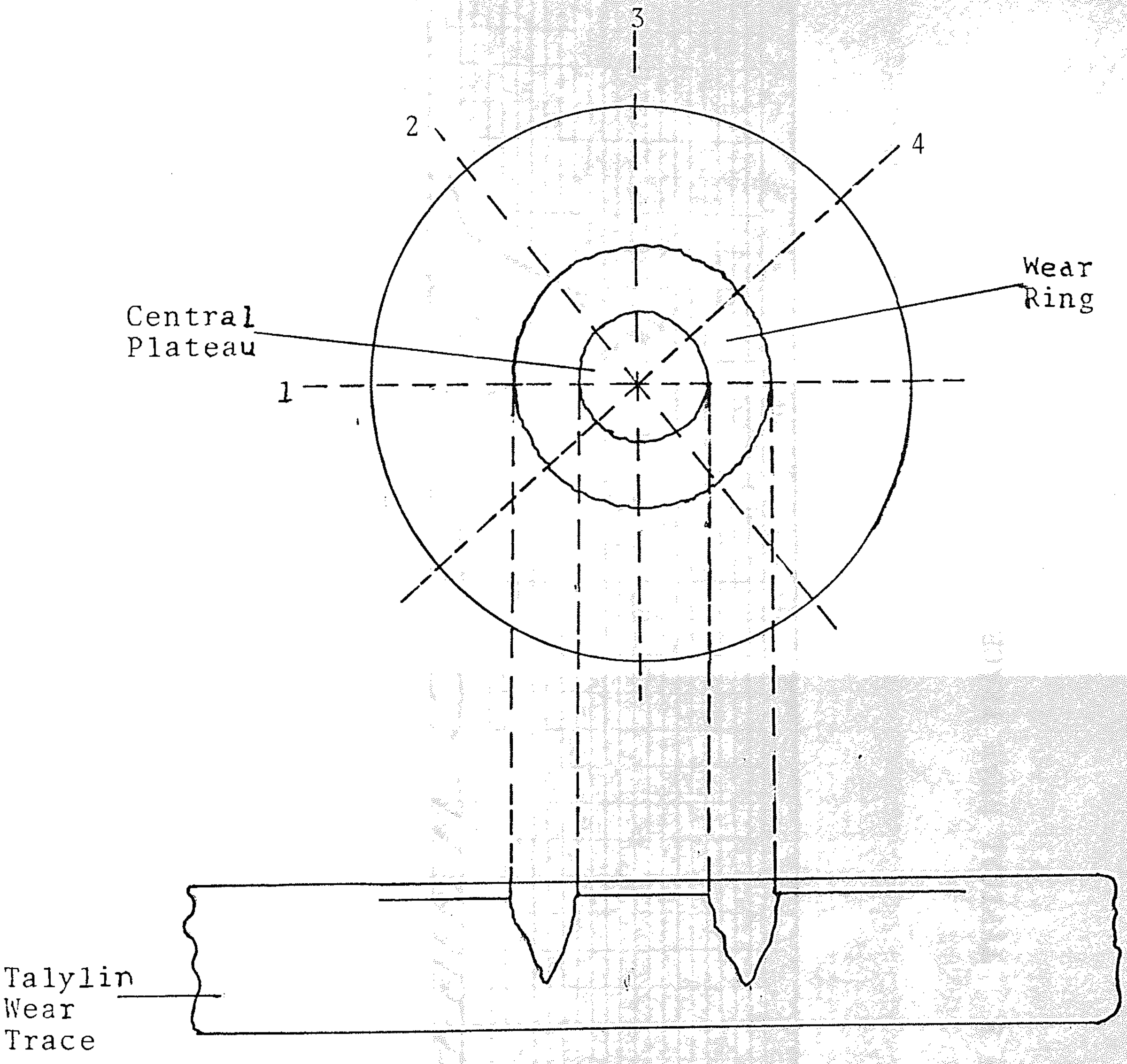
To obtain good adhesion of the deposit, the dies were subjected to the same preplating sequence as described in section 3.10. Etching time is critical, an etch time of 1.5-1.75 minutes being required for Electem No. 5 die steel.

The dies were jigged, the sides and back being stopped off with a lacquer and plated for 4-5 hours to ensure that a deposit thickness of between 40-60 μm was obtained in the centre of the die. The deposit on the die was then ground flat; this was essential to allow the automatic billet feed mechanism to function correctly and to fix a datum surface for subsequent wear measurements. The surface was ground in a manner such that the least possible thickness of deposit was removed from the centre of the disc.

i) Measurement of Wear

The amount of wear occurring during the forging operation was evaluated by obtaining a wear pattern from the surface

FIGURE 7 POSITIONS AT WHICH WEAR TRACES WERE OBTAINED ON DIE SURFACE



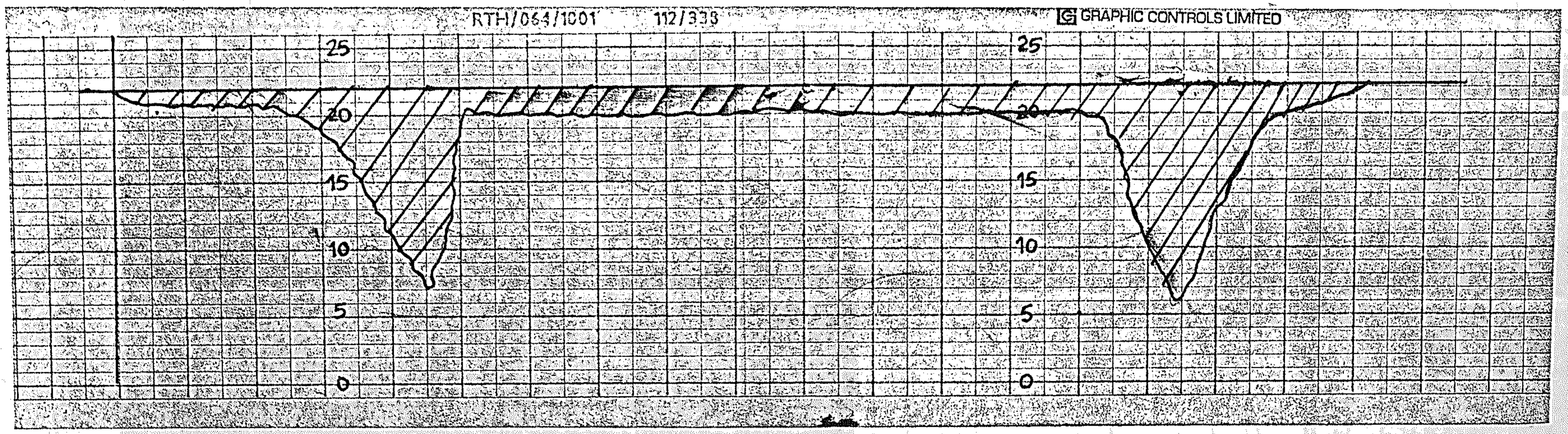


FIGURE 8 TYPICAL WEAR TRACE

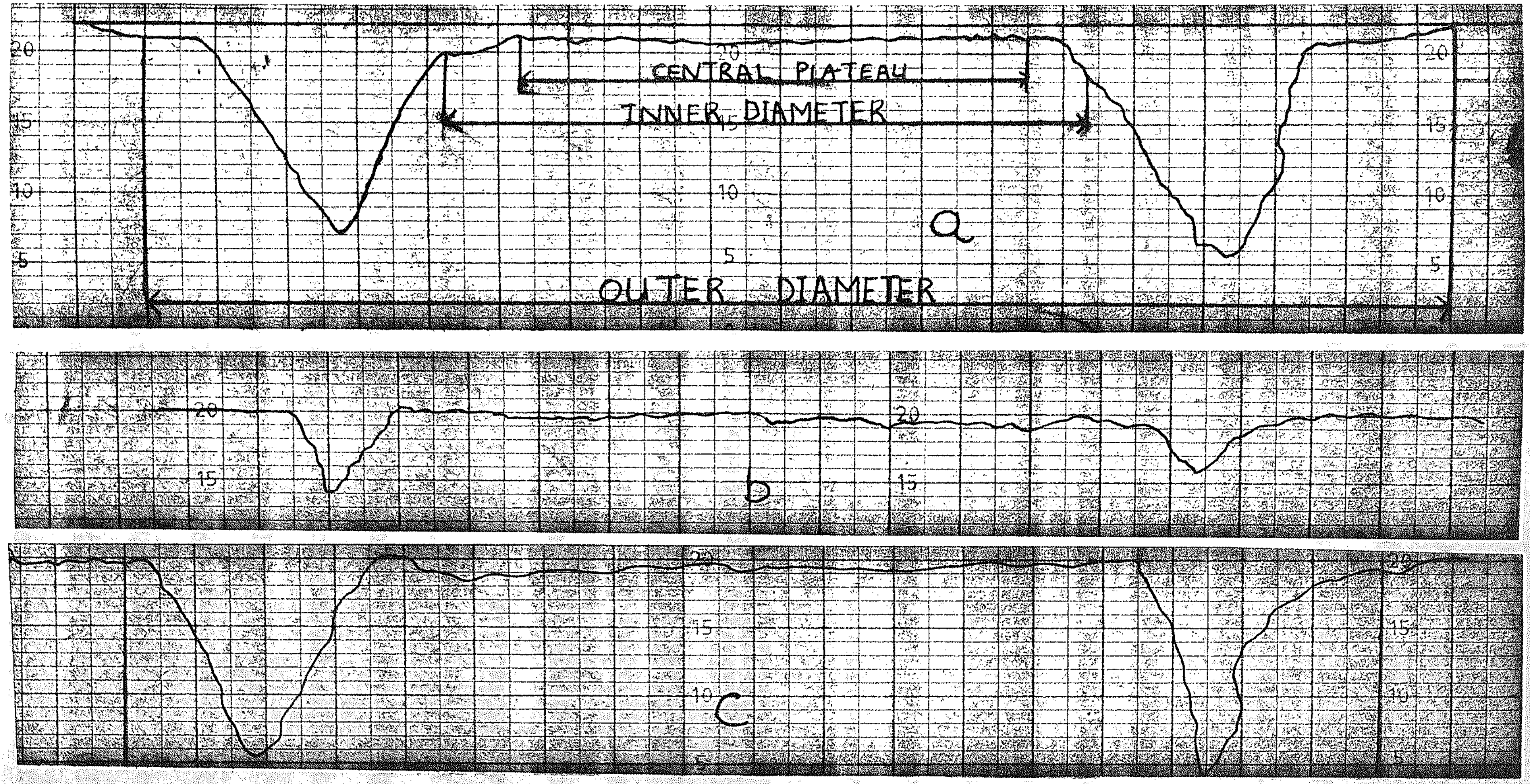


FIGURE 9 WEAR TRACES
a) SHOWING THE INNER AND OUTER DIAMETER OF WEAR RING
b) SHOWING LITTLE WEAR, LOW MAGNIFICATION x1000
c) SHOWING LITTLE WEAR, HIGH MAGNIFICATION x4000

of the die using a Taylor Hobson Talylin surface analyser. After forging the surface of the die was descaled electrolytically. The back and the side of the die were coated with a suitable lacquer and using a carbon rod as anode, the surface of the die was cleaned cathodically in a solution of 5% v/v H_2SO_4 containing 0.1% by weight O-tolylthiourea as an inhibitor. The solution temperature was 75^{o}C and the applied current 18-30 A/dm^2. The maximum time permitted for descaling was 1·5 minutes: this was divided into thirty second periods, each being followed by vigorous brushing of the die surface with a hard brush. After descaling the surface, four wear traces were taken at 45^{o} to each other (Fig. 7). It was possible to alter the sensitivity of the apparatus so that varying degrees of wear could be evaluated. The length of the trace obtained could also be expanded by x2, x5, and x10 (i.e. when set at x10, for each 1 cm traversed by the stylus, 10 cm of trace were produced). In the present project x5 or x4 were used. A typical trace is shown in Fig. 8. The central plateau region was of approximately the same size as the billet diameter, i.e. 1.25 cm. This represents the area of sticking friction associated with the upset forging operation; it was therefore an area of almost zero metal flow and remained virtually unworn on completion of the forging test. The wear ring extended outwards from the edge of the central plateau almost to the diameter of the forged billet, approximately 2·5 cm. This area was one of metal flow during the forging operation and consequently severe wear of the die surface occurred.

ii) Calculation of Mean Wear Volume

In order to calculate the amount of wear a line was drawn across the wear trace connecting the two original surfaces, Fig. 8(a). The outer and inner extremities of the wear ring were then marked and the diameter measured. From these measurements the mean wear diameter was calculated using the expression:-

$$\text{mean wear dia} = \text{inner dia} = \frac{(\text{outer dia} - \text{inner dia})}{2}$$

The area bounded by the wear trace and the original surface line was determined using a planimeter. This gave the apparent wear area, in cm^2, which was dependent upon the magnification employed in producing the trace. The wear volume, in cm^3 (i.e. the quantity of the deposit lost during the forging operation) was then found by rotating half the wear area about the mean wear circle, i.e.

$$\text{wear volume} = \frac{\text{Wear area}}{2} \times \text{mean wear diameter} \times \pi.$$

The mean of the four wear volumes calculated in this way was then found. This method of calculation was straightforward in the majority of cases, since well defined wear regions and central plateau regions were present, but care had to be exercised in certain instances, particularly where little wear had taken place. Typical traces of this type of situation are shown in Figs. 9(b) and 9(c). Figure (b) represents a fairly low magnification wear trace of a die which had suffered little wear; it shows that clearly defined regions are not detected on the die surface as they are in the example shown in Fig. 9(a). Consequently, the mean wear diameter is very difficult to measure due to the uncertainty of the diameter of the central plateau. If high magnifications are used in order to achieve reasonable wear traces another problem is introduced. Figure 9(c) illustrates a typical trace of this type; the original surface profile is sloping at a small angle to the horizontal because during the forging operation the die deforms very slightly into a saucer-shape and the magnification is so high that apparent wear is recorded. The original surface line could not be positioned accurately.

When these types of wear trace were encountered the wear volumes were calculated by other techniques. In the case of wear traces similar to the types shown in Fig. 9(b) the measurements required for the calculation of the mean wear diameter were obtained both by inspection of the wear trace and of the die. Evaluation of wear volumes from traces similar to those shown in Fig. 9(c) was done by extending the sloping 'original surface' line to the centre of the die as shown and measuring the wear area bounded by this line. Combination of the above two techniques were also required in certain instances.

Inclusion of the deformation mentioned above in the wear volume should be considered carefully as this represents a loss of dimensional tolerance just as much as that caused by erosion of the die. However this effect is only brought out into prominence by raising the wear trace magnification and traces taken at lower magnifications are not sensitive enough to record the deformation. It was thought therefore that it should be excluded from the wear volume when measuring under a trace of this type.

It is fortunate that such traces are only produced from dies which have suffered little wear and therefore does not mean that a wear resistant material may be overlooked by miscalculation of the wear volume.

3.14 Corrosion Resistance Testing

Mild steel panels were coated with electroless and composite deposits to test the corrosion resistance of the deposits. Three different methods were then used to determine the corrosion behaviour of the deposits in the following ways.

(i) Salt spray test

Mild steel panels 10.0 cm x 7.5 cm were plated with equal thicknesses of electroless and electroless composite deposits.

Some of the panels were subjected to the salt spray test in a Cass cabinet. The solution is 5% sodium chloride with acetic acid added to make pH 3.5 and the temperature is maintained at 34°C for a duration of one hundred and twenty four hours, with the solution being continuously sprayed onto the panels.

(ii) Outdoor exposure

Another set of panels was subjected to outdoor exposure in the city centre of Birmingham for six months. The panels were held with Tufnol clamps on frames at 45^{o}C and the test was started in late summer.

(iii) Potentiostatic Measurements

Polarisation curves were produced potentiodynamically using a microprocessor controlled potentiostat.

Sections 6 cm long and 0.5 cm wide were cut from the panels plated with electroless and electroless composite deposits. Some of these panels were heat treated at 400^{o} and 600^{o}C for one hour in vacuum. Mild steel panels were plated with Watts nickel and bright nickel and their sections were also prepared for comparison. The sides of the sections were painted with lacquer to prevent the attack of corrosive liquid on the mild steel directly.

Initially, the potential was set at -1000 mv to find the corrosion potential. Afterwards the potentiostat was programmed at -650 mv and the scanning rate was set at 1 mv/sec. The scanning was continued until the cathodic potential changed to anodic. In this way the corrosion potential of the deposits was determined. Each experiment was repeated 3-4 times to obtain an average value.

3.15 Tensile Testing

A five ton capacity tensile machine was used to determine the ductility of the deposits.

Cylindrical tensometer test pieces of B-brass were used for determining the ductility of the deposits. The length and diameter of the tensometer specimen were measured before and after the plating to find the deposit thickness.

Load deflection curves of the plated and unplated specimens were produced, the specimen in each case being tested to failure. All tests were carried out at cross head speeds of 0.5 cm per minute.

Yield stress is calculated by dividing that load at which plastic deformation occurs indicated by the curve in the straight line with the cross-sectional area of the specimen and ultimate tensile stress is calculated by dividing the cross-sectional area with that load at which failure takes place.

4. RESULTS

4.1 Quantimet Analysis

Results are given in Table I. They show that there is essentially no difference in the volume % inclusion of the chromium carbide particles in the deposits with an increase in the concentration of particles in the solution.

TABLE I

Result of the Quantimet Analysis

Concentration of particles in the solution	Volume % inclusion in the deposit
10	27.2 (1.92)
20	26.4 (1.56)
40	25.3 (1.64)
60	23.4 (1.93)
80	25.1 (1.64)
100	26.3 (1.68)
150	24.2 (1.62)
200	25.1 (1.64)

NOTE: Figure in the bracket indicates the standard deviation of at least eight readings.

4.2 Electron Microprobe Analysis

The results of the microprobe analysis summarised in Table II reveal that the amount of phosphorus in the composite coating is less than the electroless coating itself.

TABLE II

Electron Microprobe Analysis Results

Type of the deposit	Composition				
	%Ni	%Co	%P	%Cr	%Cr_2C_3
Electroless nickel	90.82	-	9.07	-	-
Electroless nickel + chromium carbide	64.81	-	7.15	-	27%
Electroless nickel + chromium	51.84	-	5.15	40%	-
Electroless cobalt	-	90.56	6.84	-	-
Electroless cobalt + chromium carbide	-	64.15	4.95	-	27%
Electroless cobalt + chromium	-	63.15	3.75	31	-

4.3 Microhardness Measurement

The effect of heat treatment in air and vacuum at various times and temperatures on the microhardness of the deposits are presented isochronally and isothermally in the Figures 10-47. Tables of the result are given in the Appendix.

The hardness change with heat treatment essentially follows the same trend for all deposits. The hardness increases from the initial as deposited value to a peak and then decreases to a hardness value less than the as plated hardness after heating at 800°C. Generally the peak hardness obtained by heating in vacuum is higher than that produced after heating in air, and the composite deposit hardness is higher than the simple deposit, see Table III. Some deposits also show a second peak hardness, for example as shown in Figs. 36, 37, 39, 41, 45.

The as plated and heat treated hardness of the nickel composite deposits containing carbide particles, whether titanium carbide or tungsten carbide or chromium carbide, were nearly the same.

TABLE III

Maximum Hardness of the Deposit

Type of Deposit	Heat Treatment			Hardness	
	Temperature °C	Time hours	Condition	As plated	Heat treated
Electroless nickel	200	5	Vacuum	515	1155
Electroless nickel	400	1	Air	515	1000
Electroless nickel + chromium carbide	500	5	Vacuum	645	1225
Electroless nickel + chromium carbide	500	12	Air	645	1195
Electroless nickel + tungsten carbide	500	5	Vacuum	640	1190
Electroless nickel + tungsten carbide	500	12	Air	640	1175
Electroless nickel + titanium carbide	500	5	Vacuum	650	1240
Electroless nickel + titanium carbide	500	12	Air	650	1210
Electroless nickel + chromium	400	2	Vacuum	850	1650
Electroless nickel + chromium	400	2	Air	850	1600
Electroless cobalt	400	1	Vacuum	600	1300
Electroless cobalt	200	5	Air	600	1235
Electroless Cobalt + chromium carbide	400	2	Vacuum	800	1405
Electroless cobalt + chromium carbide	400	5	Air	800	1370
Electroless cobalt + chromium	400	5	Vacuum	650	1440
Electroless cobalt + chromium	400	2	Air	650	1400

FIGURE 10 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS NICKEL COATINGS. HEAT TREATMENT IN AIR

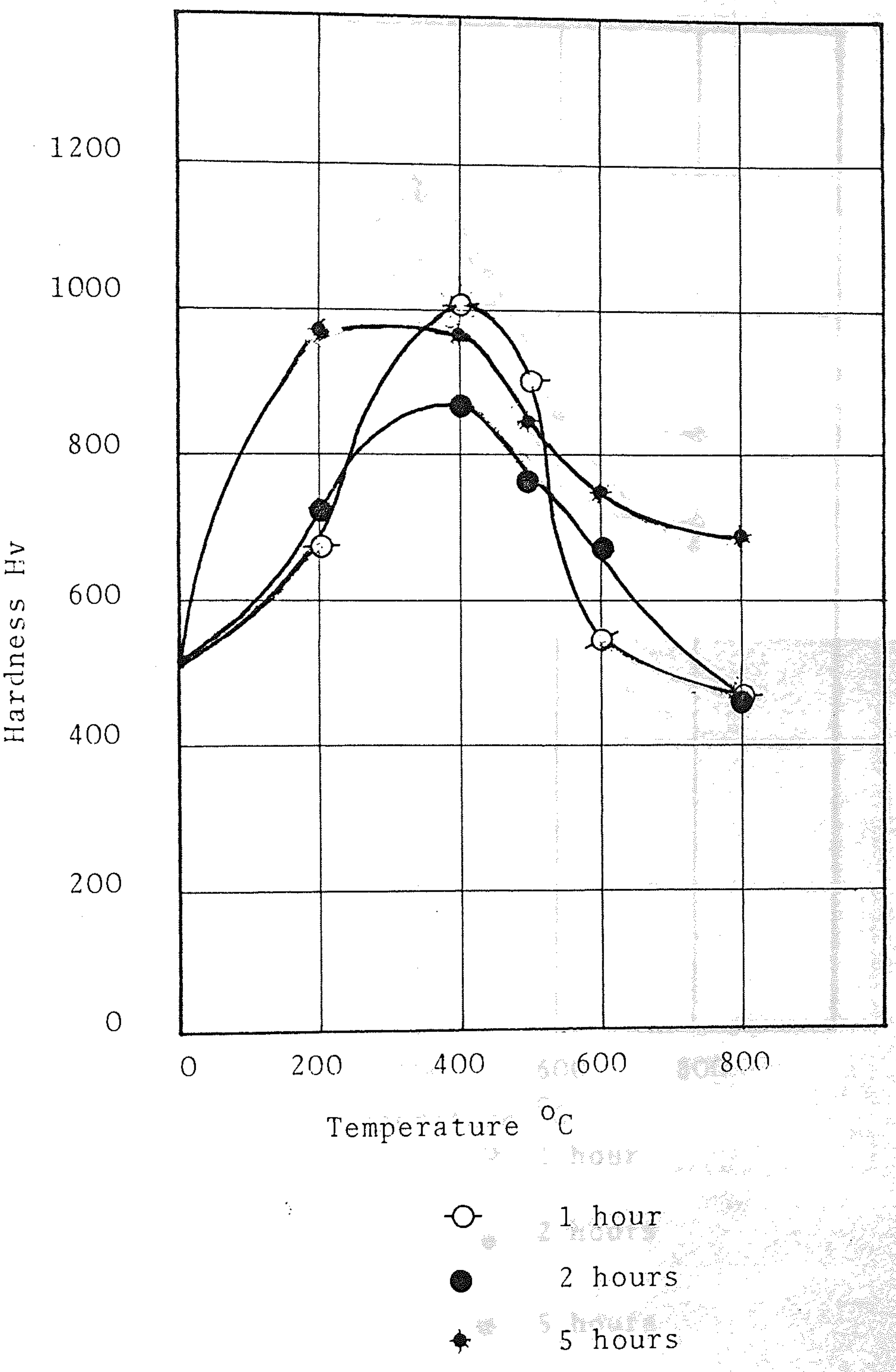


FIGURE 11 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS NICKEL-CHROMIUM CARBIDE COMPOSITE COATINGS. HEAT TREATMENT IN AIR

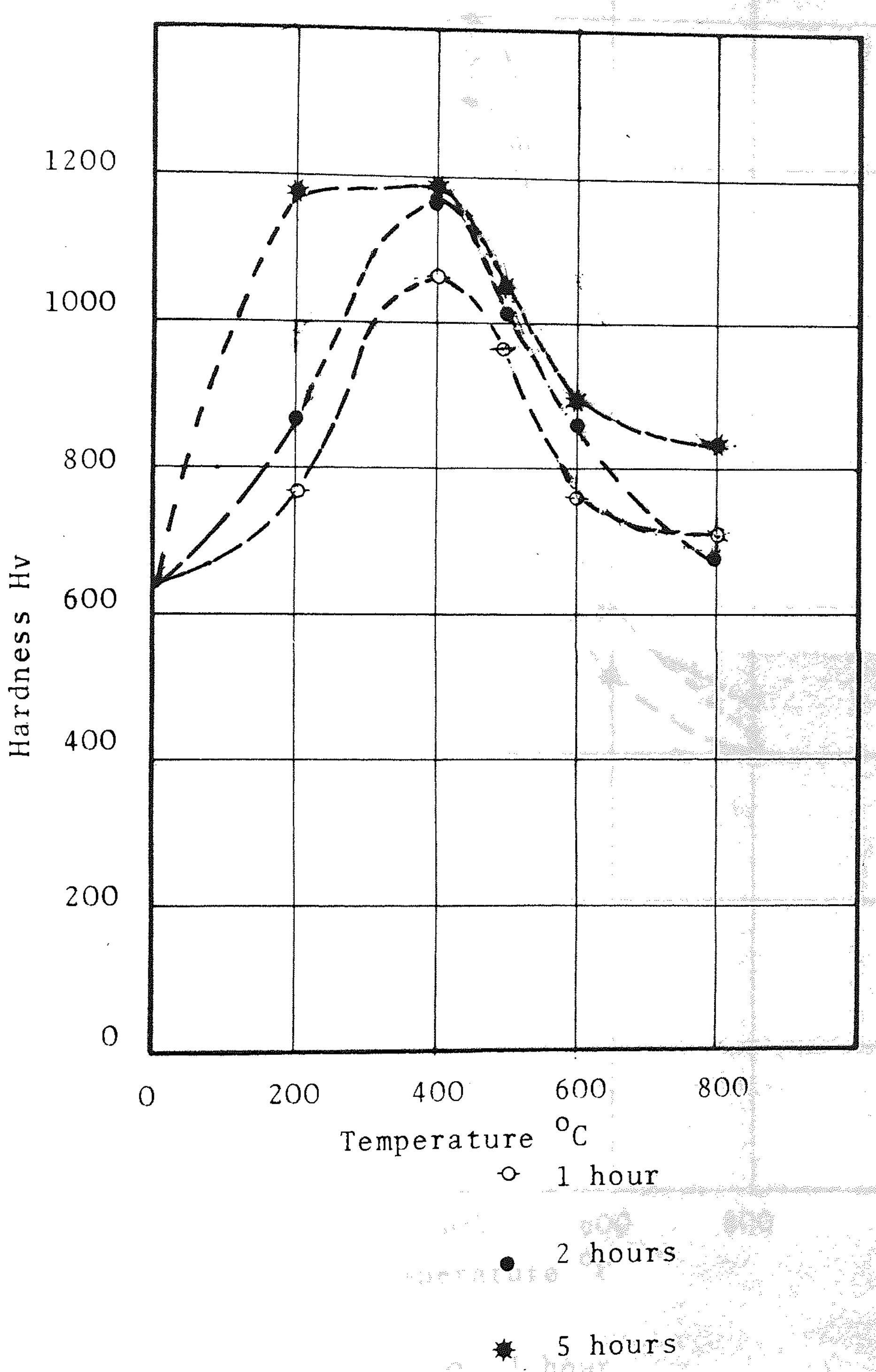


FIGURE 12 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS NICKEL+CHROMIUM COMPOSITE COATINGS. HEAT TREATMENT IN AIR

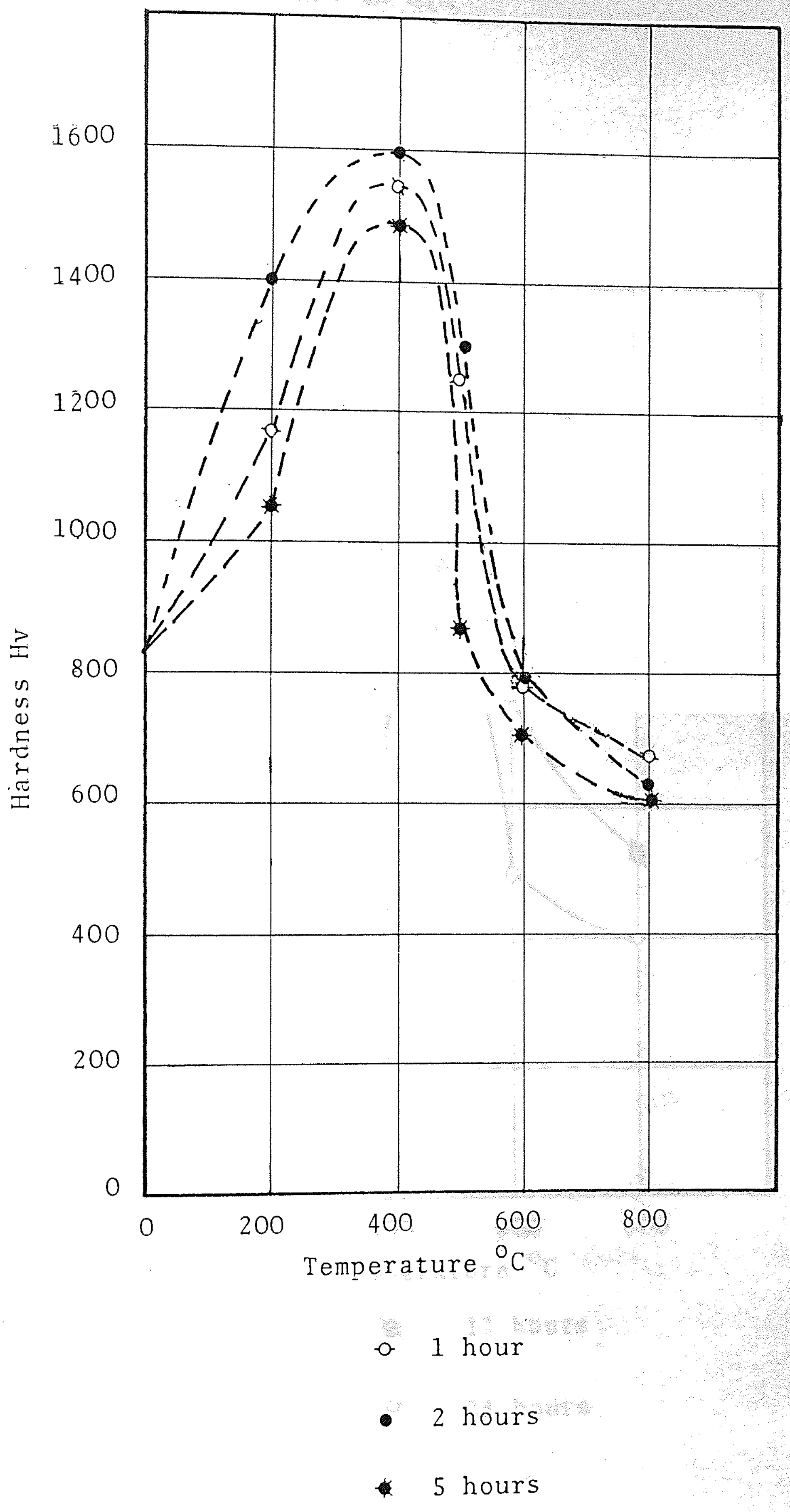


FIGURE 13 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS NICKEL COATINGS. HEAT TREATMENT IN AIR

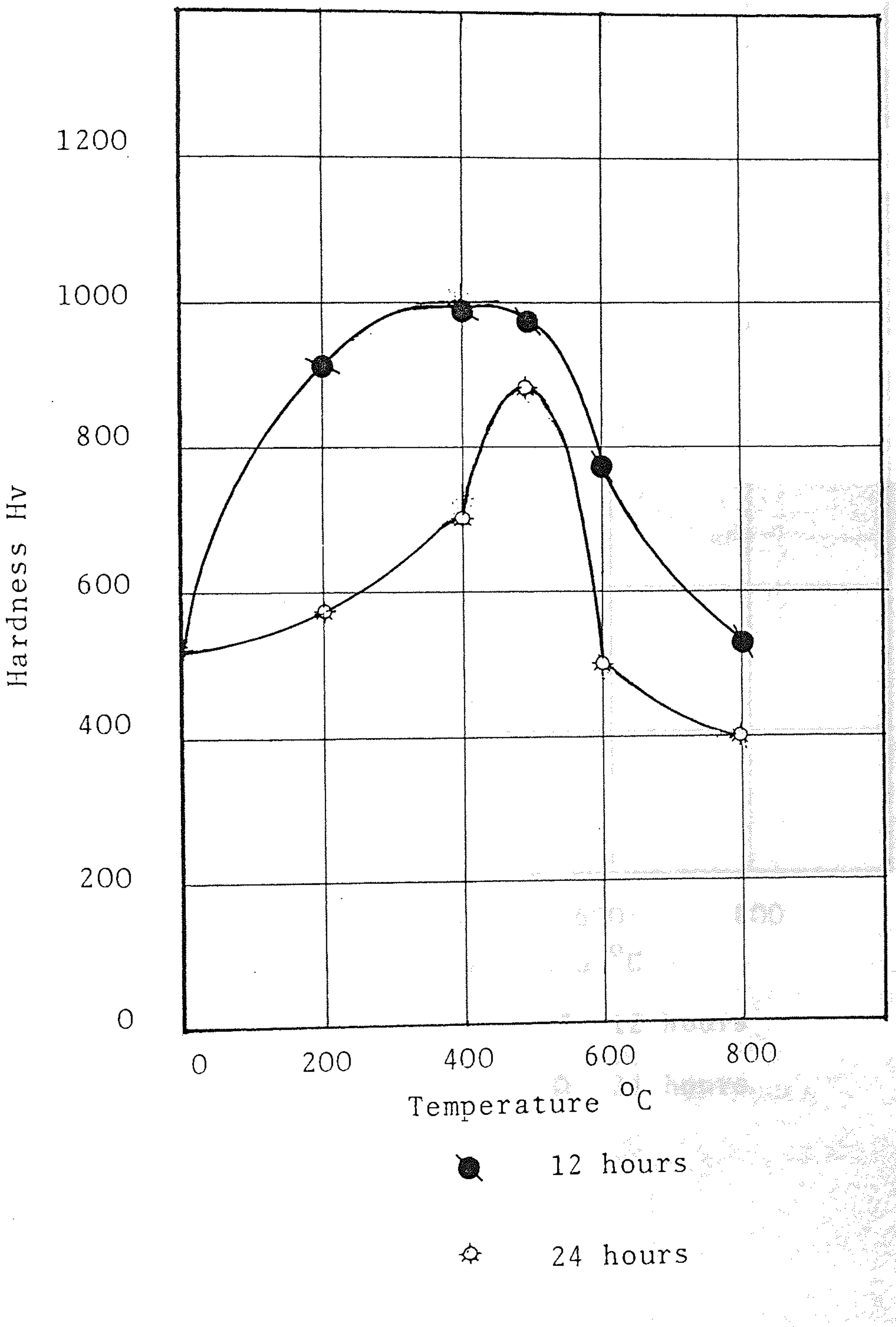


FIGURE 14 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS NICKEL CHROMIUM CARBIDE COMPOSITE COATINGS. HEAT TREATMENT IN AIR

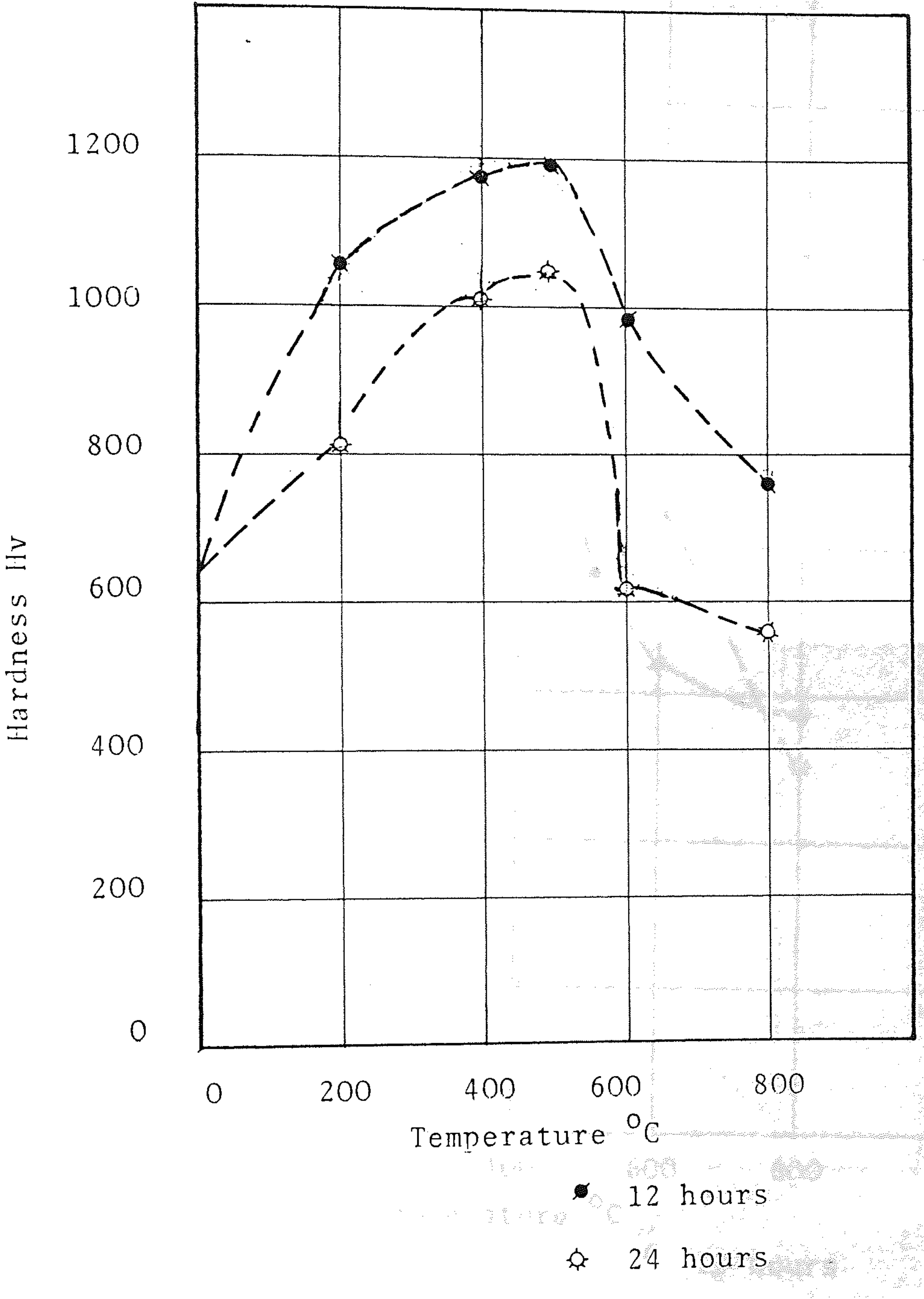


FIGURE 15 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS NICKEL+CHROMIUM COMPOSITE COATINGS. HEAT TREATMENT IN AIR

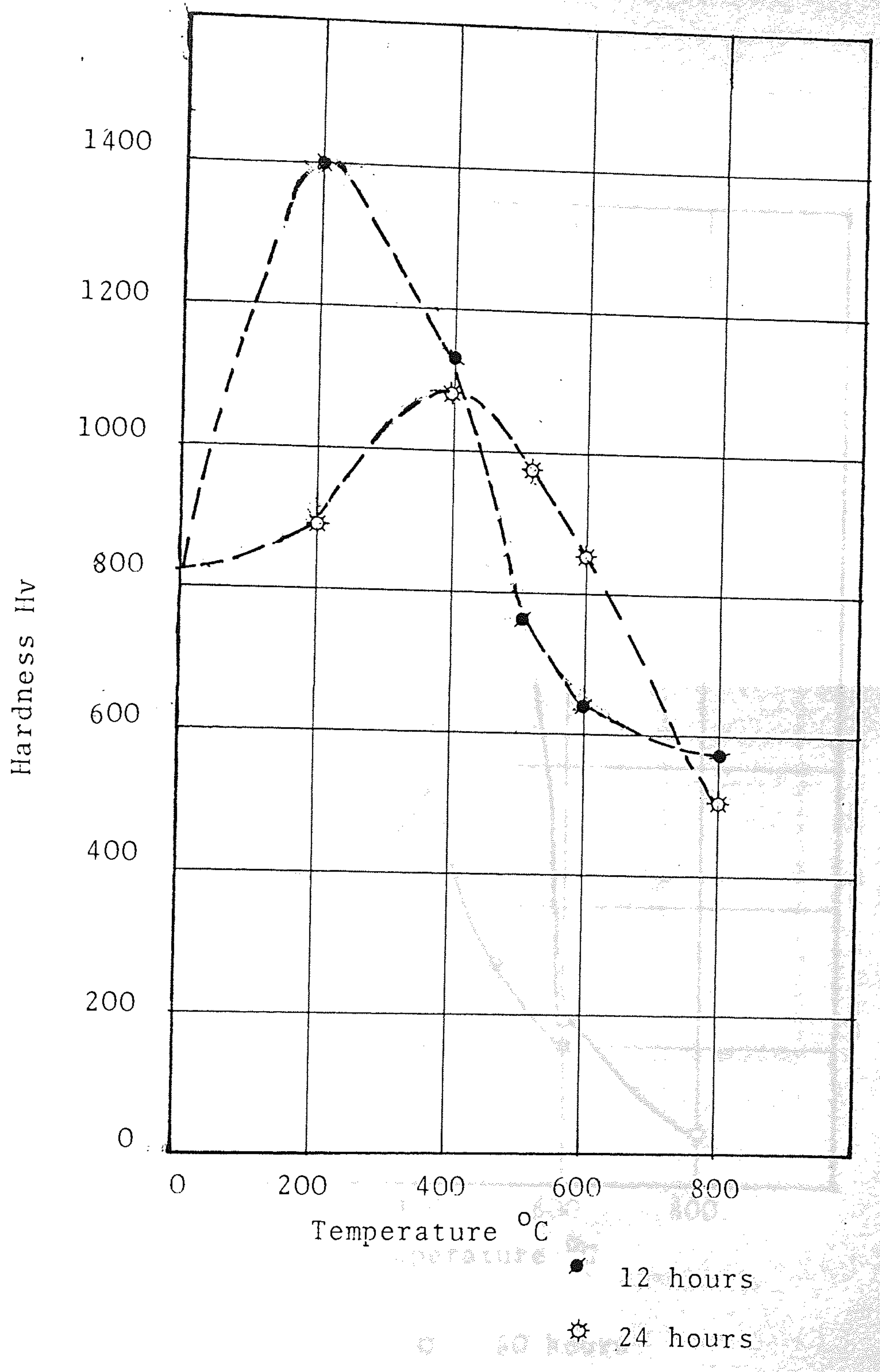


FIGURE 16 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS NICKEL COATINGS. HEAT TREATMENT IN AIR

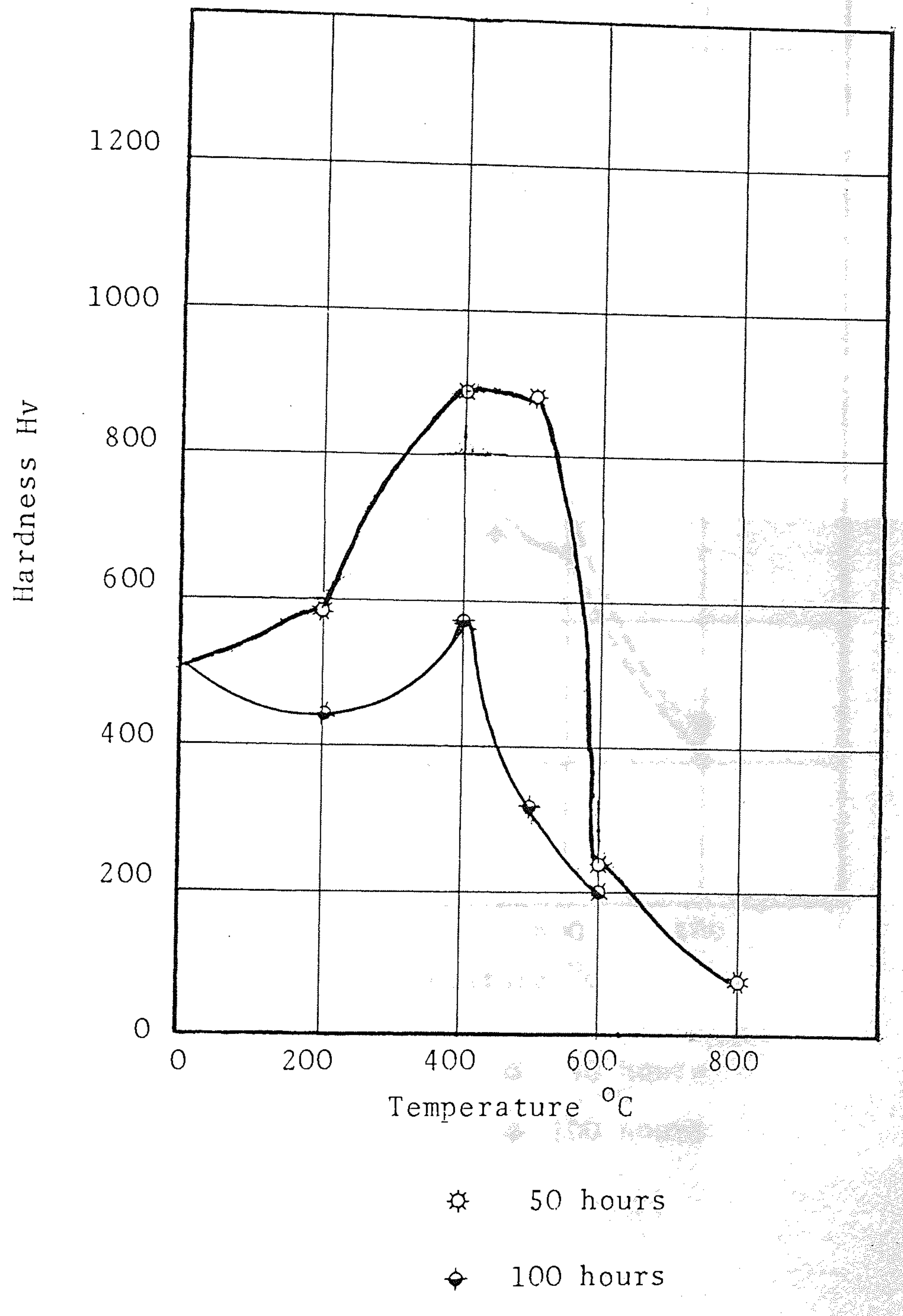


FIGURE 17 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS NICKEL+CHROMIUM CARBIDE COMPOSITE COATINGS. HEAT TREATMENT IN AIR

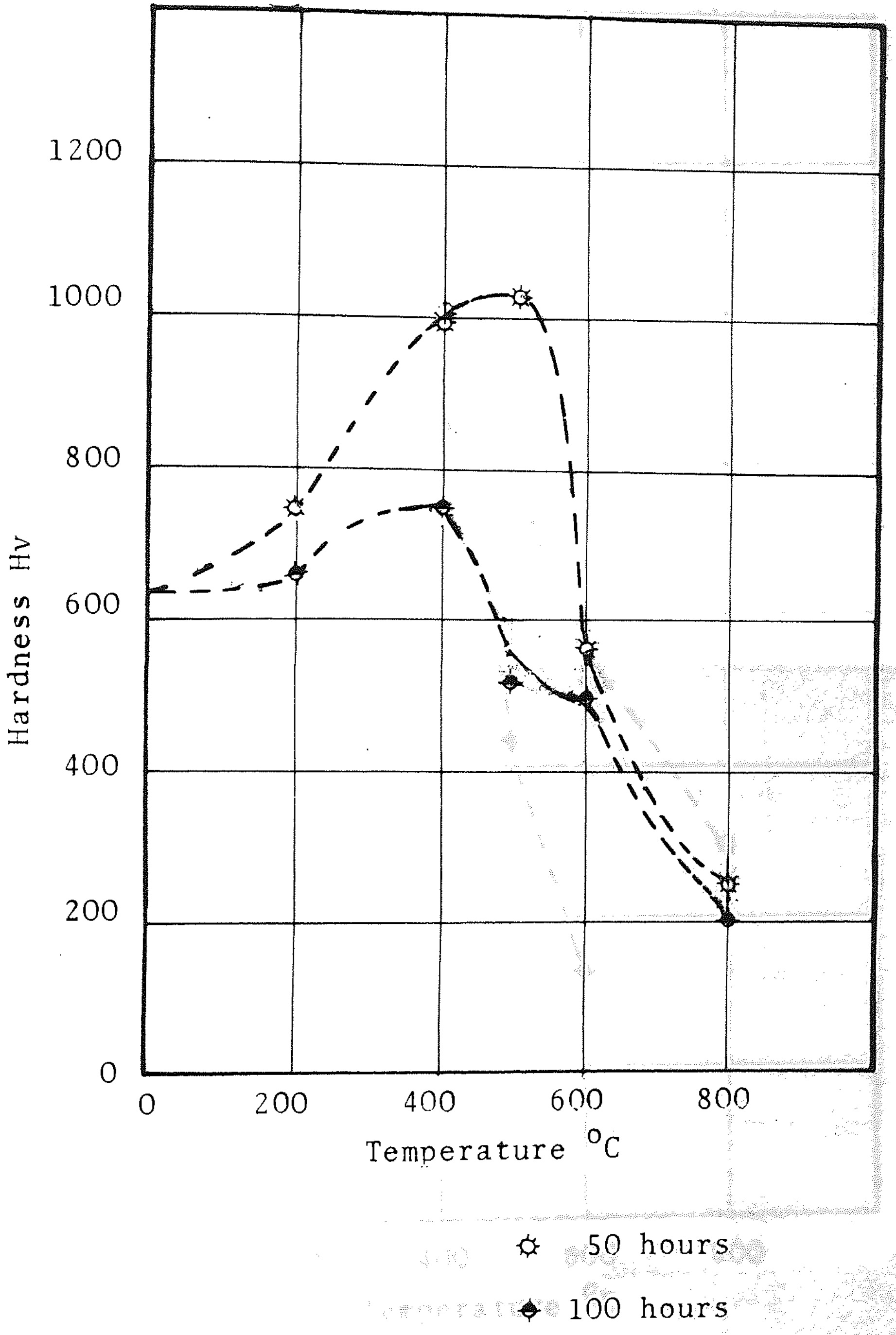


FIGURE 18 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS NICKEL+CHROMIUM COMPOSITE COATINGS. HEAT TREATMENT IN AIR

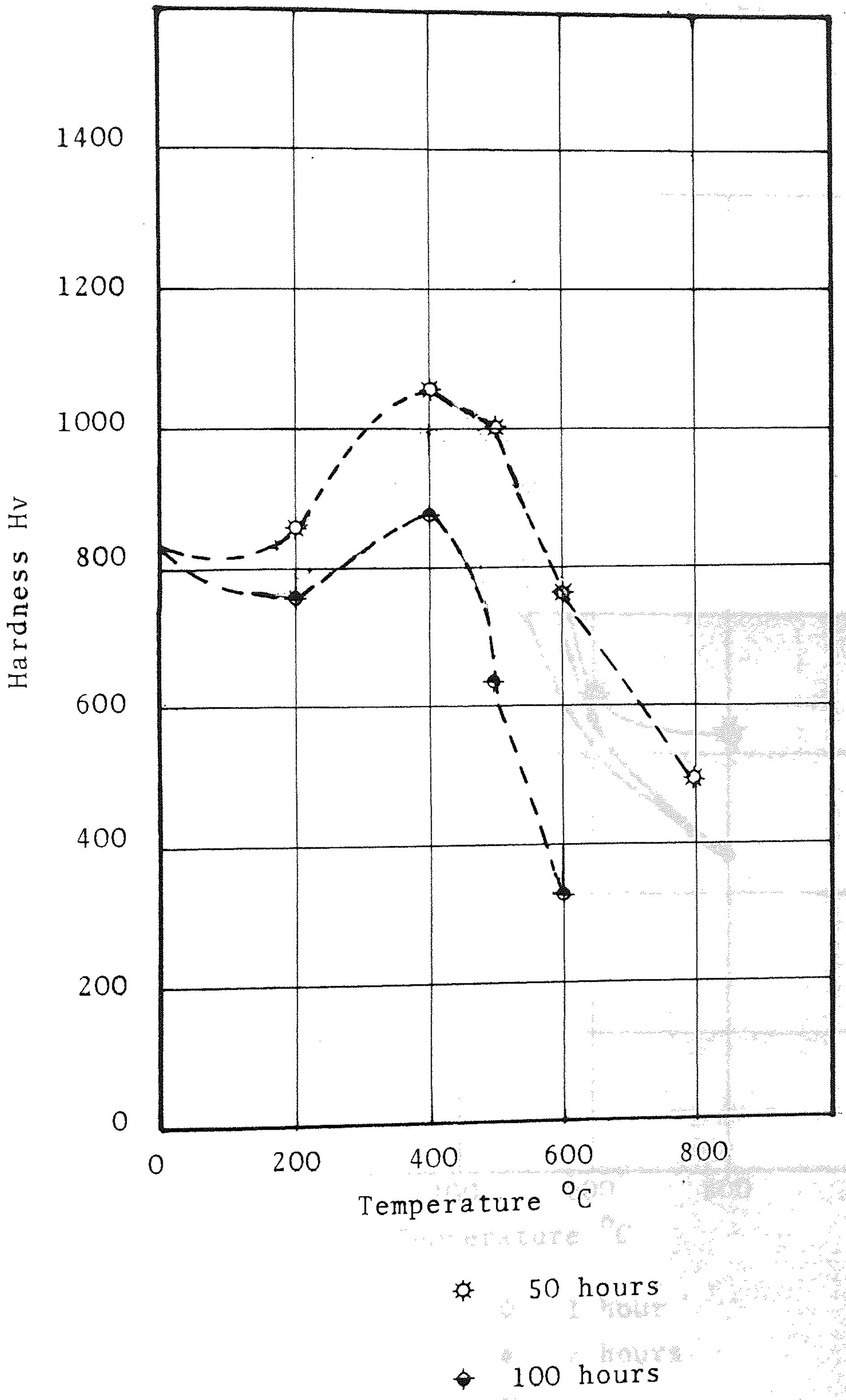


FIGURE 19 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS NICKEL COATINGS. HEAT TREATMENT IN VACUUM

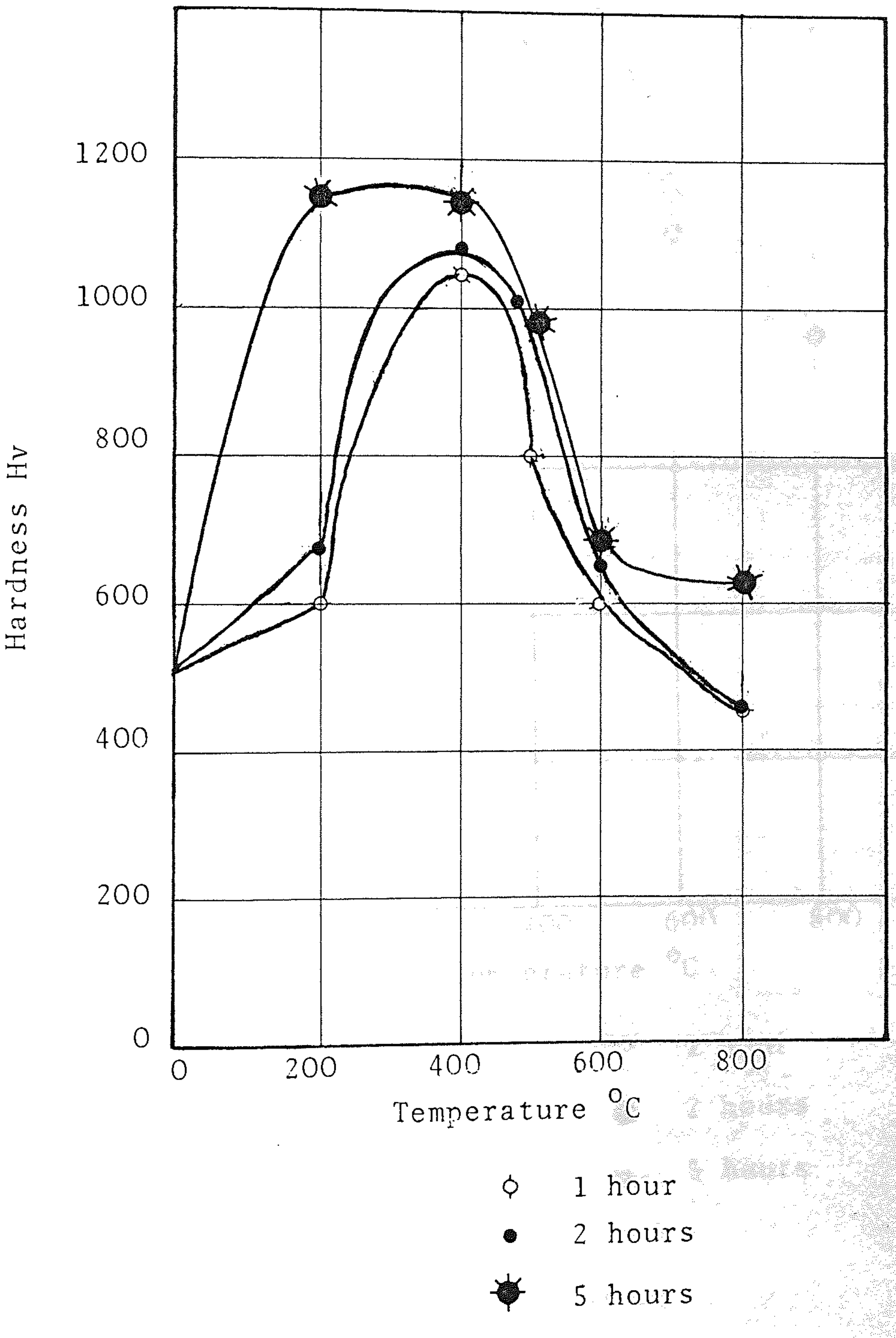


FIGURE 20 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS NICKEL+CHROMIUM CARBIDE COMPOSITE COATING. HEAT TREATMENT IN VACUUM

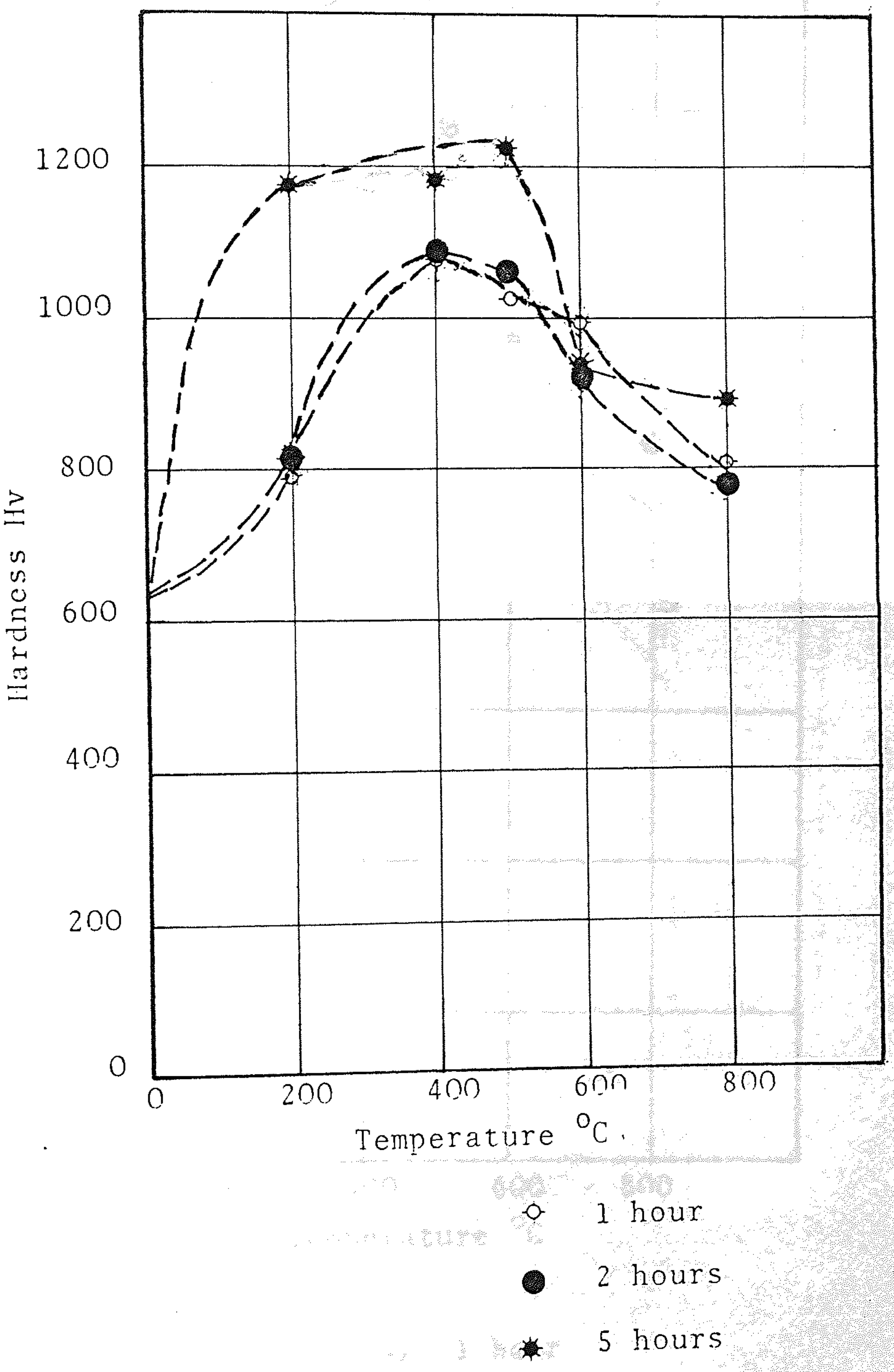


FIGURE 21 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS NICKEL+CHROMIUM COMPOSITE COATINGS. HEAT TREATMENT IN VACUUM

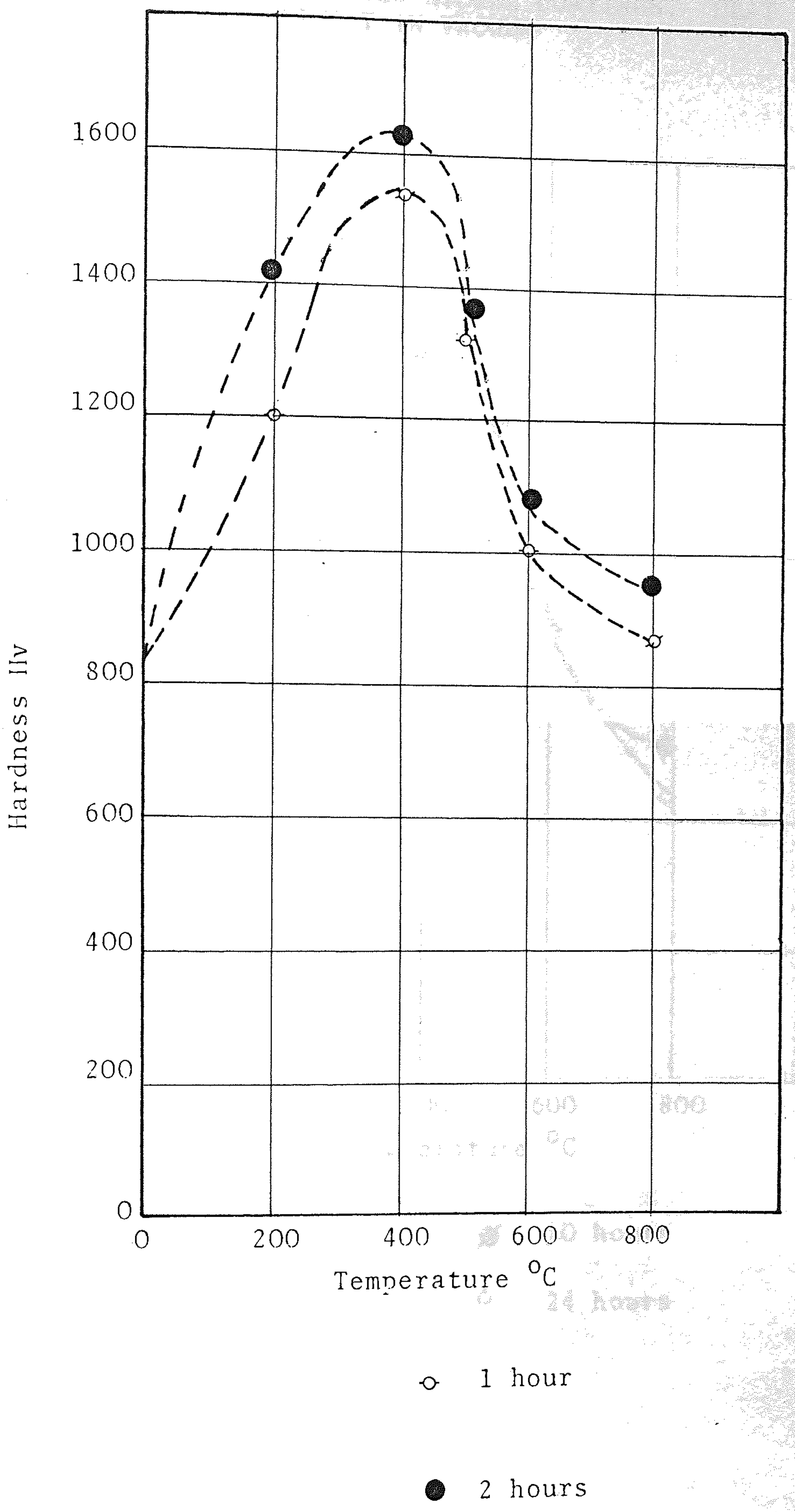


FIGURE 22 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS NICKEL COATINGS. HEAT TREATMENT IN VACUUM

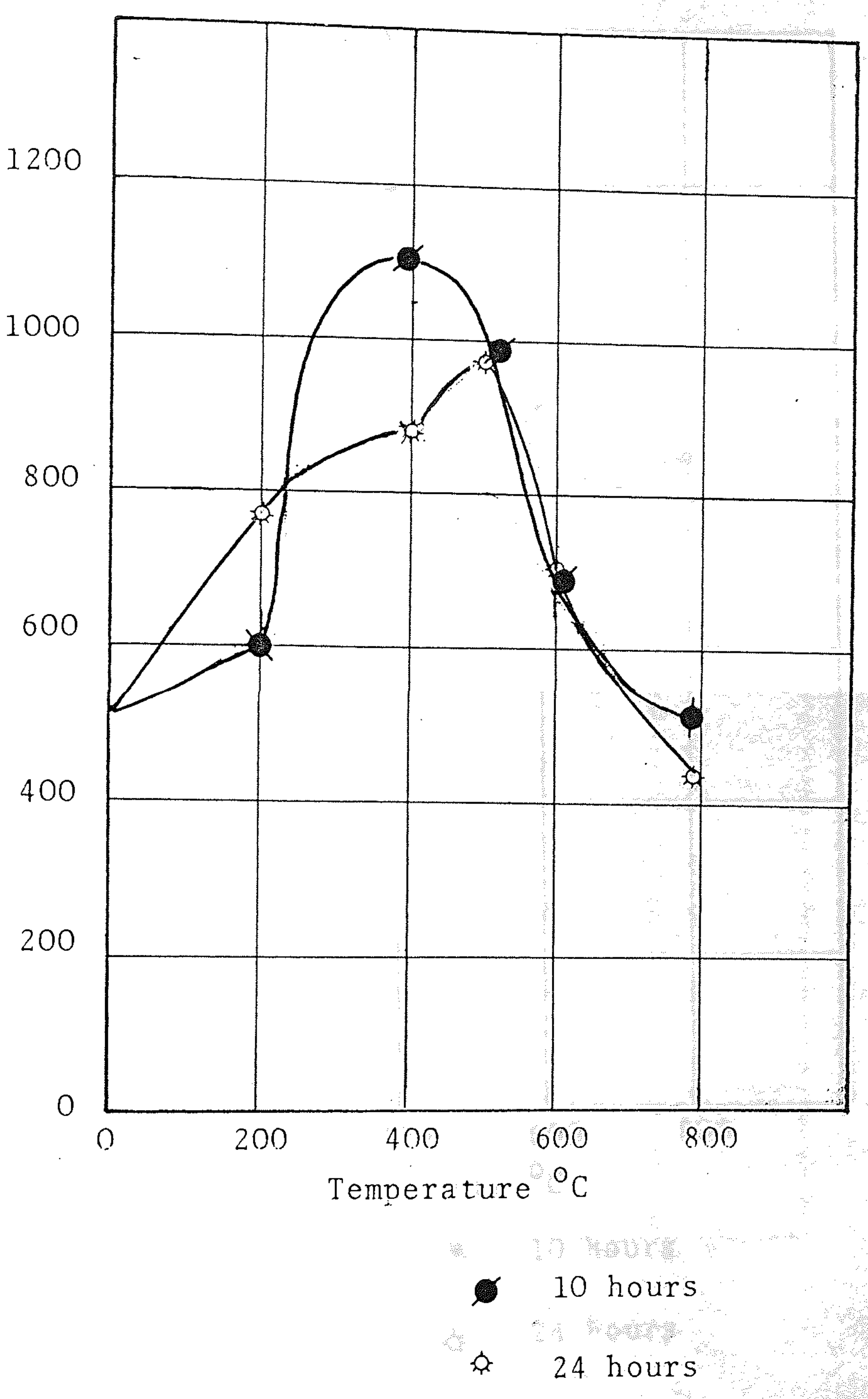


FIGURE 23 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS NICKEL+CHROMIUM CARBIDE COMPOSITE COATINGS. HEAT TREATMENT IN VACUUM

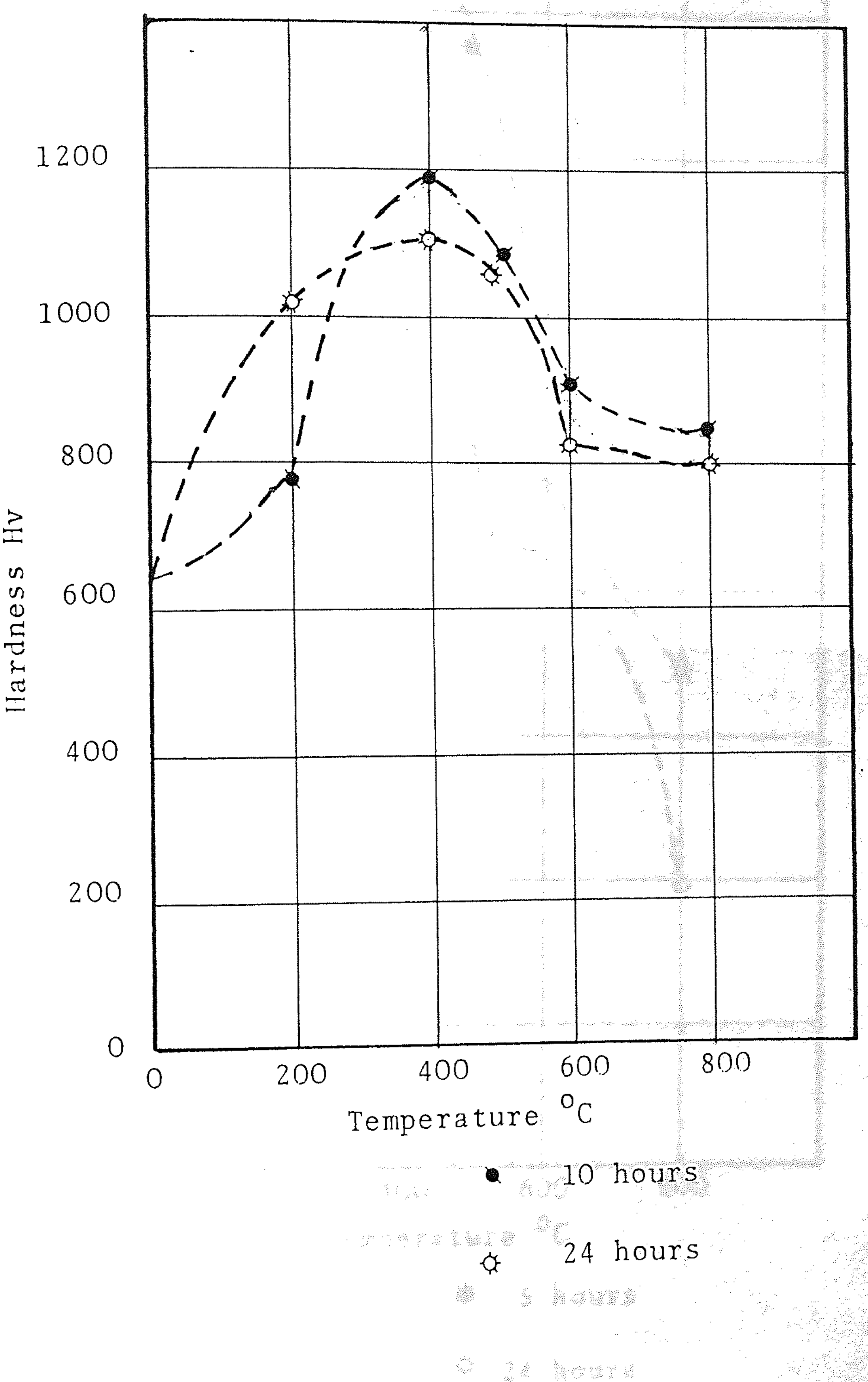


FIGURE 24 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS NICKEL+CHROMIUM COMPOSITE COATINGS. HEAT TREATMENT IN VACUUM

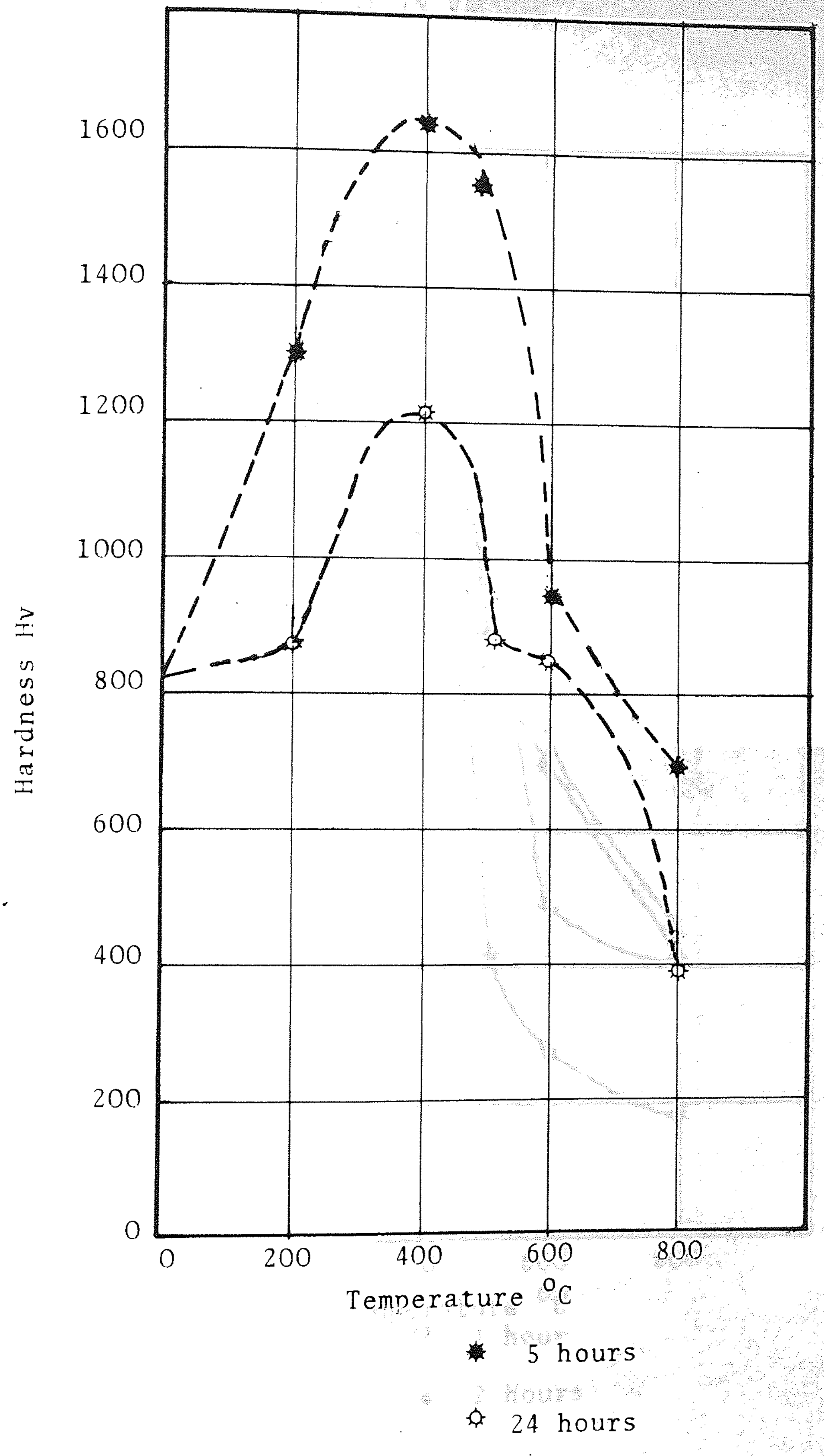


FIGURE 25 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS COBALT COATINGS. HEAT TREATMENT IN VACUUM

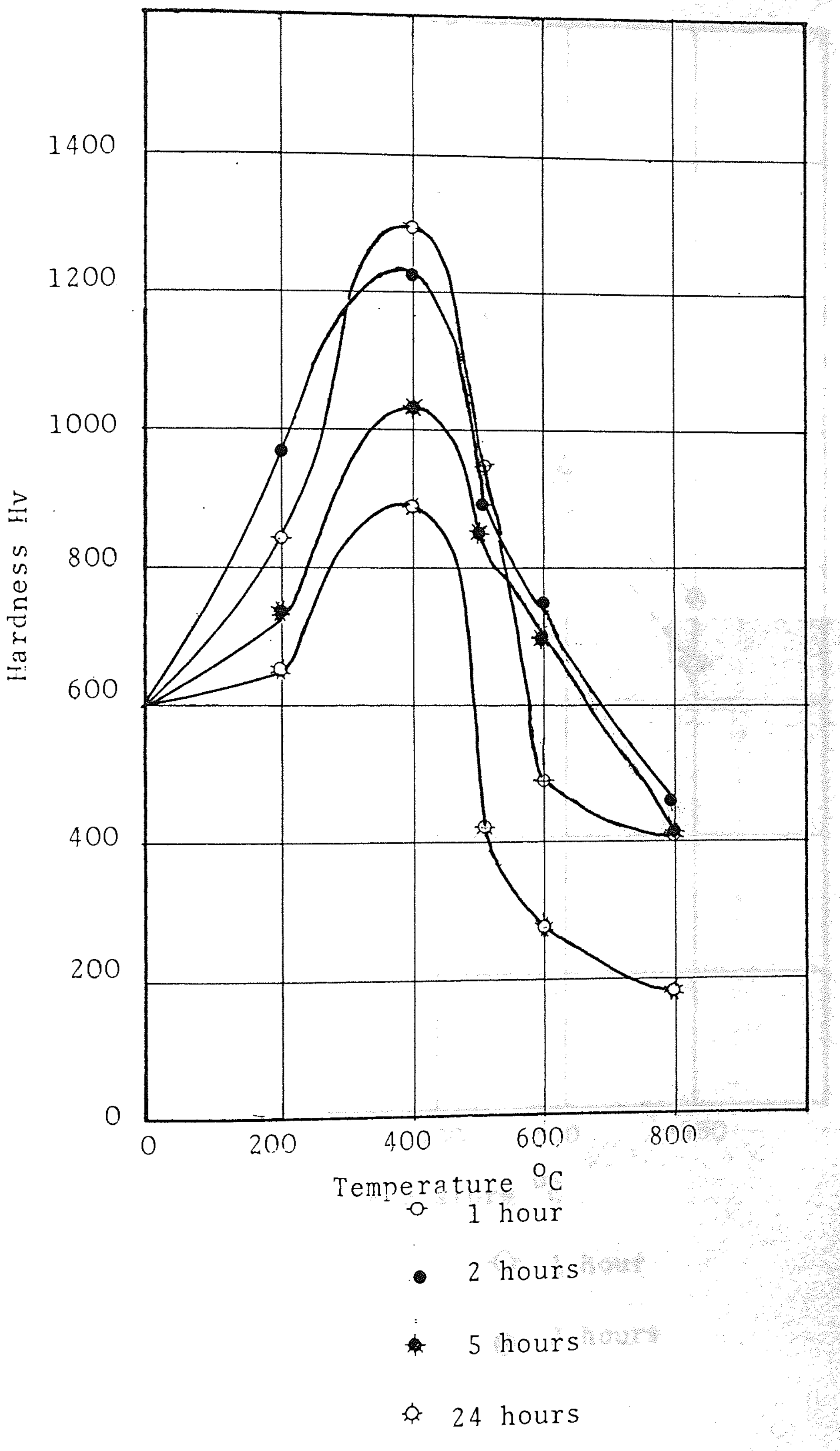


FIGURE 26 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS COBALT+CHROMIUM CARBIDE COMPOSITE COATINGS. HEAT TREATMENT IN VACUUM

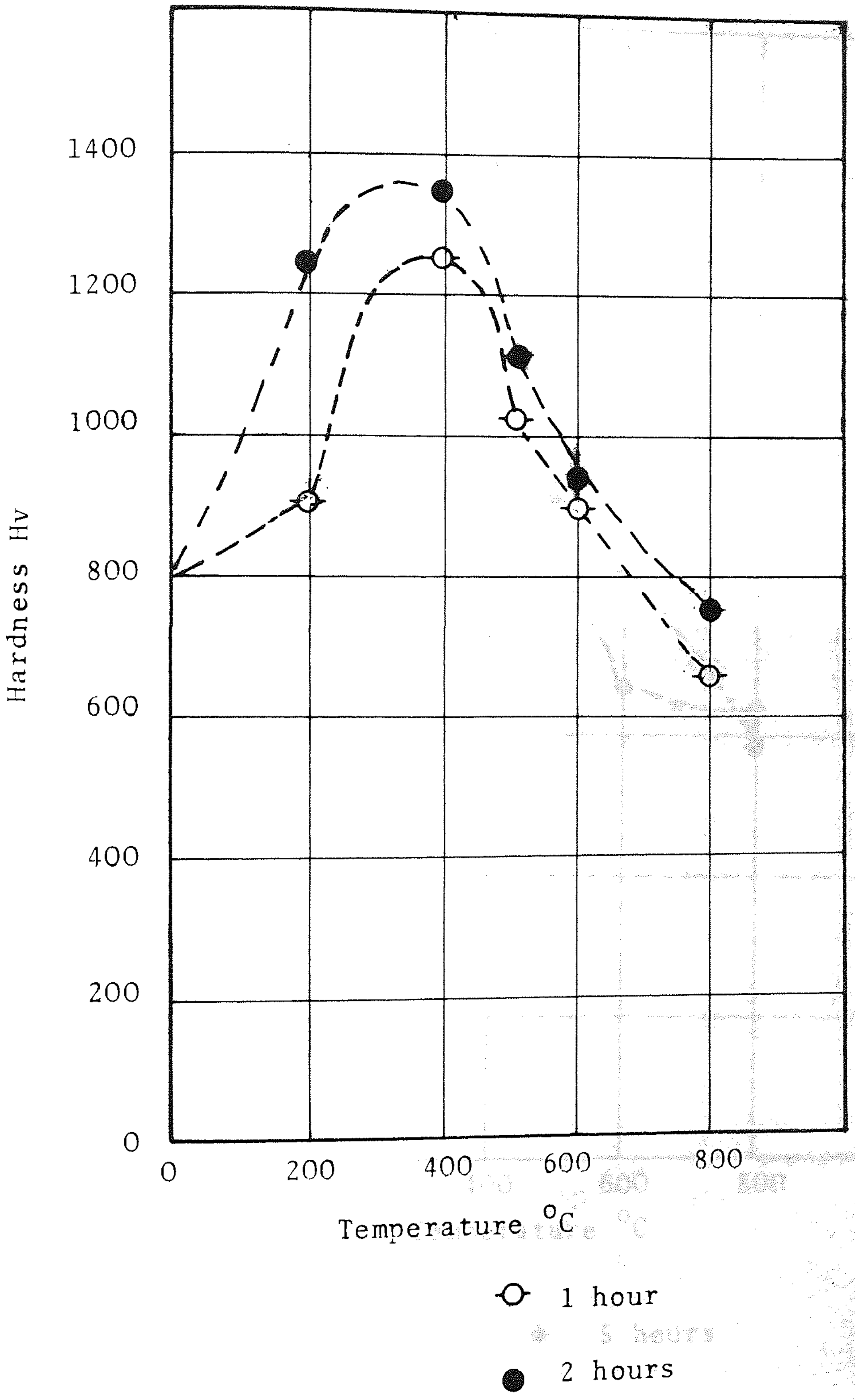


FIGURE 27 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS COBALT+CHROMIUM CARBIDE COMPOSITE COATINGS. HEAT TREATMENT IN VACUUM

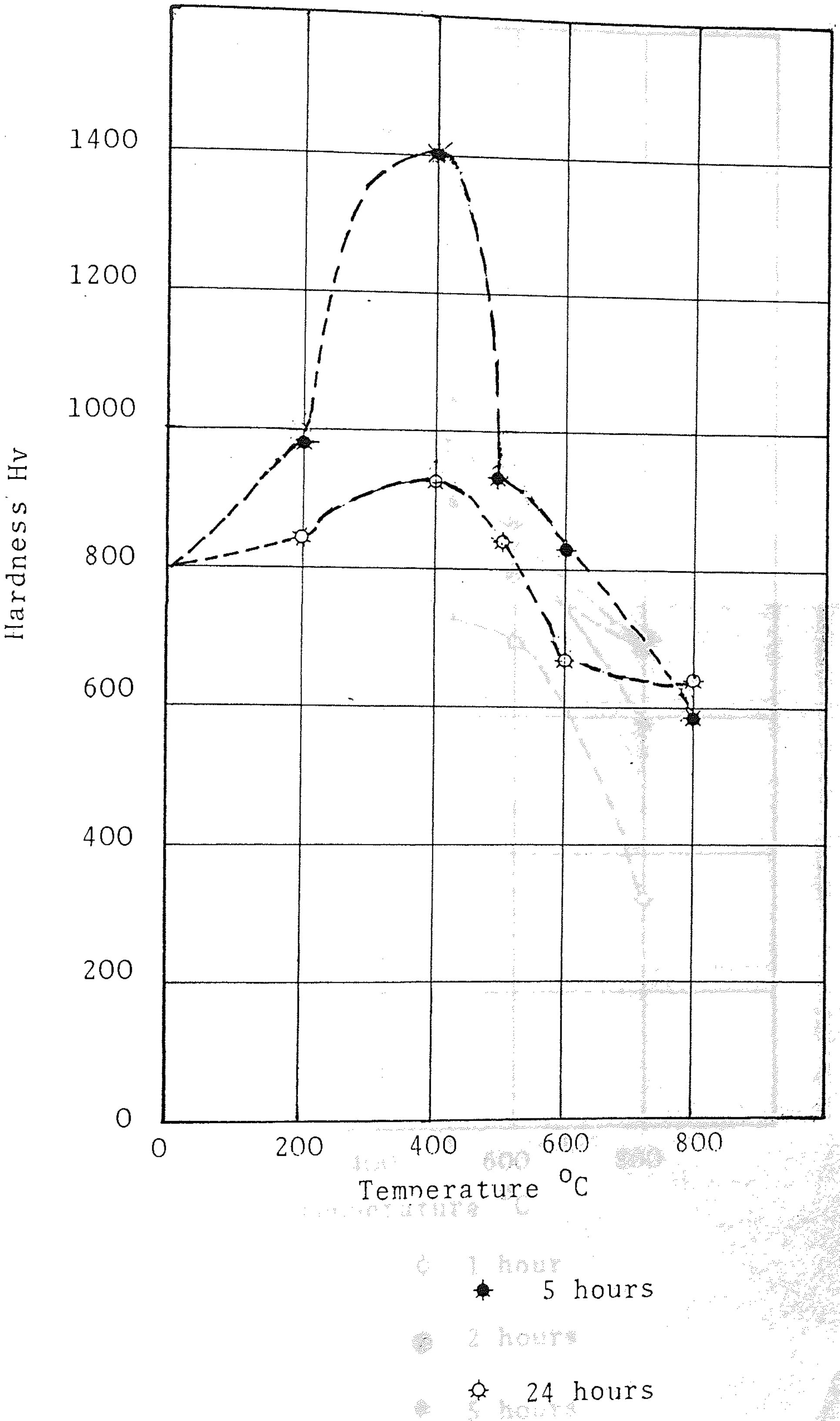


FIGURE 28 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS COBALT+CHROMIUM COATINGS. HEAT TREATMENT IN VACUUM

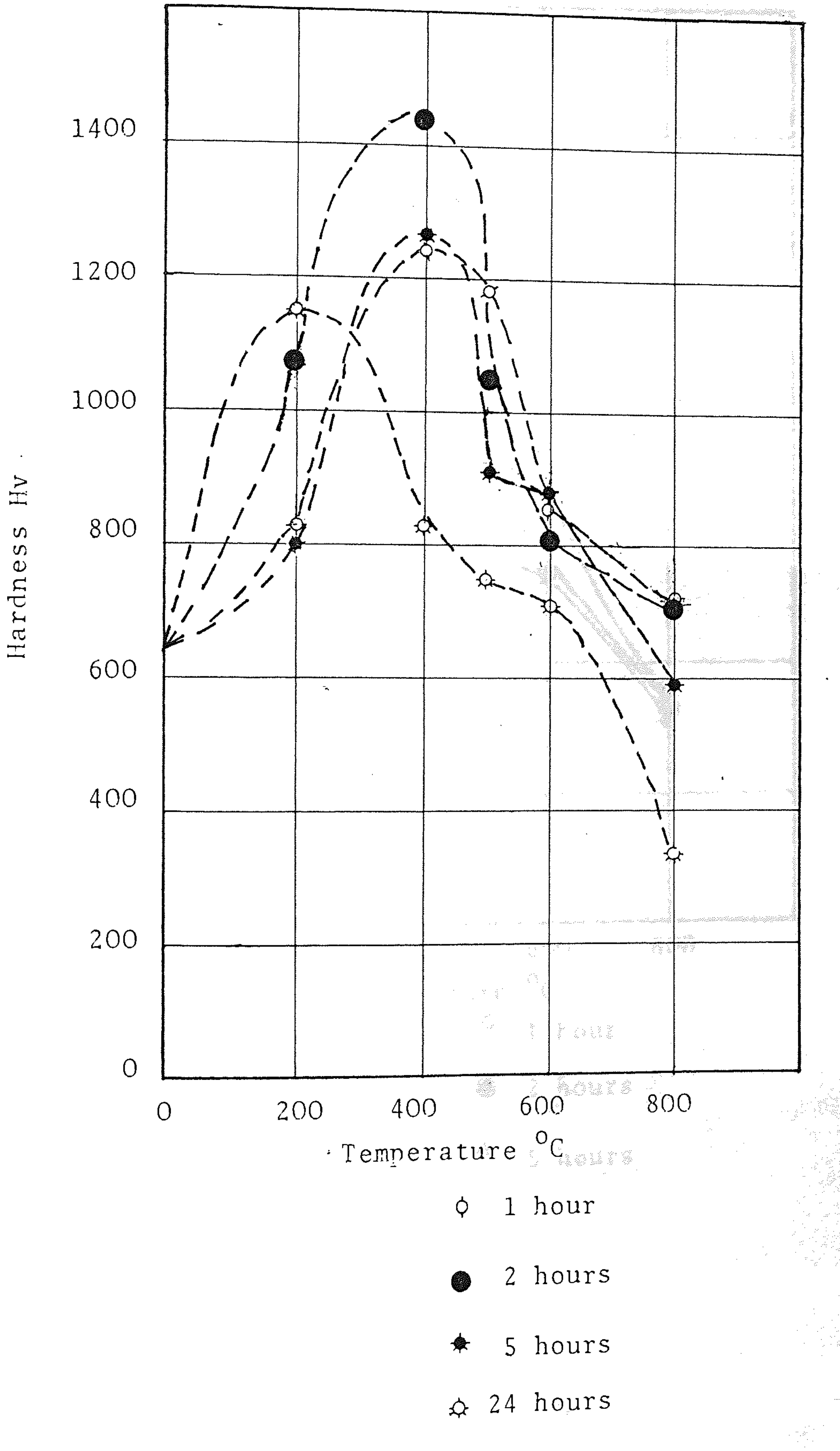


FIGURE 29 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS COBALT COATINGS. HEAT TREATMENT IN AIR

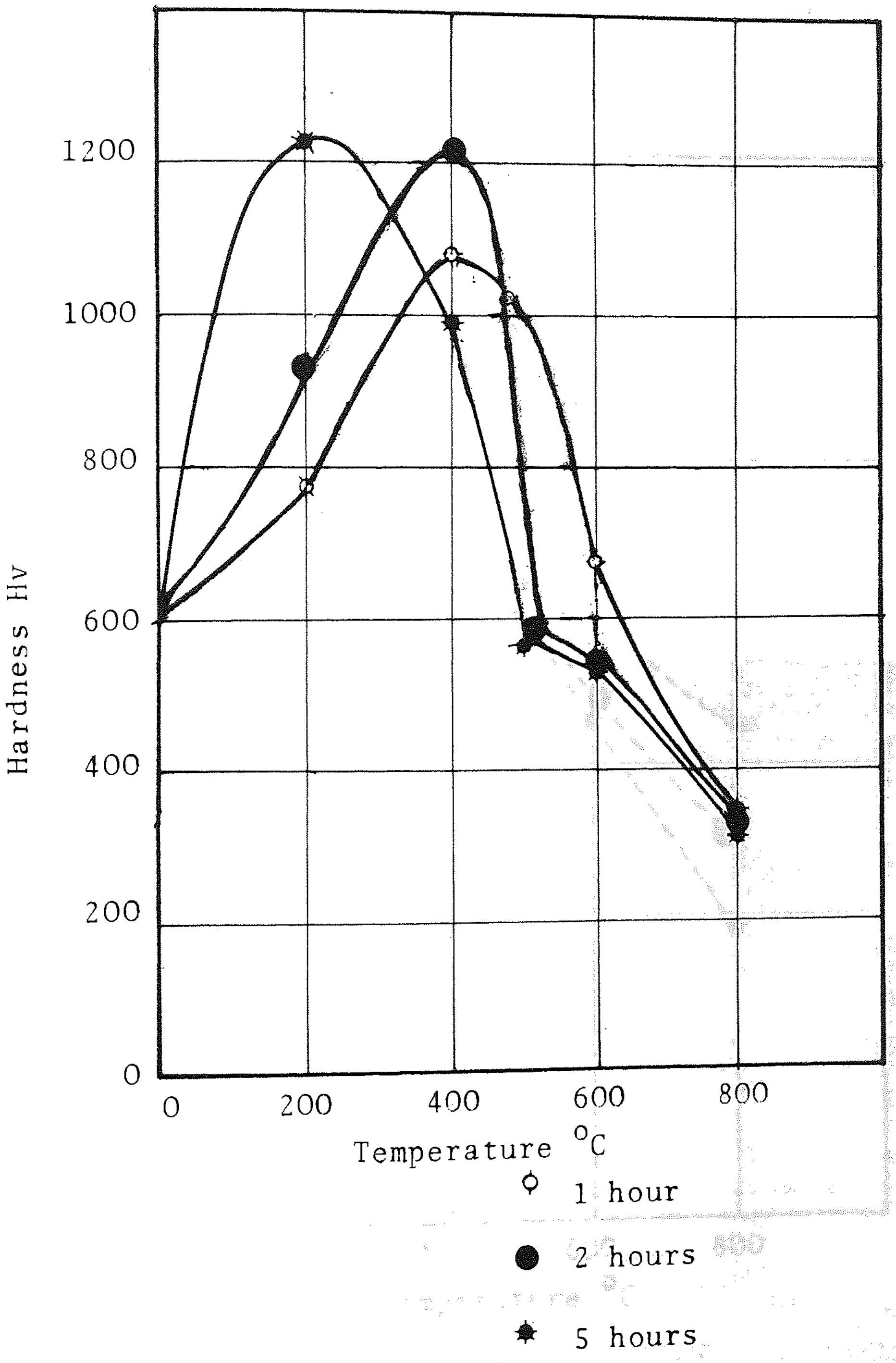


FIGURE 30 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS COBALT+CHROMIUM CARBIDE COMPOSITE COATINGS. HEAT TREATMENT IN AIR

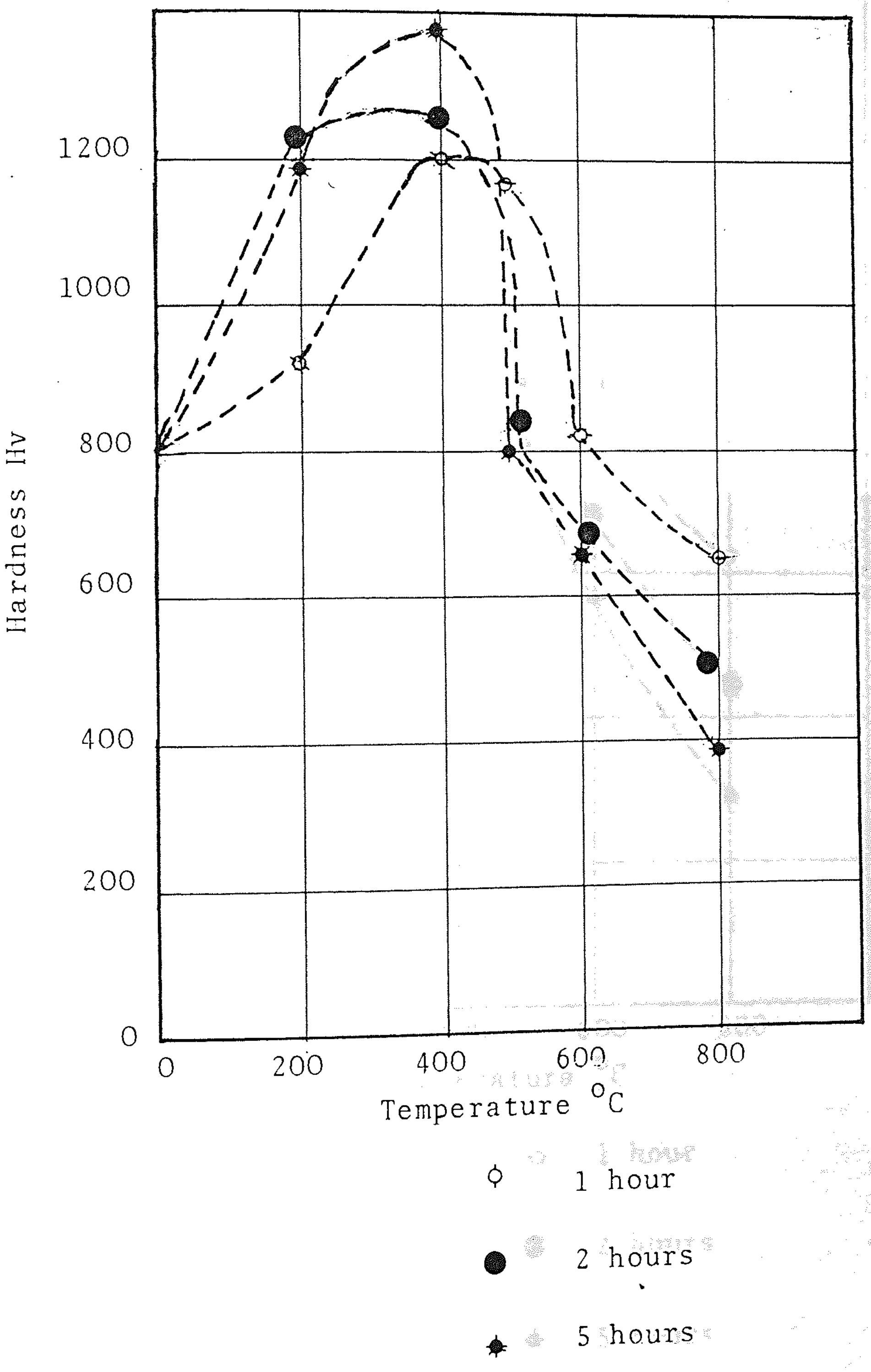


FIGURE 31 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS COBALT+CHROMIUM COMPOSITE COATINGS. HEAT TREATMENT IN AIR

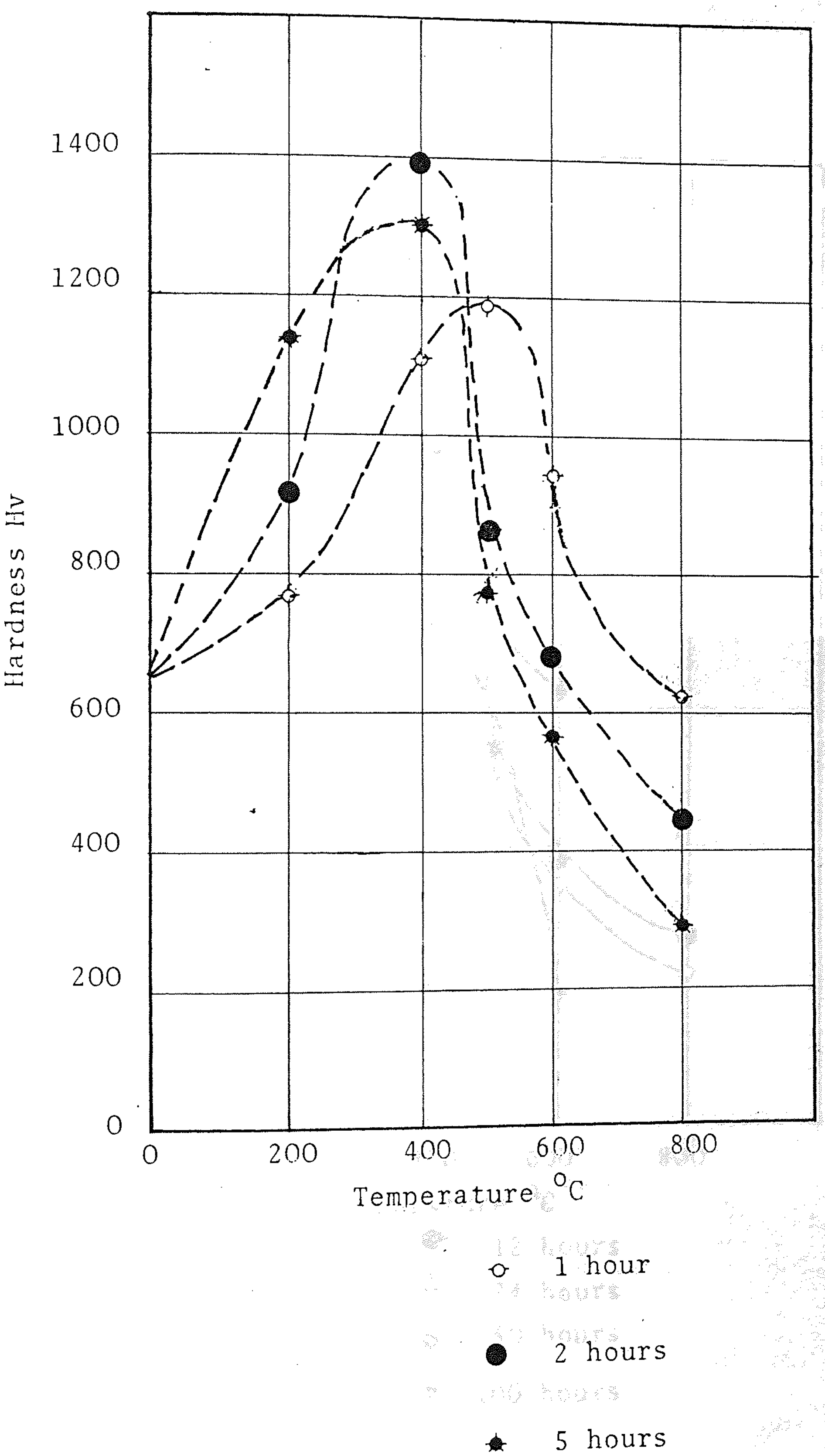


FIGURE 32 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS COBALT COATINGS. HEAT TREATMENT IN AIR

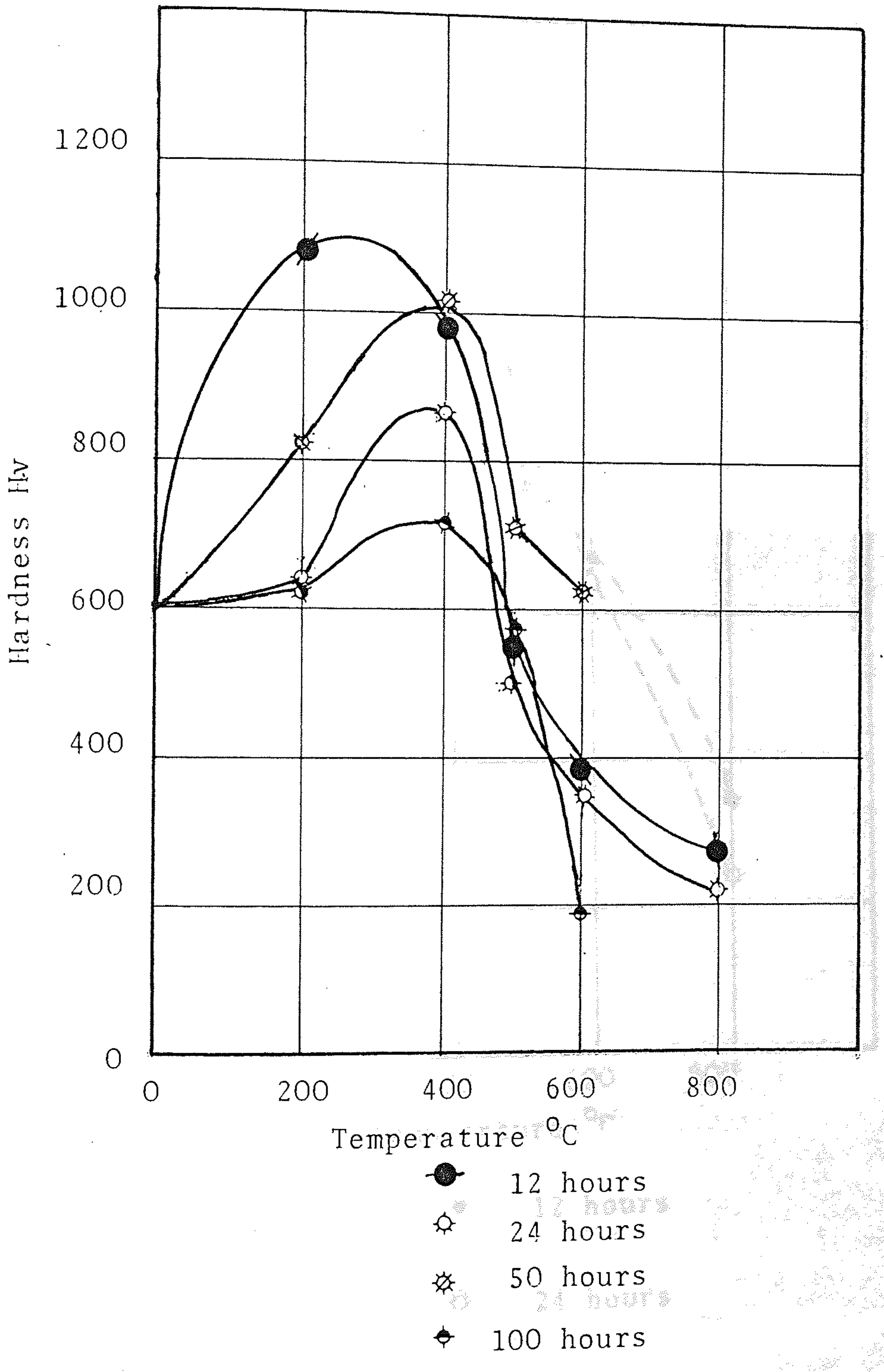


FIGURE 33 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS COBALT+CHROMIUM CARBIDE COMPOSITE COATINGS. HEAT TREATMENT IN AIR

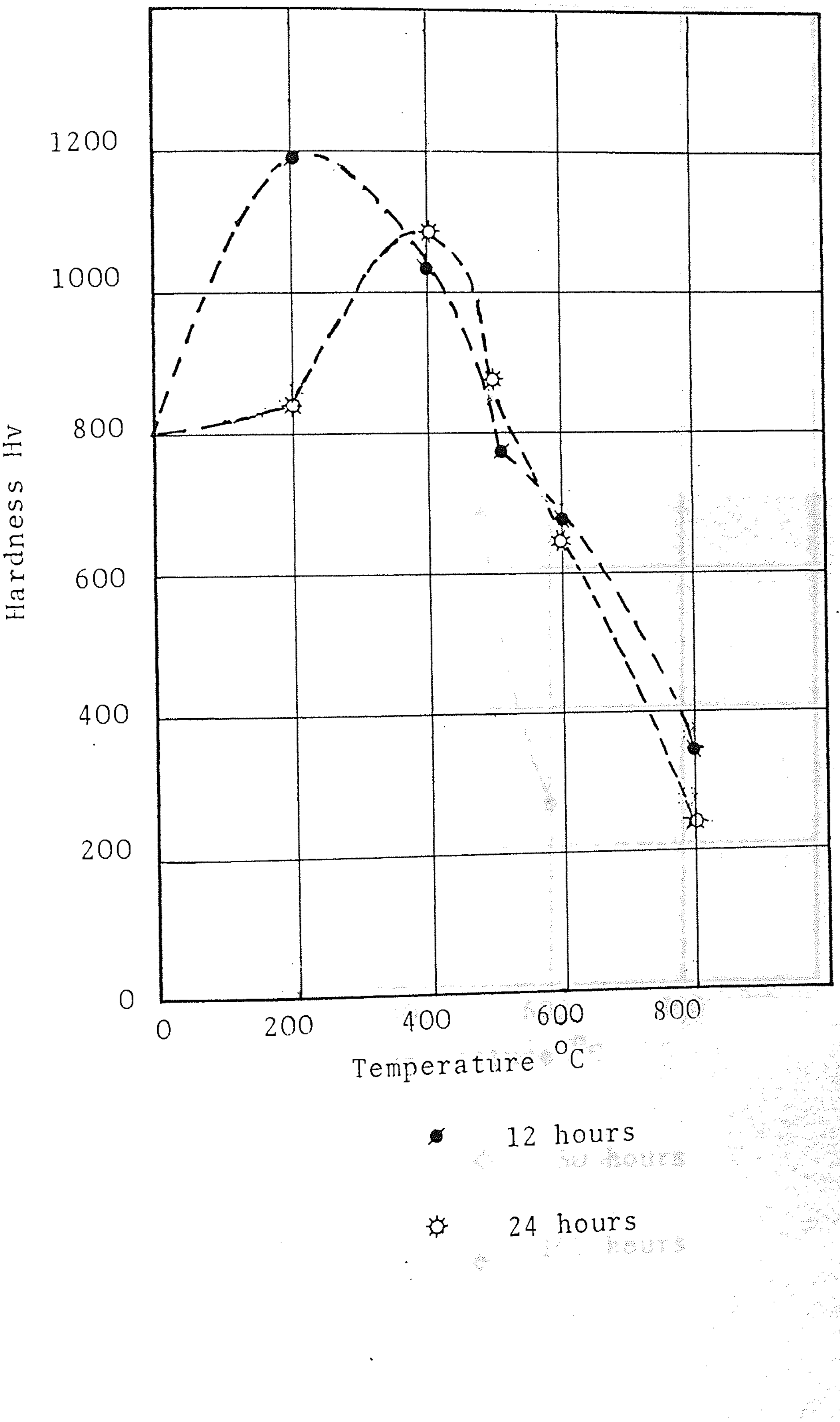


FIGURE 34 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS COBALT+CHROMIUM CARBIDE COMPOSITE COATINGS. HEAT TREATMENT IN AIR

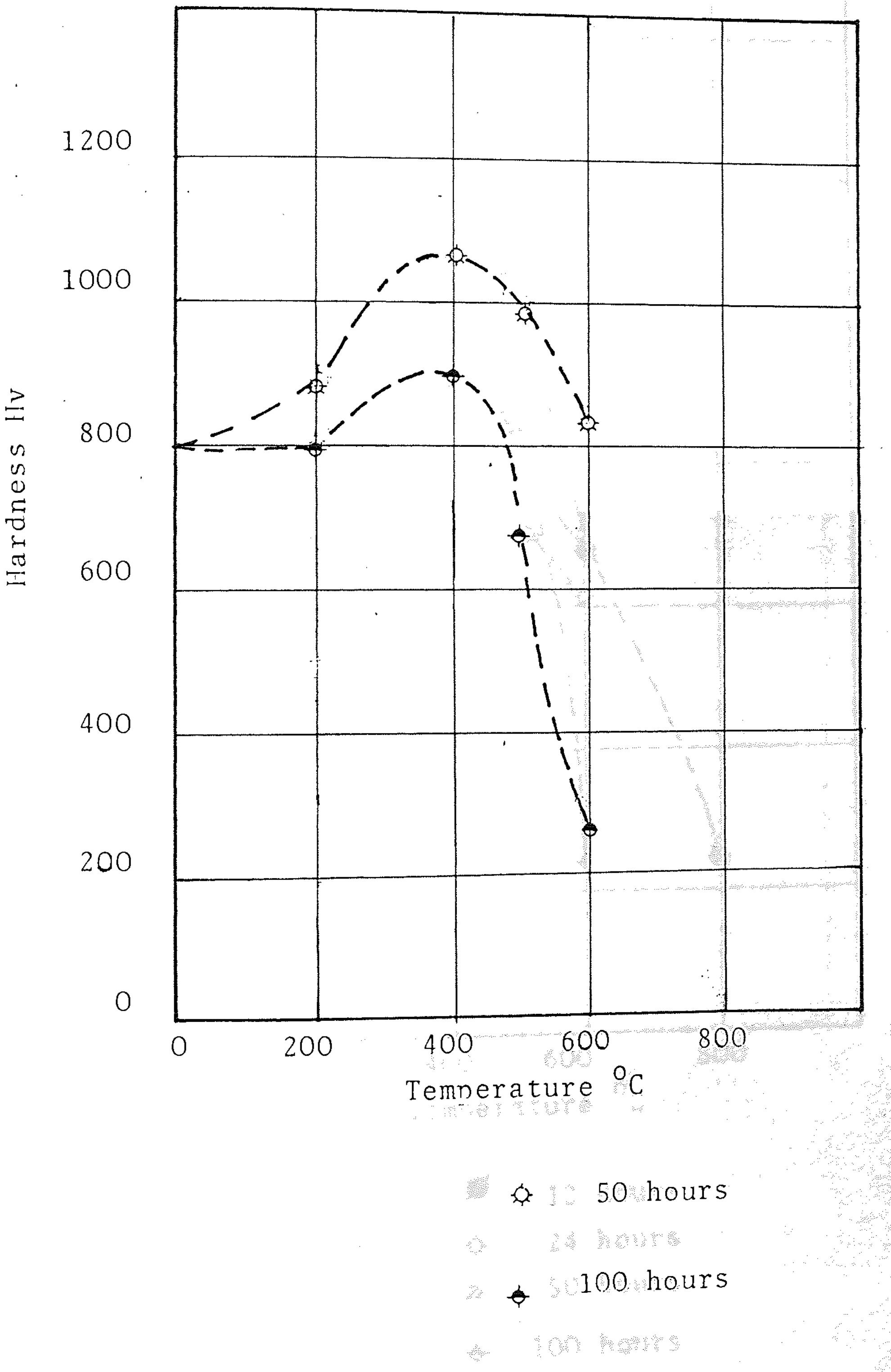


FIGURE 35 HARDNESS VERSUS TEMPERATURE CURVES OF ELECTROLESS COBALT+CHROMIUM COMPOSITE COATINGS. HEAT TREATMENT IN AIR

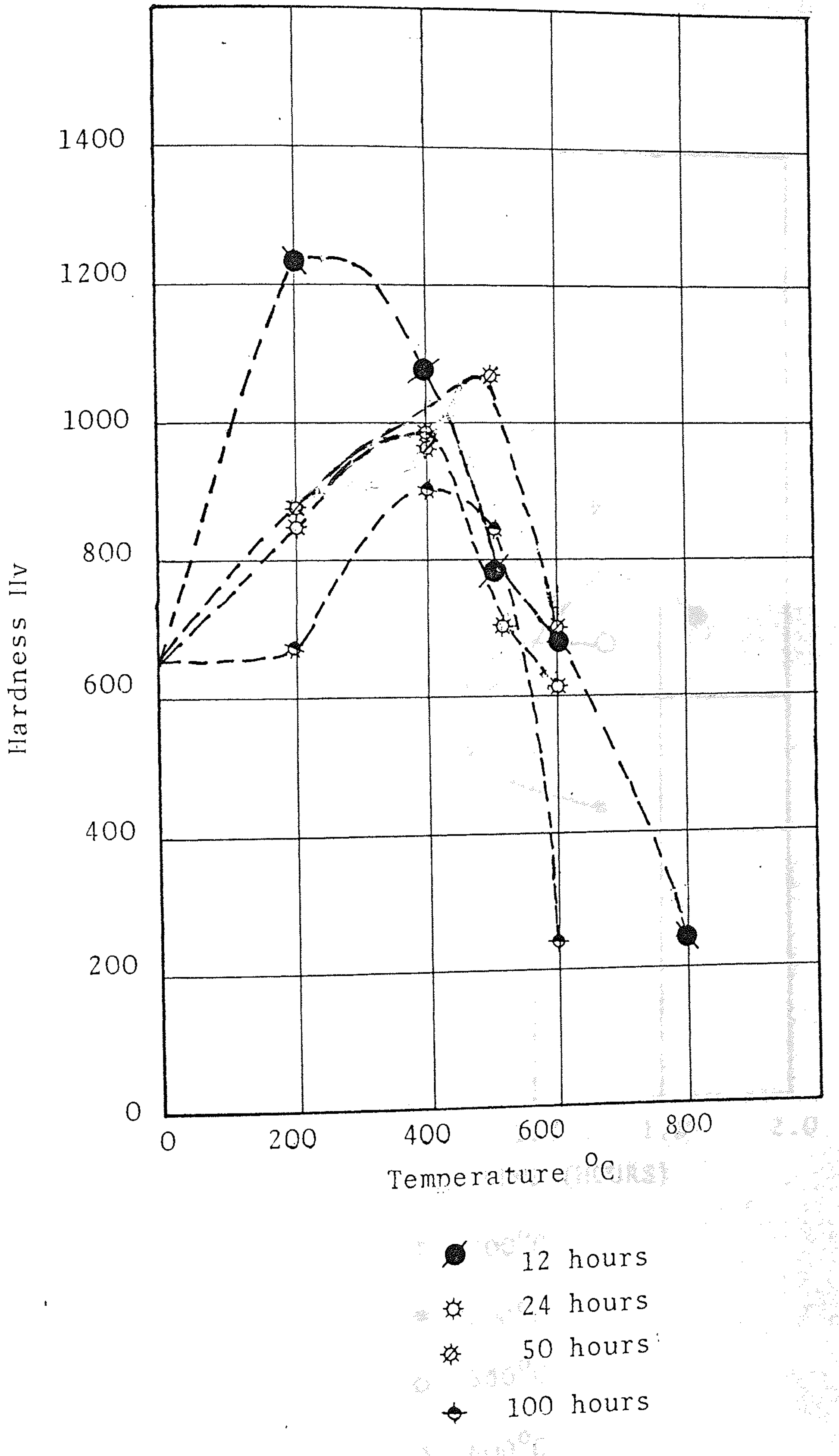


FIGURE 36 HARDNESS VERSUS LOG TIME CURVES OF ELECTROLESS NICKEL COATINGS. HEAT TREATMENT IN VACUUM

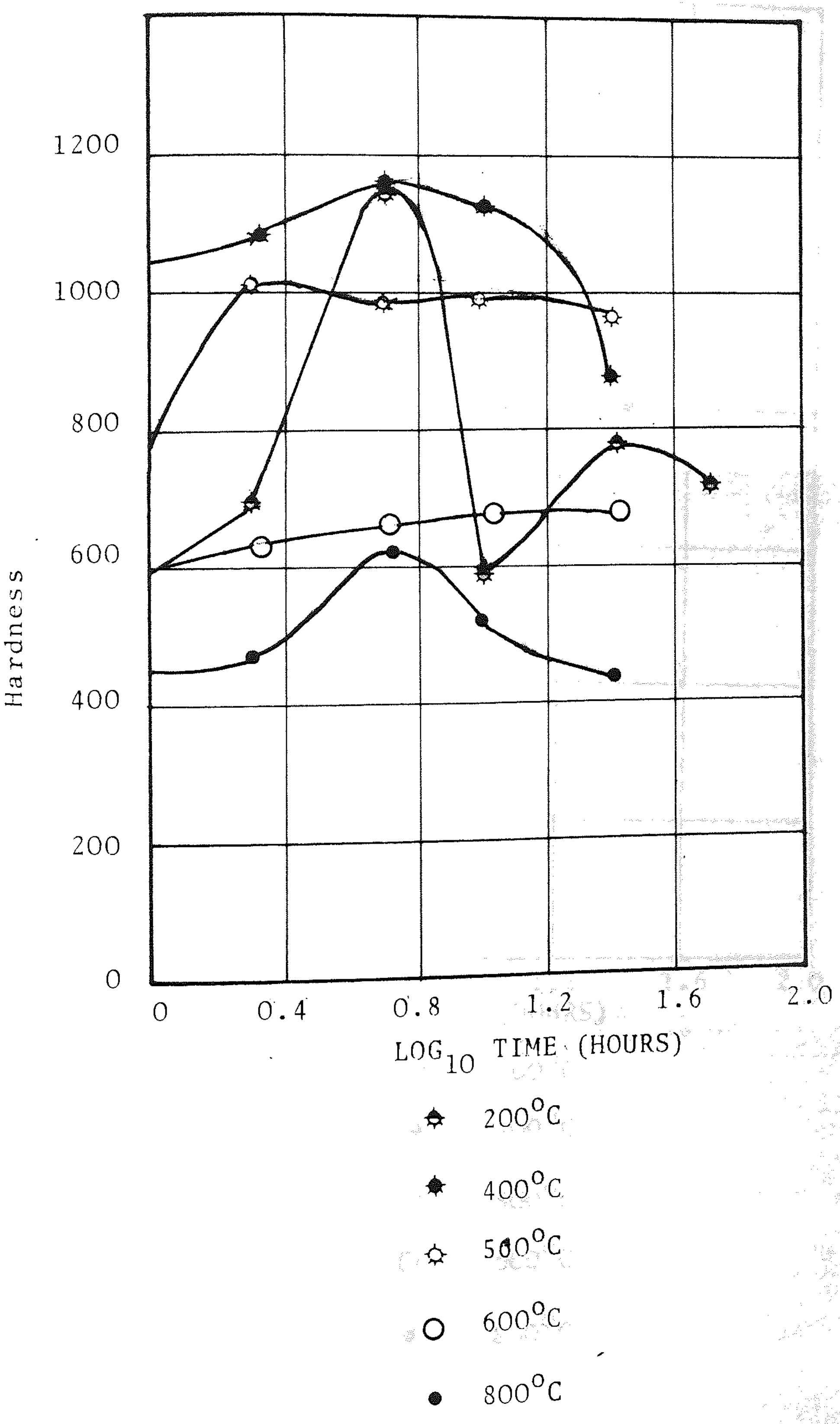


FIGURE 37 HARDNESS VERSUS LOG TIME CURVES OF ELECTROLESS NICKEL+CHROMIUM CARBIDE COMPOSITE COATINGS. HEAT TREATMENT IN VACUUM

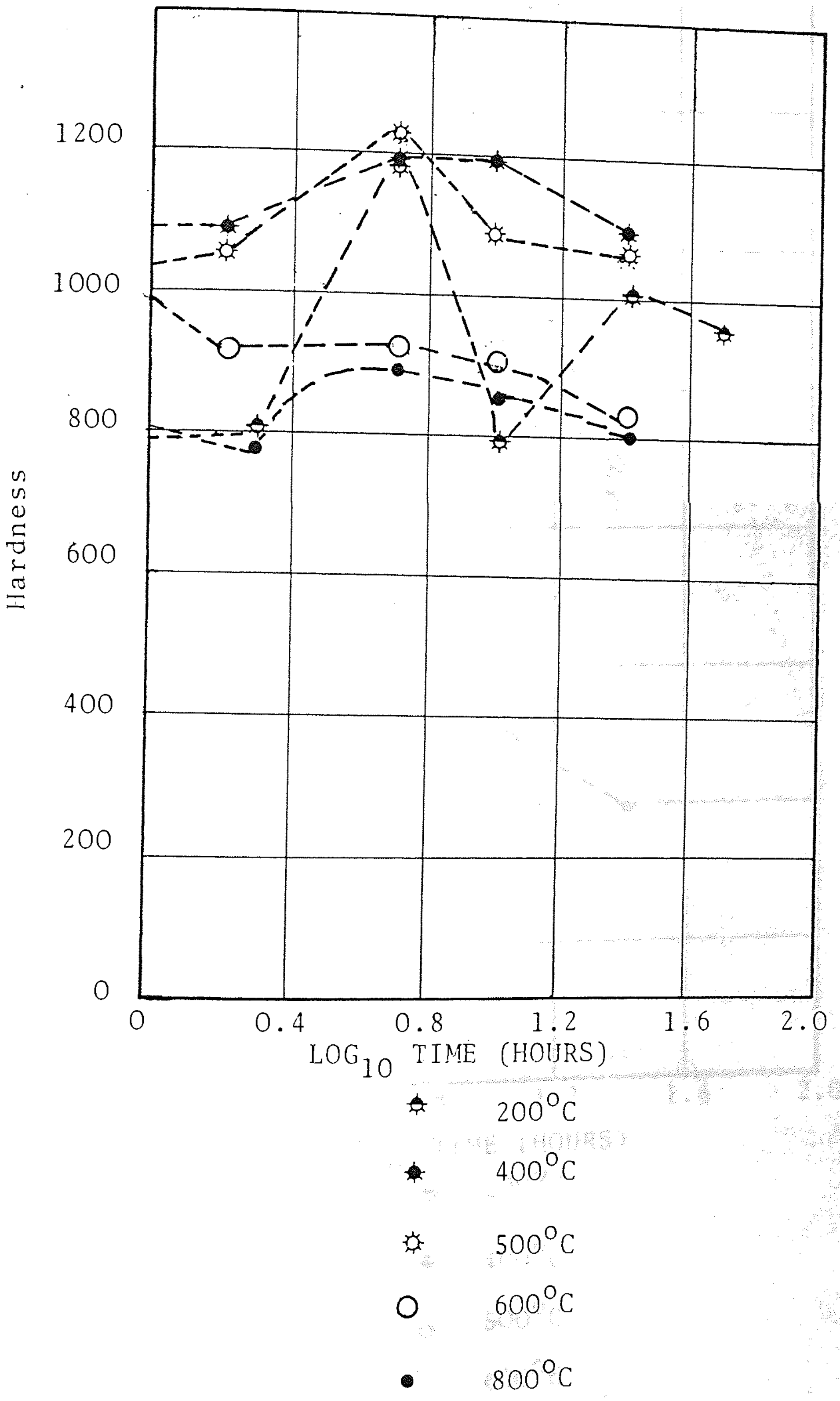


FIGURE 38 HARDNESS VERSUS LOG TIME CURVES OF ELECTROLESS NICKEL+CHROMIUM COMPOSITE COATINGS. HEAT TREATMENT IN VACUUM

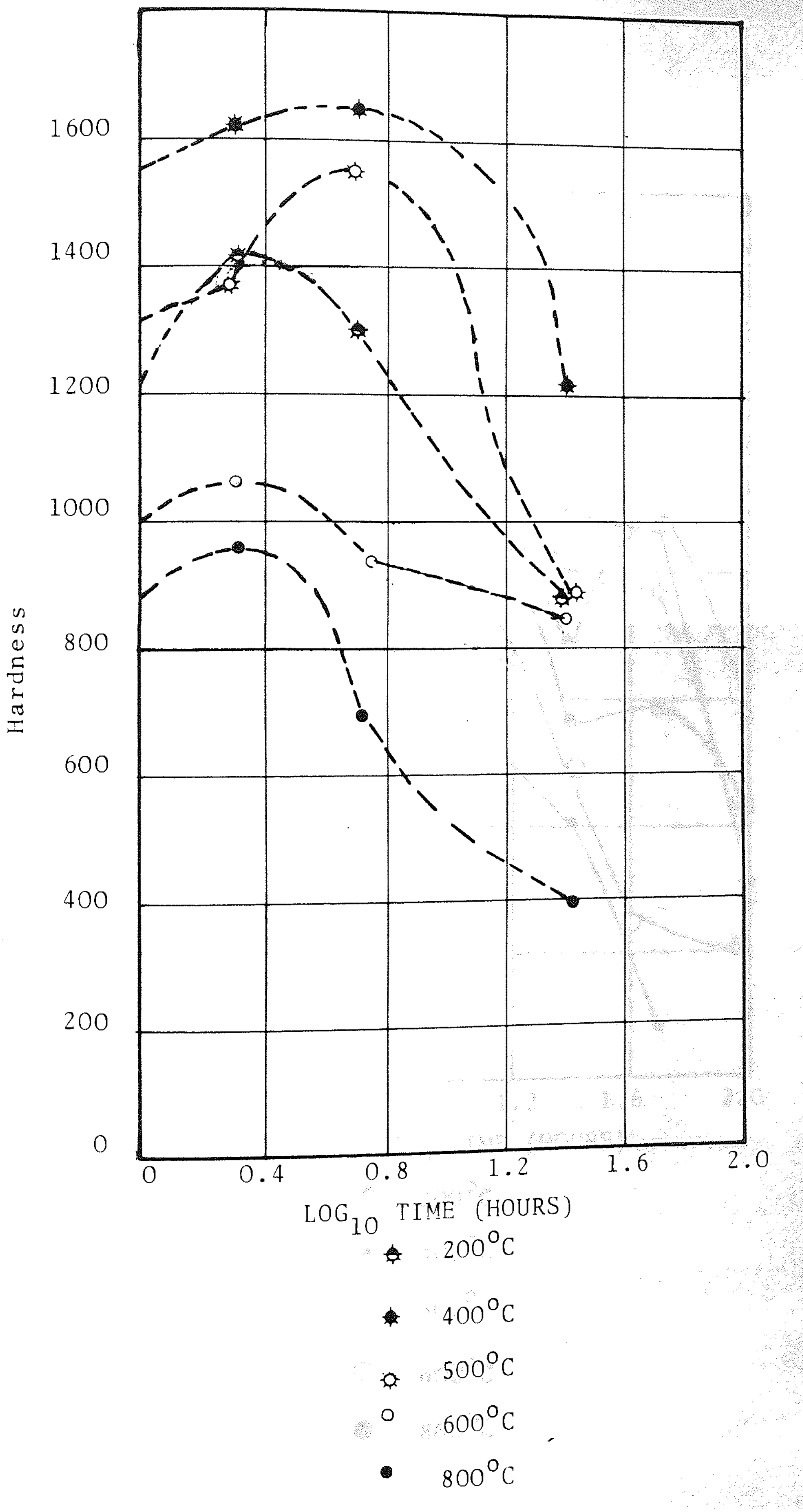


FIGURE 39 HARDNESS VERSUS LOG TIME CURVES OF ELECTROLESS NICKEL COATINGS. HEAT TREATMENT IN AIR

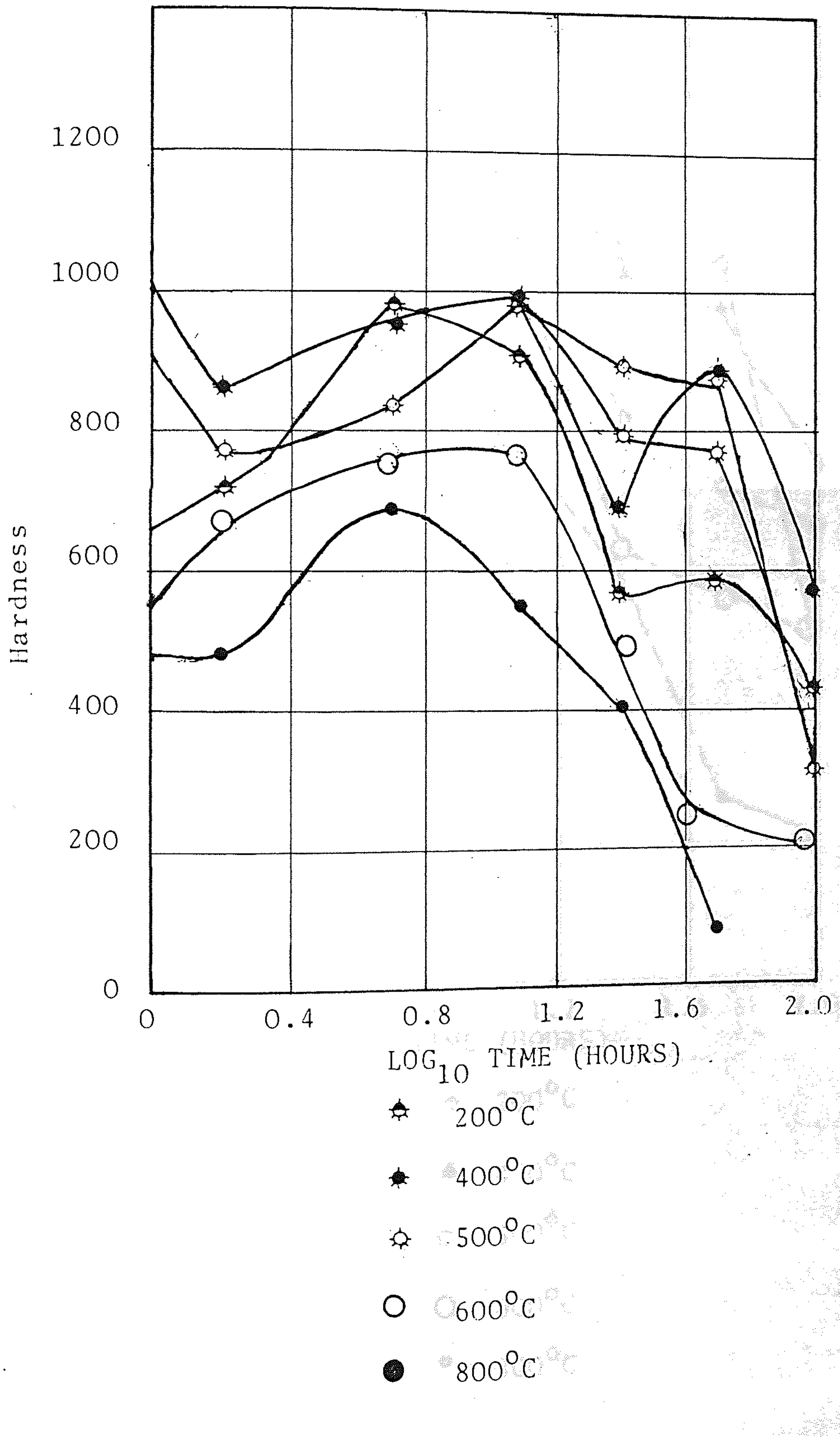


FIGURE 40 HARDNESS VERSUS LOG TIME CURVES OF ELECTROLESS NICKEL+CHROMIUM CARBIDE COMPOSITE COATINGS. HEAT TREATMENT IN AIR

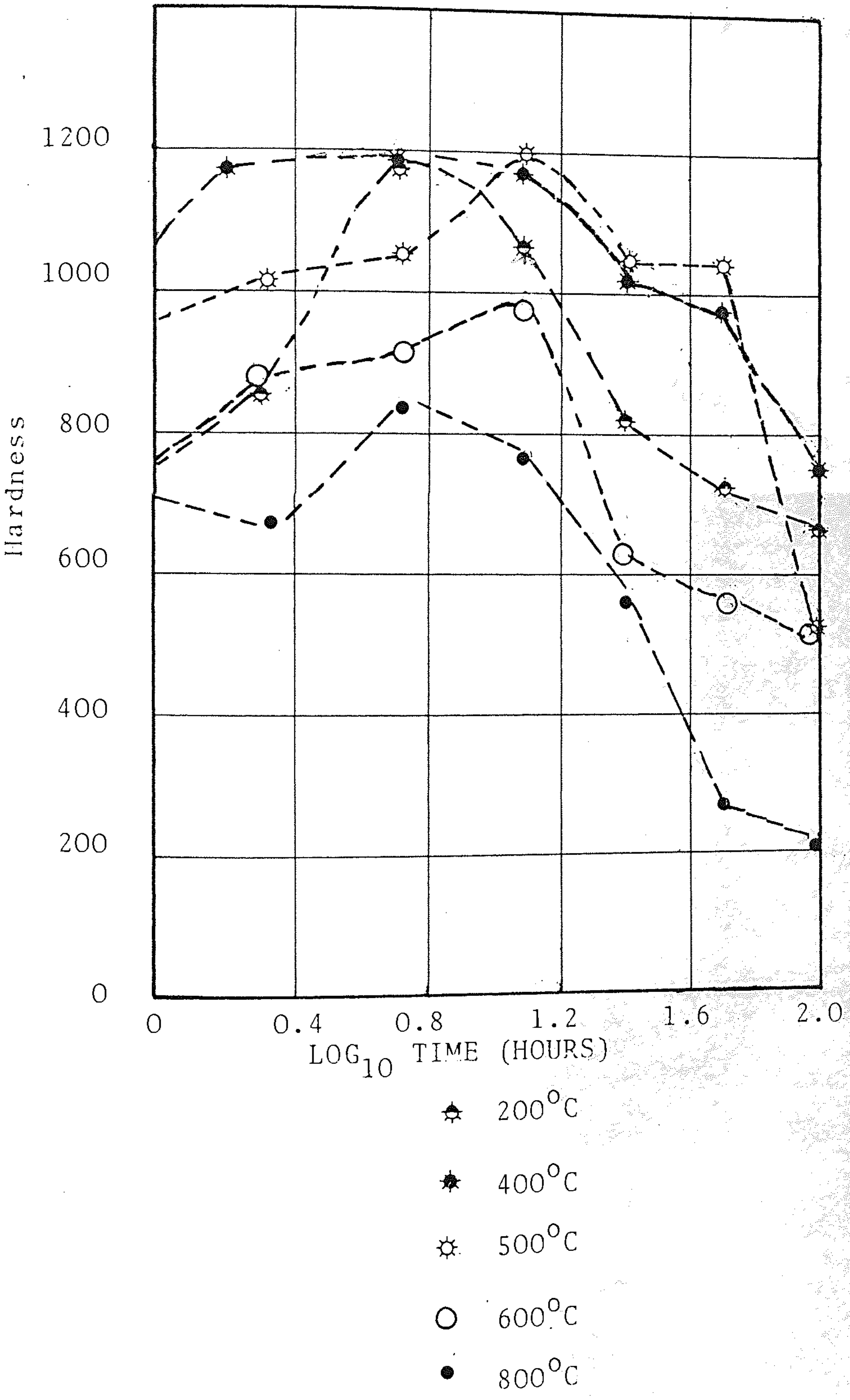


FIGURE 41 HARDNESS VERSUS LOG TIME CURVES OF ELECTROLESS NICKEL+CHROMIUM COMPOSITE COATINGS. HEAT TREATMENT IN AIR

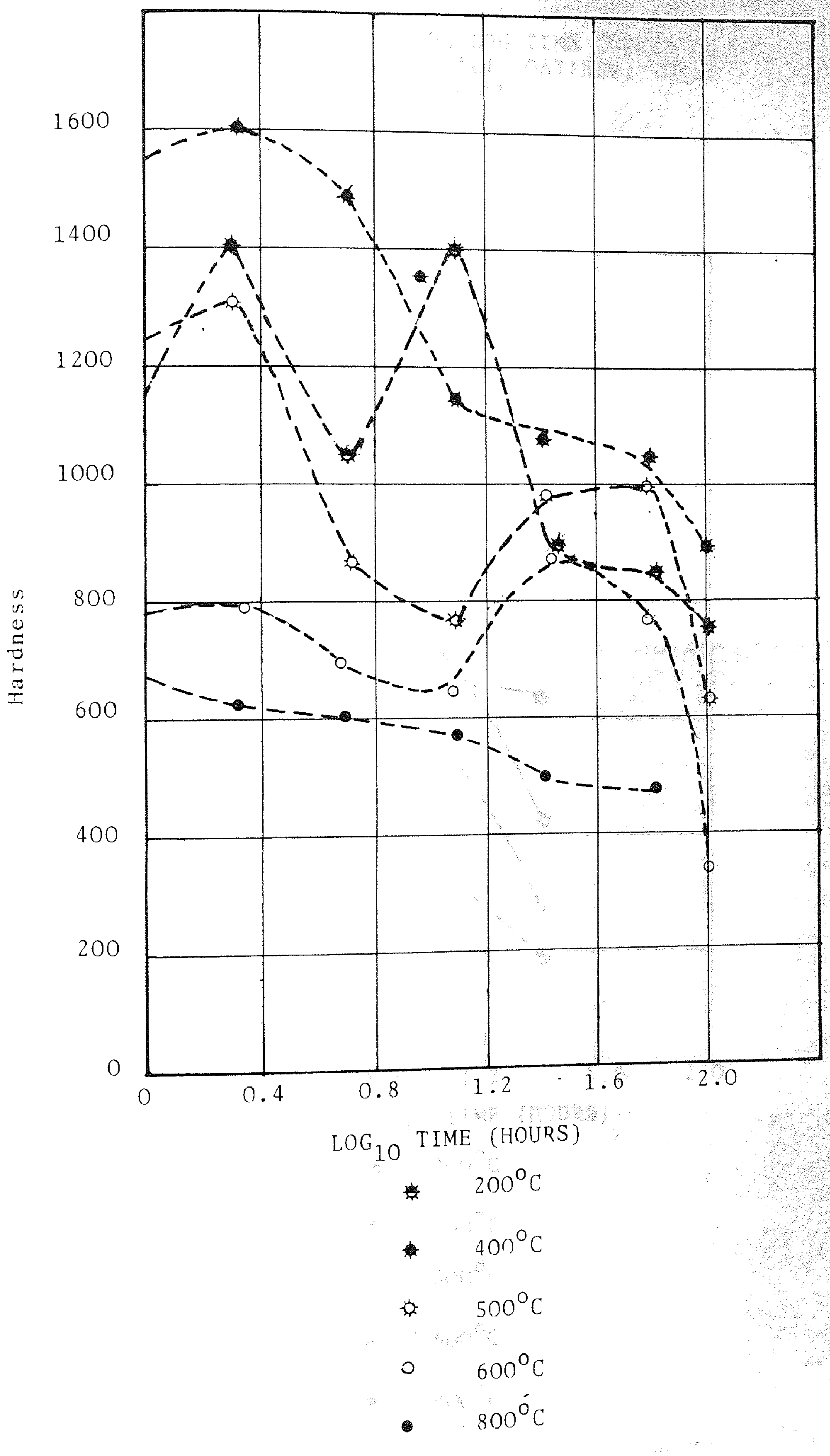


FIGURE 42 HARDNESS VERSUS LOG TIME CURVES OF ELECTROLESS COBALT COATINGS. HEAT TREATMENT IN VACUUM

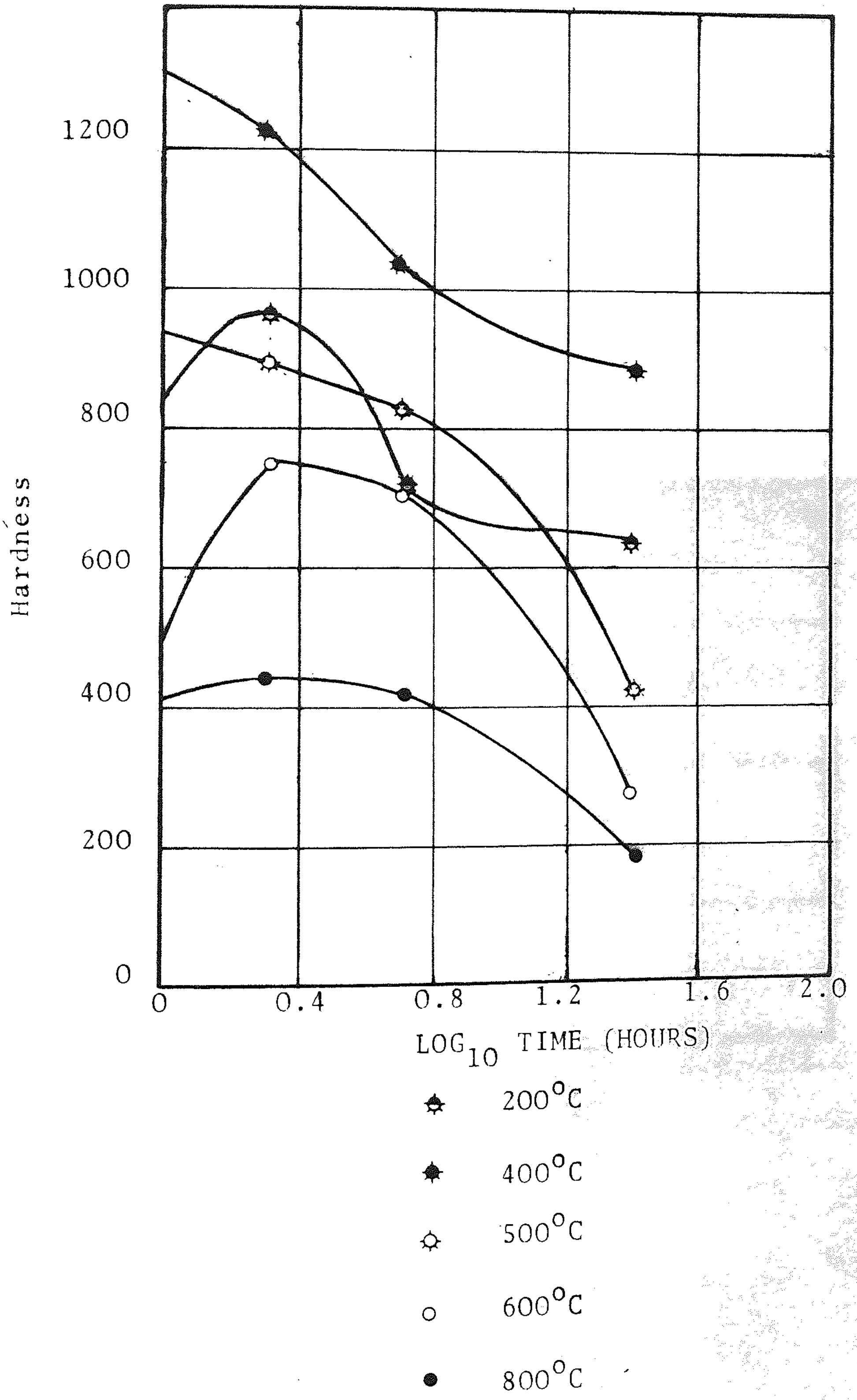


FIGURE 43 HARDNESS VERSUS LOG TIME CURVES OF ELECTROLESS COBALT+CHROMIUM CARBIDE COMPOSITE COATINGS. HEAT TREATMENT IN VACUUM

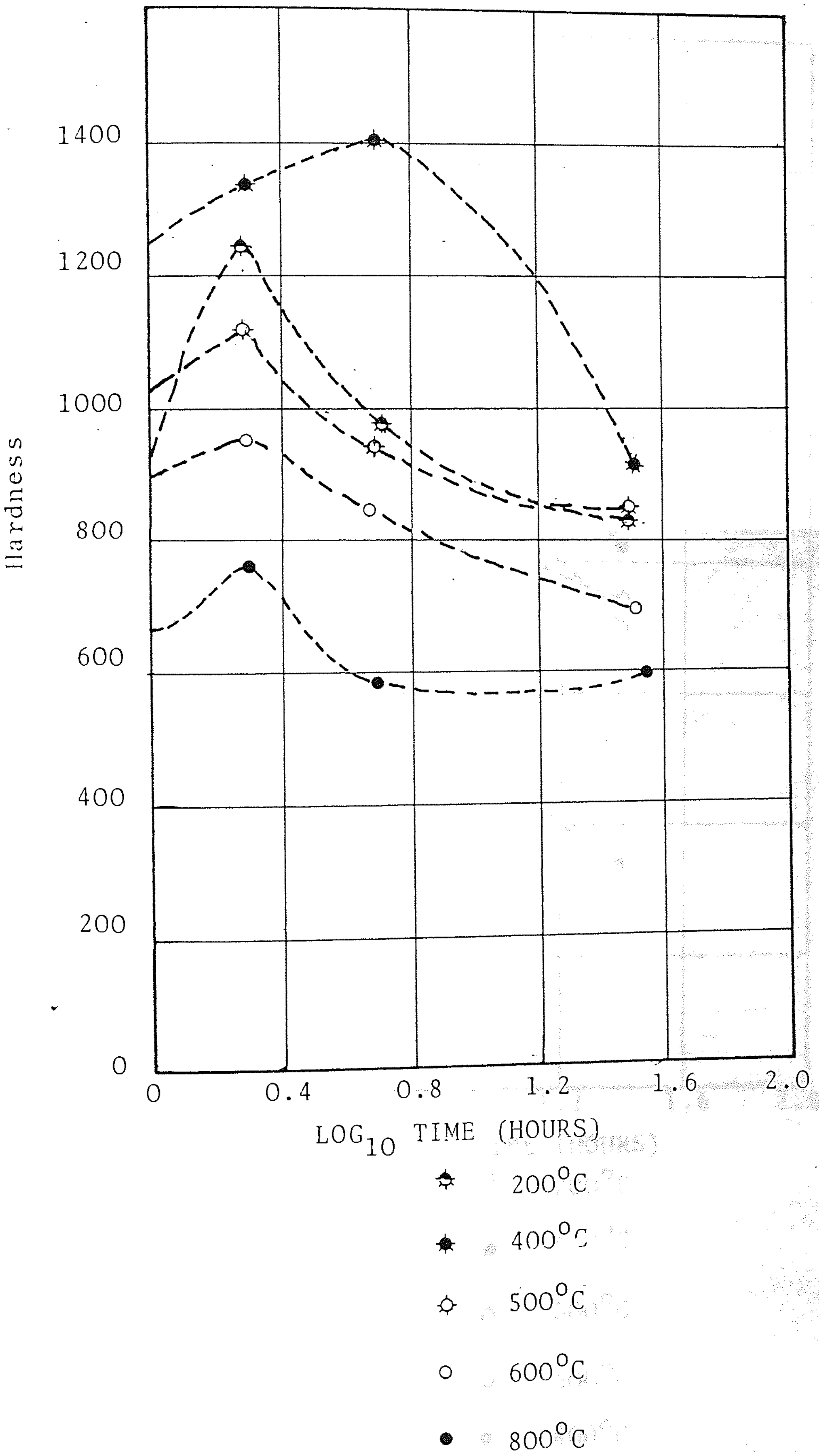


FIGURE 44 HARDNESS VERSUS LOG TIME CURVES OF ELECTROLESS COBALT+CHROMIUM COMPOSITE COATINGS. HEAT TREATMENT IN VACUUM

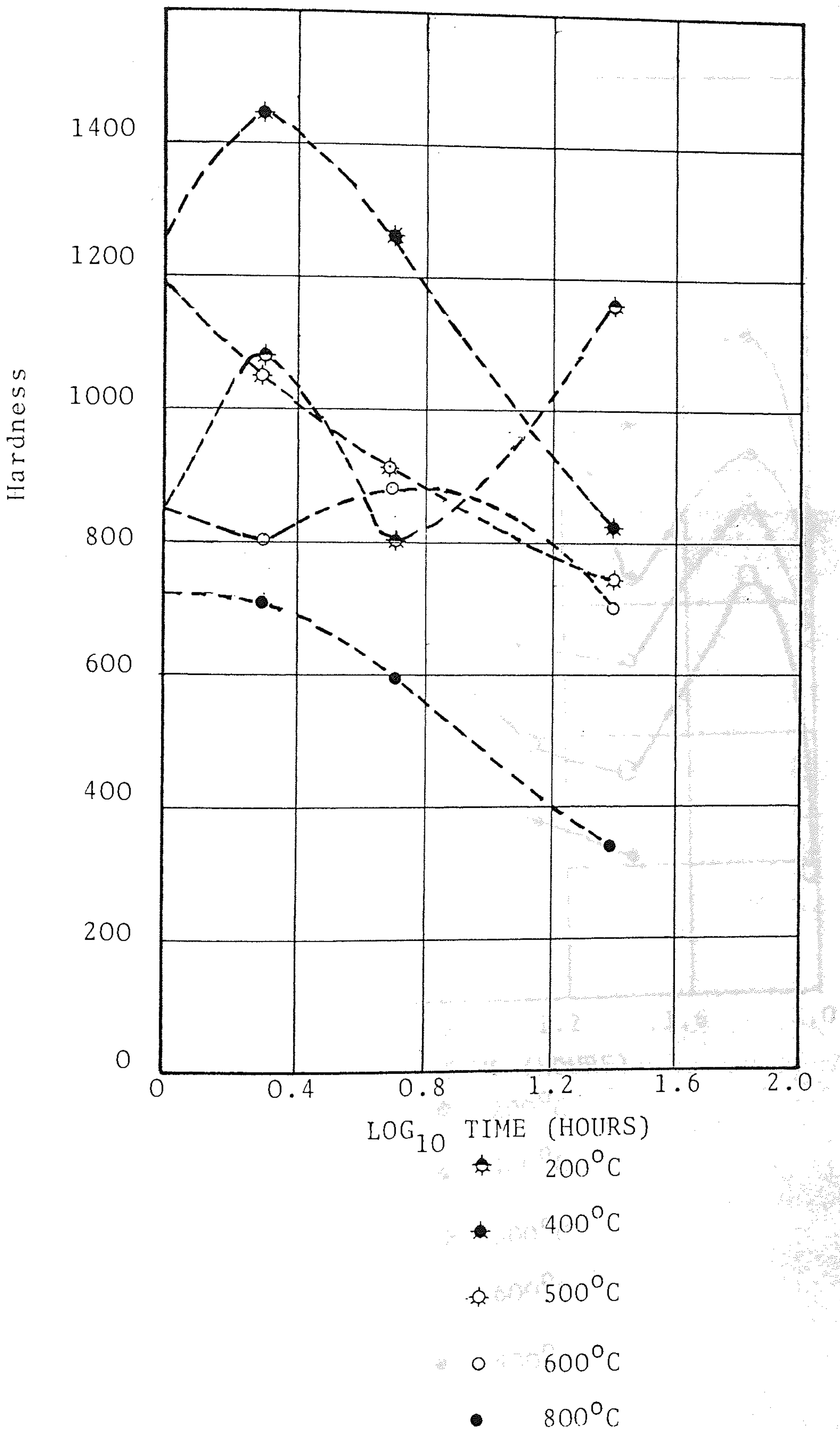


FIGURE 45 HARDNESS VERSUS LOG TIME CURVES OF ELECTROLESS COBALT COATINGS. HEAT TREATMENT IN AIR

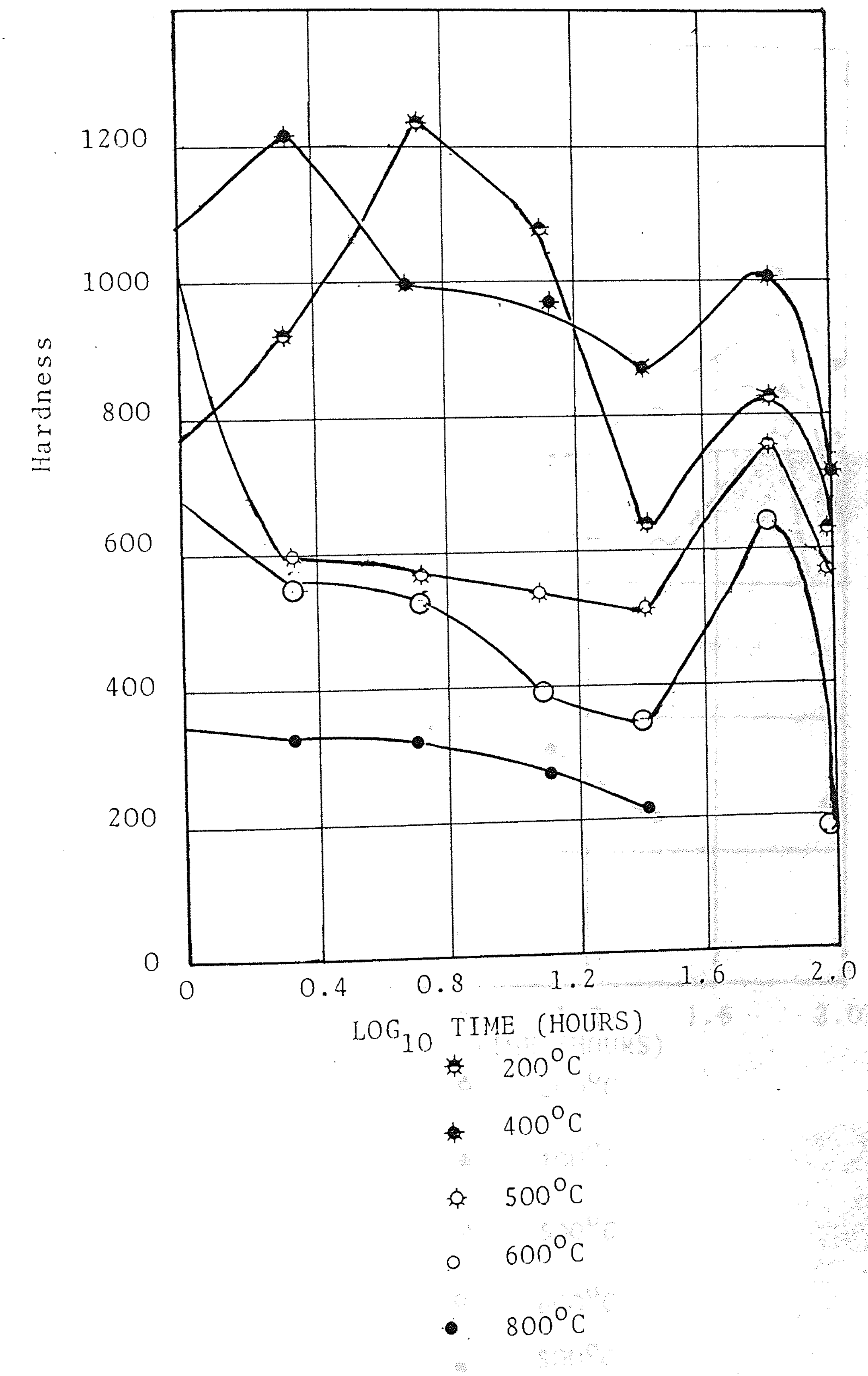


FIGURE 46 HARDNESS VERSUS LOG TIME CURVES OF ELECTROLESS COBALT+CHROMIUM CARBIDE COATINGS. HEAT TREATMENT IN AIR

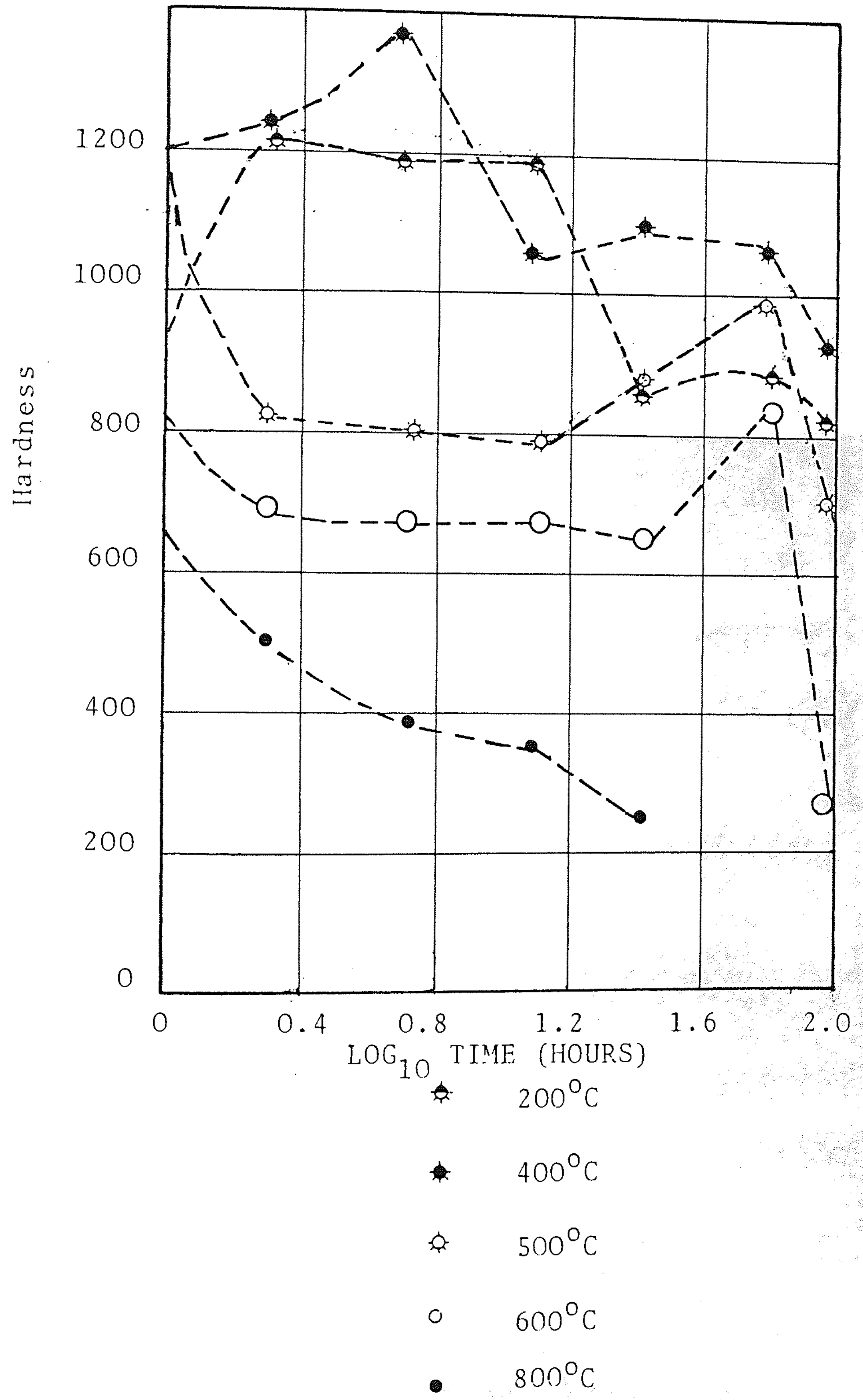
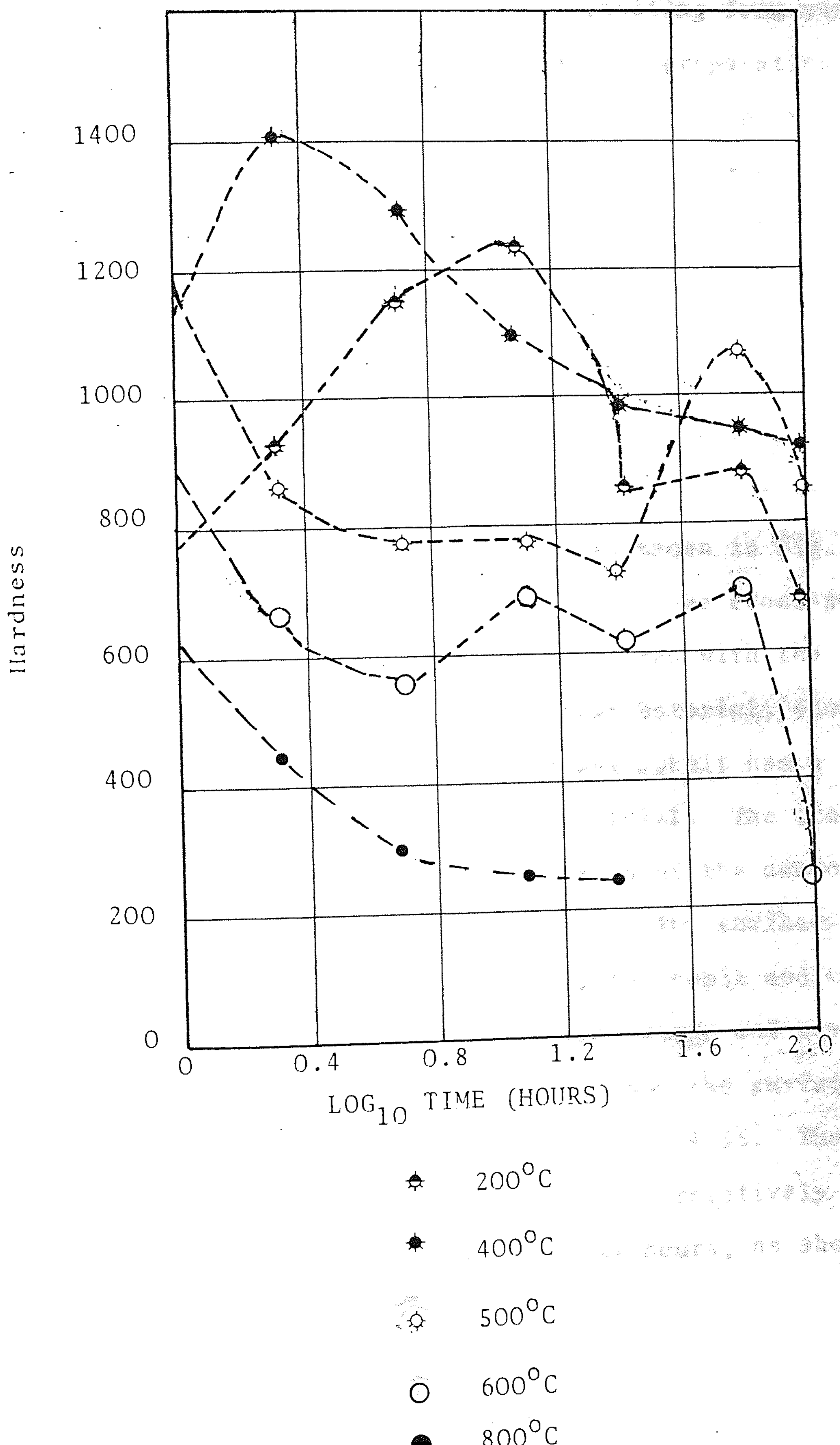


FIGURE 47 HARDNESS VERSUS LOG TIME CURVE OF ELECTROLESS COBALT+CHROMIUM COMPOSITE COATINGS. HEAT TREATMENT IN AIR



4.4 Optical Examination

Figure 48 shows a cross-sectional view of the nickel + chromium carbide composite deposit. The chromium carbide particles (light and angular ones) are evenly distributed throughout the matrix of electroless nickel. The larger black areas are probably voids resulting from particles being pulled out during the specimen preparation and the smaller voids are porosity resulting from poor deposition conditions. Figure 49 shows that cobalt + chromium carbide composite deposits produced are nodular and the porosity is interconnecting, unlike those in the nickel deposits.

4.5 Scanning Electron Microscope Examination

Scanning electron micrograph of etched cross-section of the as deposited electroless nickel is shown in Fig. 50. The banded structure is clearly shown in the cross-section of electroless nickel and may be compared with the x-ray fluorescent photograph of the same material, shown in Fig. 51. As deposited electroless cobalt has a similar banded structure to electroless nickel. The scanning electron micrographs of the surface of the composite deposits are shown in Figs. 52-55. The surfaces of both the nickel and chromium carbide, and cobalt and chromium carbide plated for ½ hour are less rough and have fewer crevices, as shown in Figs. 52, 53, than the surface of the deposits plated for six hours, Figs. 54,55. The surface of the nickel and chromium composite is relatively smooth after plating for one hour and six hours, as shown in

FIGURE 48 CROSS-SECTION OF NICKEL-CHROMIUM CARBIDE COMPOSITE DEPOSIT (x1500 OPTICAL MICROGRAPH)

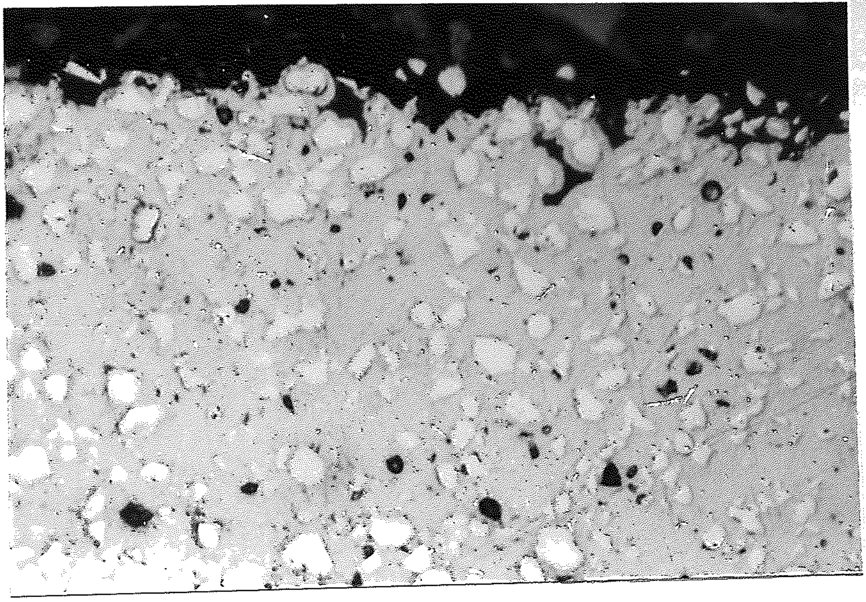


FIGURE 49 CROSS-SECTION OF COBALT-CHROMIUM CARBIDE COMPOSITE DEPOSIT (x1500 OPTICAL MICROGRAPH)

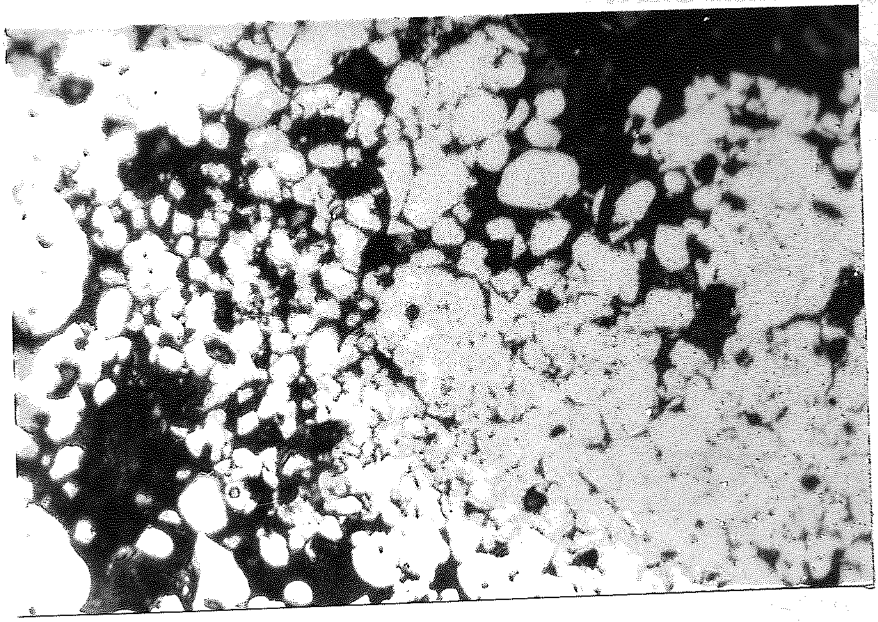


FIGURE 50 CROSS-SECTION OF AS-PLATED AND ETCHED ELECTROLESS NICKEL SHOWING BANDING
(SCANNING ELECTRON MICROGRAPH)

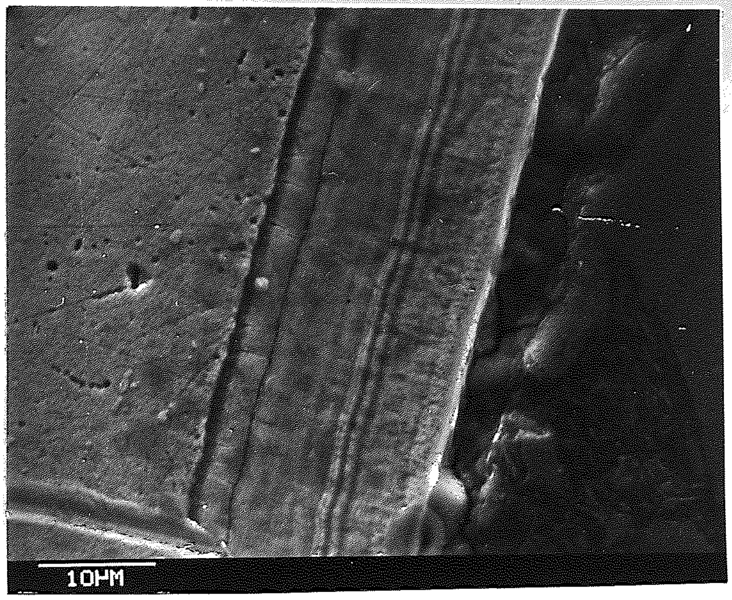


FIGURE 51 X-RAY FLUORESCENT PHOTOGRAPH OF ELECTROLESS NICKEL
(SCANNING ELECTRON MICROGRAPH)

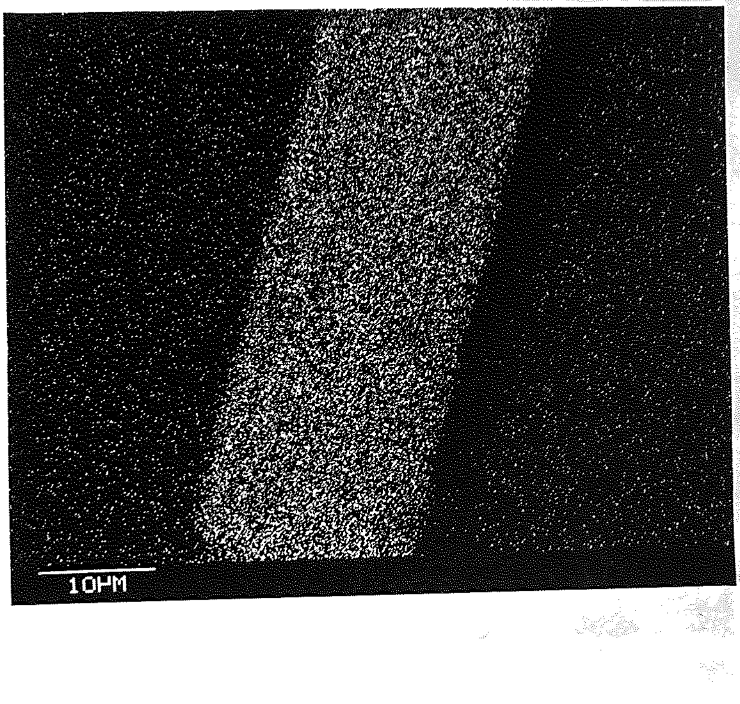


FIGURE 52 SURFACE OF NICKEL+CHROMIUM CARBIDE COMPOSITE DEPOSIT AFTER ½ HOUR PLATING (SCANNING ELECTRON MICROGRAPH)

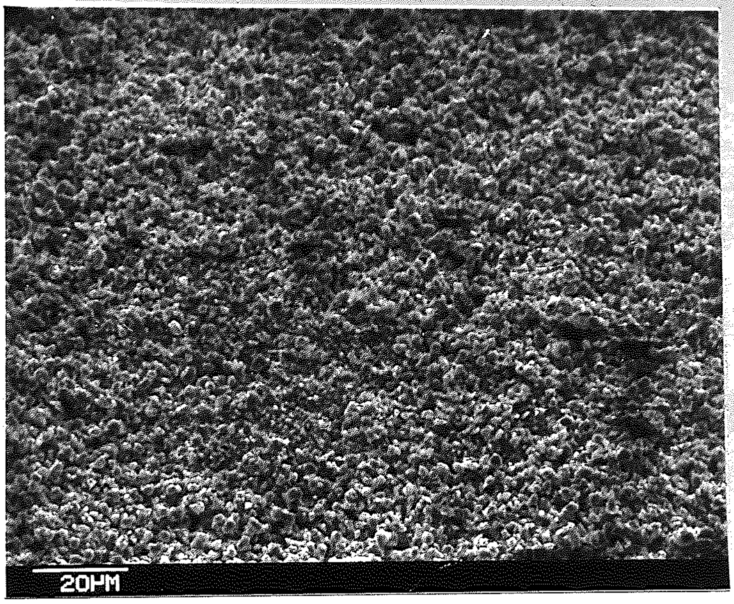


FIGURE 53 SURFACE OF COBALT+CHROMIUM CARBIDE COMPOSITE DEPOSIT AFTER ½ HOUR PLATING (SCANNING ELECTRON MICROGRAPH)

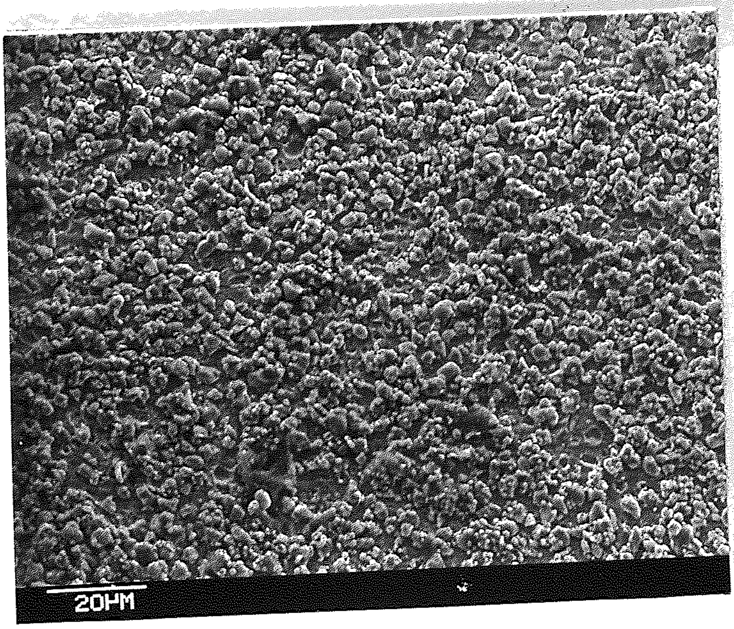


FIGURE 54 SURFACE OF NICKEL+CHROMIUM CARBIDE COMPOSITE DEPOSIT AFTER 6 HOURS PLATING (SCANNING ELECTRON MICROGRAPH)

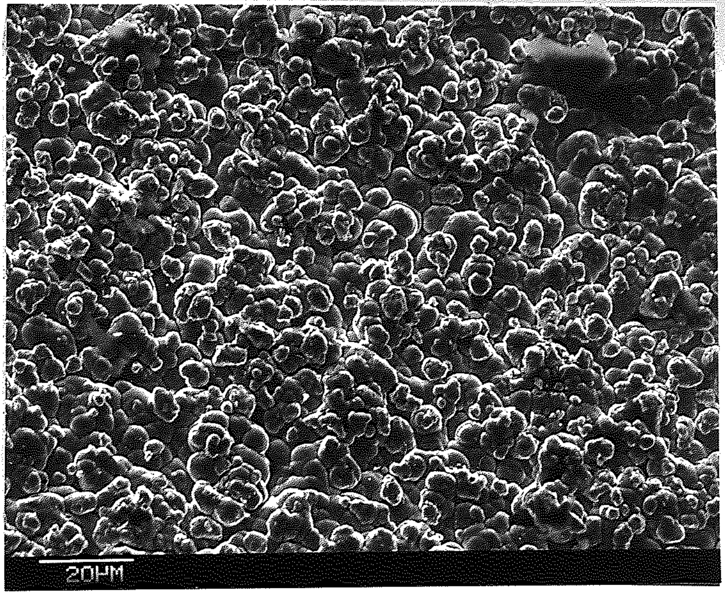


FIGURE 55 SURFACE OF COBALT+CHROMIUM CARBIDE COMPOSITE DEPOSIT AFTER 6 HOURS PLATING (SCANNING ELECTRON MICROGRAPH)

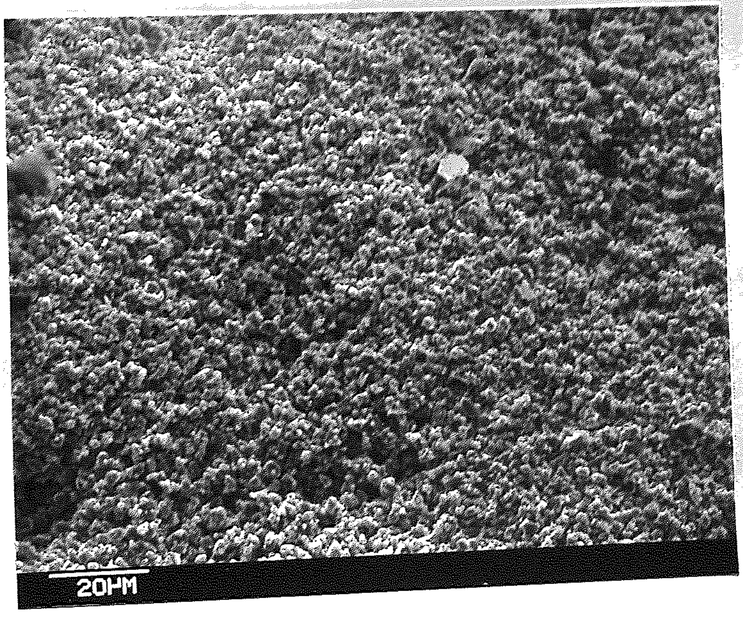


FIGURE 56 SURFACE OF NICKEL+CHROMIUM COMPOSITE DEPOSIT AFTER 12 HOURS PLATING (x 1000 SCANNING ELECTRON MICROGRAPH)

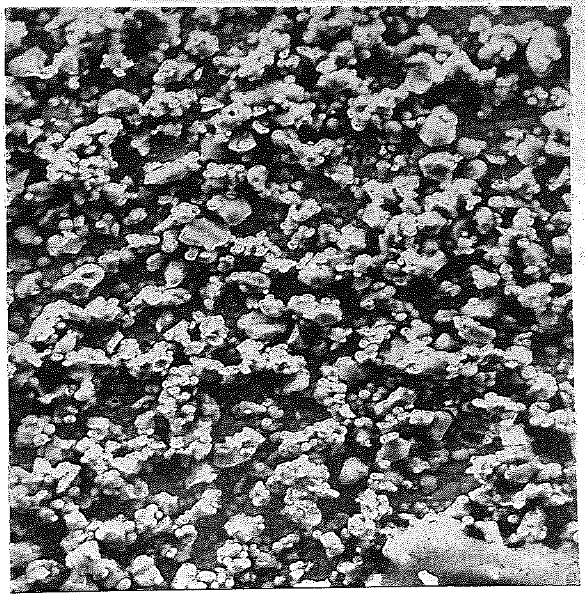


FIGURE 57 SURFACE OF NICKEL+CHROMIUM COMPOSITE DEPOSIT AFTER 6 HOURS PLATING (SCANNING ELECTRON MICROGRAPH)

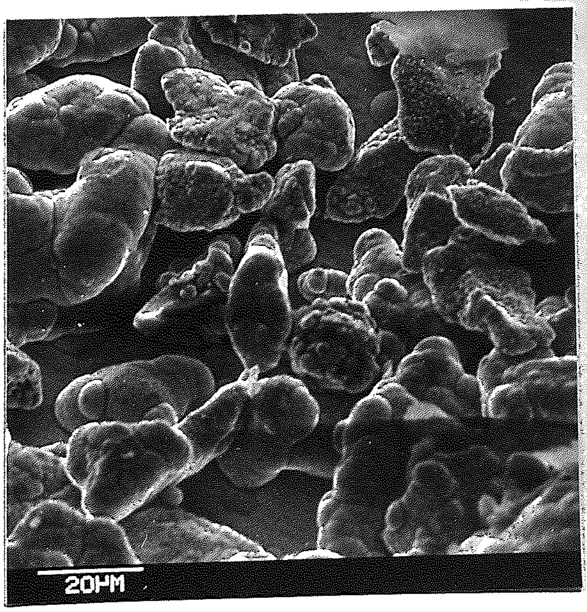


FIGURE 58 CROSS-SECTION OF NICKEL+CHROMIUM CARBIDE COMPOSITE DEPOSIT (SCANNING ELECTRON MICROGRAPH)

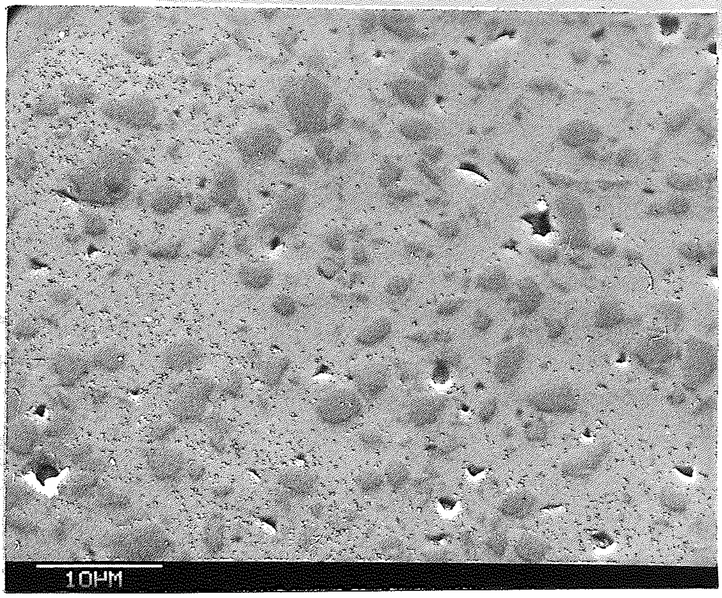


FIGURE 59 CROSS-SECTION OF COBALT+CHROMIUM CARBIDE COMPOSITE DEPOSIT (SCANNING ELECTRON MICROGRAPH)

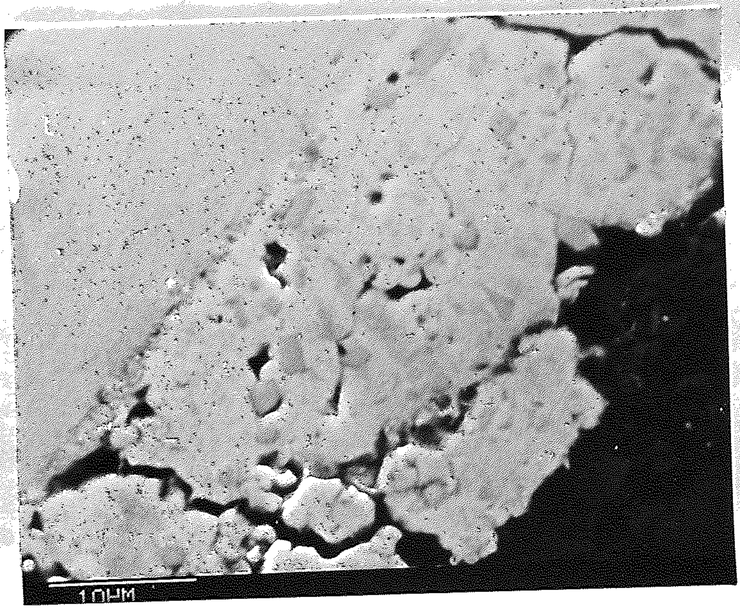


FIGURE 60 X-RAY FLUORESCENCE OF NICKEL+CHROMIUM COMPOSITE DEPOSITS (SCANNING ELECTRON MICROGRAPH)

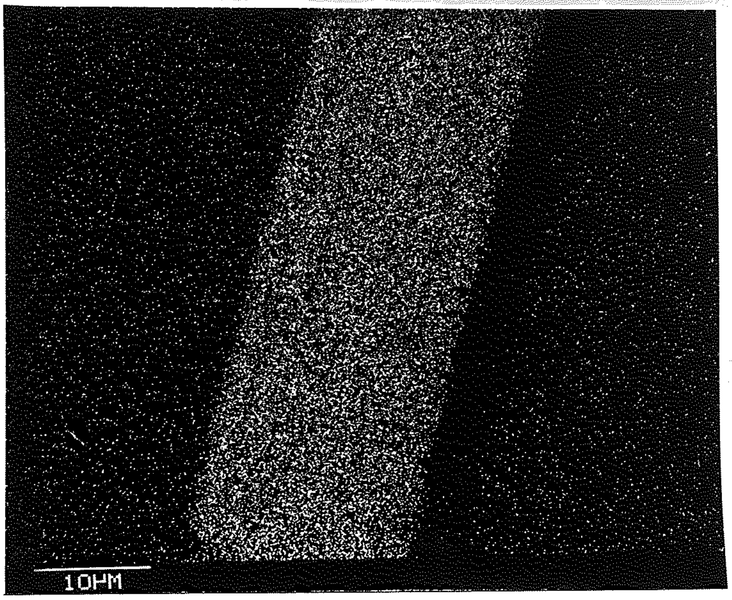
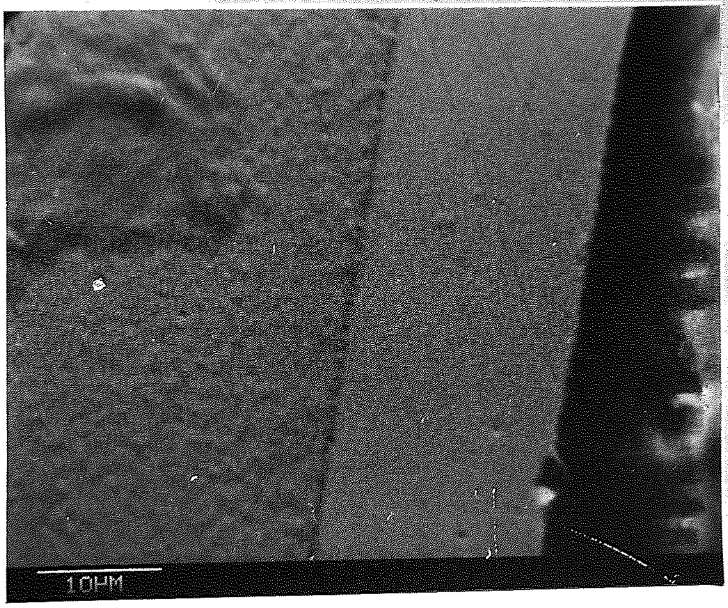


FIGURE 61 CROSS-SECTION OF NICKEL+CHROMIUM COMPOSITE DEPOSIT (SCANNING ELECTRON MICROGRAPH)



Figs. 56 and 57. Scanning electron micrographs of cross sections of nickel + chromium carbide and cobalt + chromium carbide composite deposits shows the same feature as optical micrographs. It should be noted that banding is not visible in the cross-sections of the composite material, Figs. 58 and 59.

A scanning electron microscope X-ray fluorescent photograph of a nickel + chromium composite deposit is shown in Fig. 60. A cross section of the deposits plated for six hours is shown in Fig. 61.

4.6 Wear Rate and Coefficient of Friction Measurements

The results obtained for the wear rate and the coefficient of friction of the deposits by rubbing against EN31, as measured on the pin and disc wear rig, are shown in Table IV. Each result given is an average of four tests. The composite deposit of nickel-chromium carbide has a lower rate of wear than the other deposits. Its wear rate decreases, more particularly when the deposits are heated to 400°C for 1 hour in vacuum, and its wear rate becomes equal to the wear rate of electroplated hard chromium deposits.

TABLE IV

Wear Rate and Coefficient of Friction Results

Type of Deposit	Wear rate 10^{-7}mm/cm	Coefficient of Friction	
		Initial	Final
Untreated steel	9.10		
Electroless nickel (As plated)	2.37	0.30	0.21
Electroless nickel (heated for 1 hr at 400°C in vacuum	1.96	0.28	0.18
Electroless nickel + chromium carbide (As plated)	2.10	0.31	0.17
Electroless nickel+chromium carbide (heated for 1 hr 400°C in vacuum	1.69	0.29	0.15
Electroless nickel+tungsten carbide (As plated)	2.18	0.30	0.19
Electroless nickel+tungsten carbide (Heated for 1 hr at 400°C in vacuum	1.78	0.29	0.16
Electroless nickel+titanium carbide (As plated)	2.25	0.32	0.19
Electroless nickel+titanium carbide (Heated for 1 hrs at 400°C in vacuum	1.72	0.31	0.16
Electroless cobalt (as plated)	2.41	0.33	0.23
Electroless cobalt (heated for 1 hr at 400°C in vacuum	2.03	0.32	0.21
Electroless cobalt+ chromium carbide (As plated)	2.18	0.34	0.17
Electroless cobalt+ chromium carbide (heated for 1 hr at 400°C in vacuum	1.79	0.30	0.18
Electroplated hard chromium	1.68	0.30	0.15

4.7 Die Forge Test

The results of the forging tests are given in Table V. The results of previous tests of dies coated with electroplated deposits of Co-Mo and Co-W are also included for comparison. Dies plated with nickel-chromium carbide (heated for 5 hours at 500°C in vacuum) and cobalt-chromium carbide (heated for 2 hours at 400°C in vacuum) have the least wear volume and a minimum amount of scale was found on their surfaces after forging.

TABLE 5

Die Forge Test Results

Type of Deposit	Wear volume 10^{-3} cm^3			Comments
	Top	Bottom	Average	
Untreated die	-	-	4.3	Heavy adherent scale
Electroplated Co-Mo	0.98	1.04	1.01	Very slight to Zero scale
Electroplated Co-W	1.27	2.10	1.7	Heavy scale
Electroless nickel (As plated)	2.31	2.47	2.39	Local heavy wear, very adherent scale
Electroless nickel (heated at 400°C for 1 hour in vacuum)	1.81	1.93	1.87	Heavy scale
Electroless nickel+ chromium carbide (As deposited)	1.98	2.08	2.03	Heavy scale
Electroless nickel+ chromium carbide (heated for 5 hours at 200°C in air)	1.68	1.88	1.78	Slight scale
Electroless nickel+ chromium carbide (heated for 5 hours at 400°C in air)	1.37	1.85	1.61	Very slight scale
Electroless nickel+ chromium carbide (heated for 5 hours at 500°C in vacuum)	1.20	1.50	1.35	Essentially zero scale
Electroless nickel+ chromium (heated for 2 hours at 400°C in vacuum)	1.82	2.04	1.93	Heavy adherent scale
Electroless cobalt+ chromium carbide (heated for 1 hour at 400°C in vacuum)	1.16	1.84	1.50	slight scale
Electroless cobalt+ chromium carbide (heated for 2 hours at 400°C in vacuum)	0.98	1.68	1.33	Very slight scale

4.8.1. Potentiostat Measurements

Corrosion potential ($E_{corrosion}$) of the deposits measured with a microprocessor controlled potentiostat are given in Table VI. The $E_{corrosion}$ values reported are an average result of four measurements.

TABLE VI

Potentiostat Measurement Results

Type of Deposit	$E_{corrosion}$
Electroless nickel (as plated)	-.591 volts
Electroless nickel (heated for 1 hour at 200°C)	-.581 volts
Electroless nickel (heated for 1 hour at 400°C)	-.598 volts
Electroless nickel (heated for 1 hour at 600°C)	-.618 volts
Bright nickel	-.592 volts
Watts nickel	-.581 volts
Electroless nickel+chromium carbide (As plated)	-.621 volts
Electroless nickel+chromium carbide (heated for 1 hour at 200°C)	-.613 volts
Electroless nickel+chromium carbide (heated for 1 hour at 400°C)	-.632 volts
Electroless nickel+chromium carbide (heated for 1 hour at 600°C)	-.607 volts
Electroless nickel+chromium (As plated)	-.506 volts
Electroless nickel+chromium (heat treated for 1 hour at 400°C)	-.480 volts
Electroless nickel+chromium (heat treated for 1 hour at 600°C)	-.491 volts
Mild steel	-.570 volts
Stainless steel 304	-.432 volts

4.8.2 Salt Spray and Outdoor Exposure Results

After spraying the coated mild steel panels for one hundred and twenty four hours in an acetic acid salt spray cabinet at $34^{o}C$, they were washed and photographed. Similarly after outdoor exposure for six months, the panels were then washed and photographed. From these photographs, Figs.62, 63 it is clear that the corrosion resistance of electroless nickel deposit is better than that of the composite deposits - also the corrosion resistance decreases with heat treatment for one hour at $400^{o}C$, but there was a slight improvement in corrosion performance after heat treatment for one hour at $600^{o}C$.

4.9 Tensile Test Results

The flow stress,ultimate tensile strength and elongation of uncoated and coated specimens are shown in Table VII.

The results listed are the average of three or four results.and they are for the composite (substrate and deposit).

TABLE VII

Tensile Test Results

Type of coating	Flow Stress Kg/mm^2	Ultimate Tensile Stress Kg/mm^2	Elongation %
Uncoated	41.23	48.75	11
Electroless nickel	41.35	48.42	13
Nickel+chromium carbide (As plated)	45.81	51.07	15
Nickel+chromium carbide (Heated for 1 hour at $400^{o}C$)	40.84	49.10	17
Electroless cobalt	38.35	42.55	14
Cobalt+chromium carbide (As plated)	42.43	49.64	15
Cobalt+chromium carbide (Heated for 1 hour at $400^{o}C$)	38.45	44.15	16

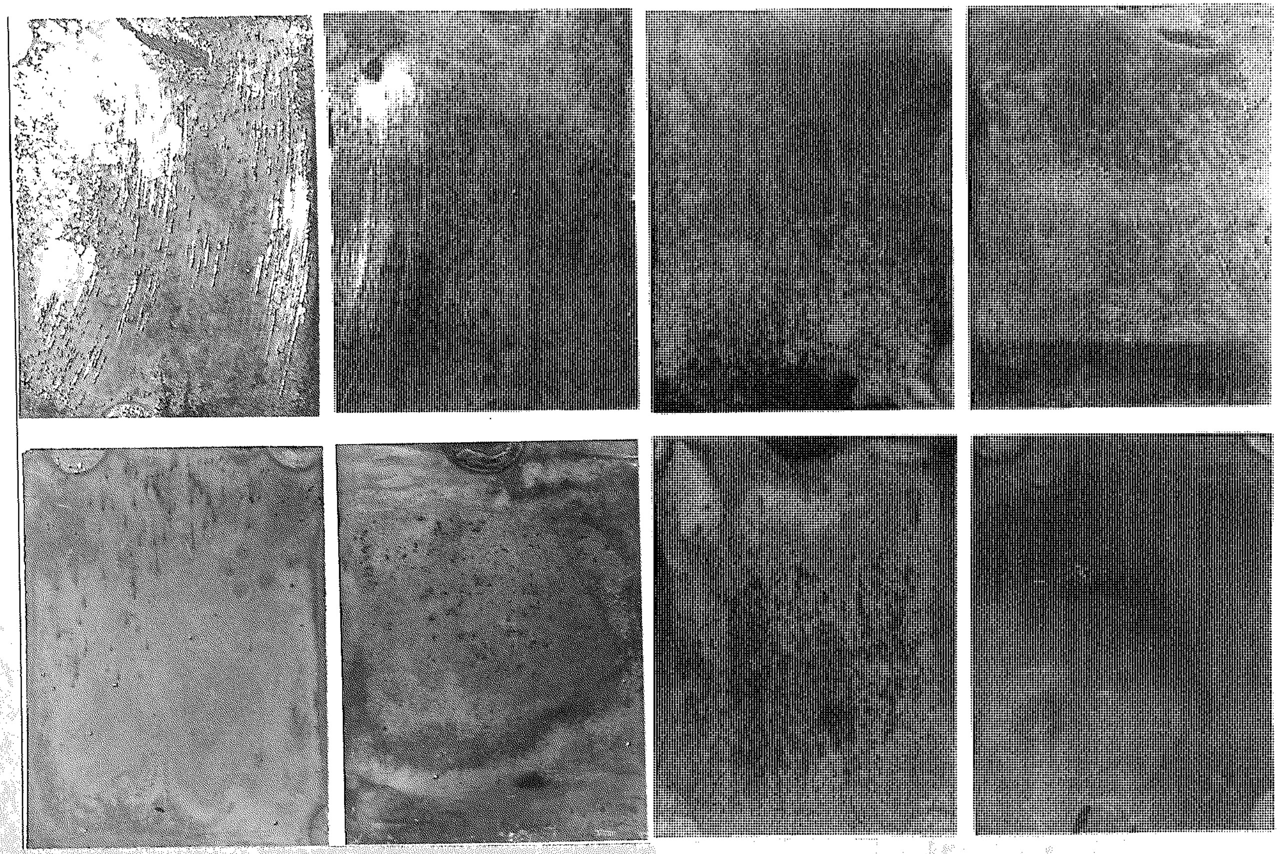


FIGURE 62 PHOTOGRAPH OF THE PANELS AFTER SALT SPRAY TEST
TOP: PANELS PLATED WITH ELECTROLESS NICKEL
BOTTOM: PANELS PLATED WITH ELECTROLESS NICKEL+CHROMIUM CARBIDE DEPOSITS
FROM LEFT TO RIGHT: i) AS PLATED; ii) HEAT TREATED AT 200^{o}C FOR 1 HOUR;
iii) HEAT TREATED AT 400^{o}C FOR 1 HOUR;
iv) HEAT TREATED AT 600^{o}C FOR 1 HOUR.

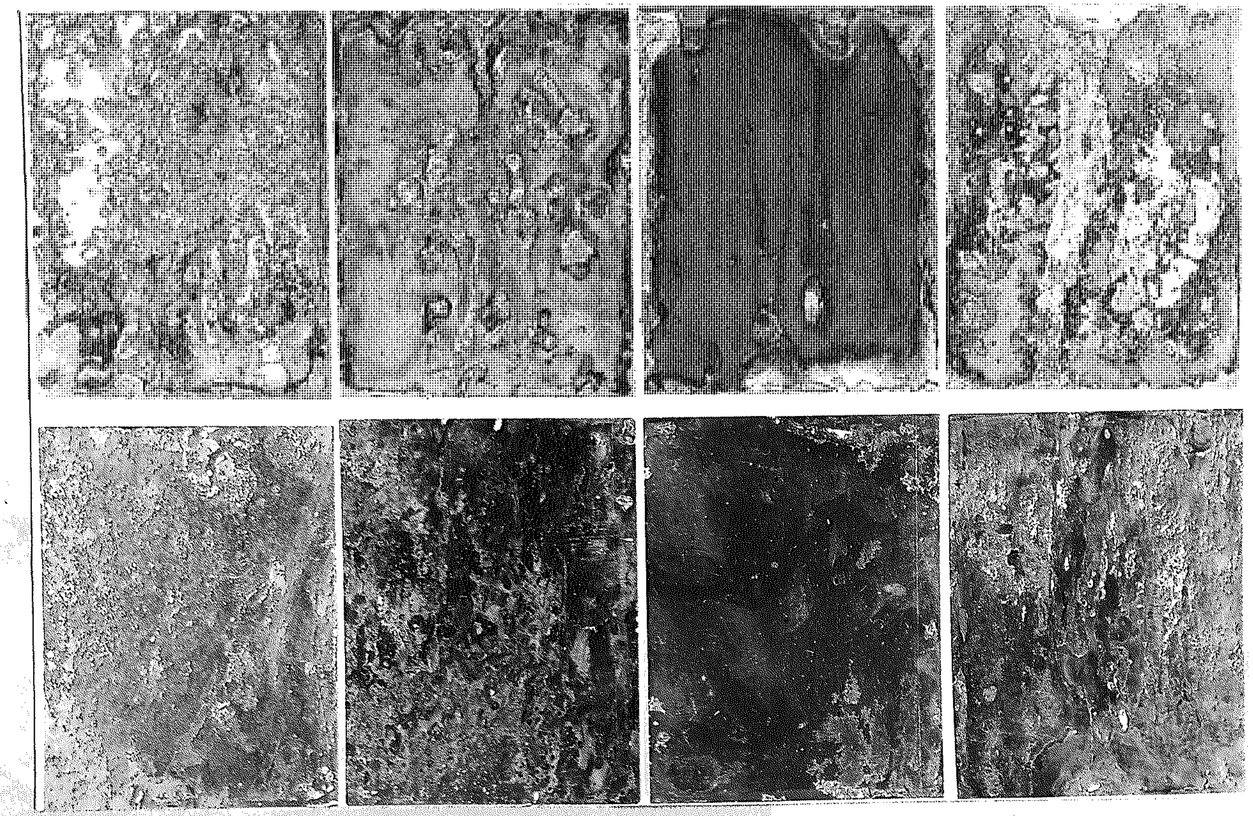


FIGURE 63 PHOTOGRAPH OF THE PANELS AFTER OUTDOOR EXPOSURE
TOP: PANELS PLATED WITH ELECTROLESS NICKEL
BOTTOM: PANELS PLATES WITH ELECTROLESS NICKEL+CHROMIUM CARBIDE
FROM LEFT TO RIGHT: i) AS PLATED; ii) HEAT TREATED AT 200°C FOR 1 HOUR; iii) HEAT TREATED AT 400°C FOR 1 HOUR; iv) HEAT TREATED AT 600°C FOR 1 HOUR.

5. DISCUSSION

5.1 Selection of the Plating Solution and Plating Conditions

The electroless plating solution undergoes changes in its composition during the deposition process. The concentrations of the metal salts, hypophosphite ions and stabilisers decrease but the hydrogen ion concentration and phosphite concentration increases.

Nifoss 80 was selected for depositing electroless and composite deposits because the reduction in the concentration of its constituent components can be easily made up by the addition of chemicals provided.

As the plating rate increases with temperature, so it was essential to select an optimum temperature to produce consistent deposit thickness at a fast rate without spontaneously decomposing the solution itself. For Nifoss 80, the rate of deposition per hour was 14 μm at 85°C, 20 μm at 92°C and 22 μm at 95°C but at the latter temperature the risk of local overheating increases which can decompose solution spontaneously, thus it was operated at 92°C for optimum plating rate as asserted by Baldwin and Such (37)

Hydrogen ions are liberated as nickel ions are reduced to the metallic state and so the pH of the solution is reduced. Consequently hypophosphite is less efficient as reducing agent and boric acid is less efficient as a buffer. The rate of deposition increases if the pH is increased by adding alkali, the deposition rate increases and it changes the hypophosphite reaction from catalytic to homogeneous which can possibly decompose the solution catastrophically. Also the solubility of nickel phosphide is decreased and it leads to the production of rough coatings. Thus pH value should be regulated in such a manner so as to obtain the most favourable condition. Therefore a pH value of 4.5 is selected as a compromise, as shown by Baldwin and Such (37)

5.2 Effect of Particle Concentration in the Solution on the Deposits

There is essentially no difference in the amount of the particles in the deposit with increase in the concentration of the particles suspended in solution; this is in agreement with previous authors (146,152). It is of interest to compare the inter-particle distance in the electroless nickel composite deposits with that of the particles in suspension in the plating medium to see if a reason may be found to explain why the particle concentration in the suspension in the range (10-200 g/l) does not affect that in the deposit. Taking average particle size to be 2.5×10^{-6}m and assuming them to be spherical, the average weight may be found from $\frac{4\pi}{3}\left(\frac{2.5\times10^{-6}}{2}\right)^3 \rho$ where $\rho = 6.7 \times 10^3$ Kg/m^3. The average weight therefore $= 5.47 \times 10^{-14}$ Kg. There are therefore approximately

2 x 10^{11} particles in 10g of Cr_3C_2 powder. Assuming the particles to be uniformly in suspension in one litre of plating solution, the average inter-particle distance may be estimated to be 1.7 x 10^{-5} m. The inter-particle distance in the deposit is calculated from the Quantimet observations which show that there are approximately 200 particles in an area of 0.0085 mm^2. Therefore the distance between the particles in the deposit = 6.50 x 10^{-6} m. These calculations indicate that the inter-particle distance in the composite is approximately one third that in the suspension for 10g/l suspension. Similarly in the most concentrated solutions (200 g/l) when the distance between the particles in the suspension is approximately 6.6 x 10^{-6} m, the distances are about the same in the deposit.

There is an important additional factor that has to be considered which is that the suspension is moving against the stationary surface being plated. If the velocity of the suspension is taken to be 10^{-1} m/sec perpendicular to the surface of the substrate then the number of the particles per second bombarding the surface is 10^{14} /m^2/sec. (Taking the average inter-particle distance in the suspension to be 10^{-5} m/sec.) Taking the deposition rate of electroless nickel to be 20 x 10^{-6} m/hours, i.e. 5 x 10^{-9} m/sec. If all the particles that strike the surface are incorporated into the deposit, there would be 10^{14} in a layer of volume 5 x $10^{-13}m^3$. This would result in an inter-particle distance of approximately 4×10^{-8} m. This shows that there is a redundancy of approximately 10^2 particles using an average suspension concentration 10g/1 and so the efficiency of incorporation is low and is not much affected by the suspension concentration.

5.3 Hardness

It is well recognised that electroless nickel and electroless cobalt, produced from hypophosphite baths contain several percent of phosphorus in the supersaturated solution, in the as plated condition and that the hardness of the deposit increases on heating, due to a precipitation hardening mechanism (78,79). The classical theory of precipitation hardening was established for aluminium-copper alloys by Silcock et al (158) and the following section summarises the essential details of this theory. Using this theory the changes of hardness with time and temperature in both Ni-P and Cu-P will be discussed. In an alloy system such as Al-Cu, when the copper is dissolved in the aluminium maxtrix at a relatively high temperature and the material is quenched the copper is retained in the aluminium matrix. This results in a supersaturated solution of copper in aluminium. On heating to a temperature below the solution treatment temperature, the copper atoms diffuse to a specific crystallographic plane with an atomic arrangement that resembles the array of atoms on a plane in the structure of the precipitate. As the copper atoms attempting to precipitate collect, they are forced to conform to the structure of aluminium. The forced coherency between atoms of the solvent and atoms attempting to form the structure of the precipitate causes severe, localised, elastic stresses that are responsible for the increase in hardness as the passage of dislocations through the lattice is restricted. When a sufficient number of solute atoms have collected, the structure of the precipitate is formed and the localised stresses are relieved because the forced coherency no longer exists. After the formation of a significant number of precipitate particles at various locations throughout the specimen, the rate of hardening decreases and the hardness approaches a maximum. If at any given temperature, ageing is allowed to proceed too far, coagulation or coarsening of the particles occurs and the numerous small particles are gradually replaced by a smaller number of more widely dispersed, coarser particles. In this state an alloy becomes softer and it is said to be in the overaged condition. In Al-Cu alloys the earlier stages of hardening are due to GP[1] zones, which are interpreted as plate like clusters of copper atoms seggregated on to planes of aluminium matrix. They then form a coherent, intermediate precipitate having definite crystal structure and are termed as GP[2] zones. These precipitates have an overall composition of $CuAl_2$. Moreover, with continuous ageing the precipitate grows, so that the strain fields become larger as it grows and peak hardness extends from one precipitate particle to the next. The strains around the precipitate particle can be relieved, however, by the formation of a stable dislocation loop around the precipitate. The long range strain fields of its precipitate and dislocation largely cancel. So it is easier for the glide dislocation to move through the lattice of the alloy containing an incoherent precipitate such as θ' than a coherent precipitate such as θ'', and the hardness falls. The equilibrium precipitate is incoherent with the matrix and its formation always leads to softening, since coherency strains disappear.

At room temperature in the electroless Ni-P systems, Ni_3P cannot precipitate as the diffusion rates are low. When the temperature is raised, atomic diffusion may occur producing aggregates of Ni_3P, which impede the progress of dislocations causing a slow rise in hardness. The Ni_3P aggregates are coherent with the matrix. Further heating causes growth of the aggregates which still retain some coherency. These aggregates are similar to the Guinier-Preston zones in aluminium-copper alloys. The thicker type causes the maximum impediment of dislocations and hardness increases rapidly on their formation. Further heating causes the agglomerates to loose coherency and becomes discrete particles of Ni_3P. This leads to the fall in hardness. On heat treating at higher temperatures the transformation proceeds nearer to equilibrium. The transformation to equilibrium produces a dispersion of Ni_3P in a nickel matrix. The reduction of hardness results from coarsening of the Ni_3P precipitates and finally to crystal growth in the nickel matrix.

According to precipitation hardening theory, only one hardness peak is expected but Ni-P alloy, like Al-Cu alloys, shows two hardness peaks (Figs. 36, 37, 39, 41, 45). Such anomalous behaviour can be explained by the fact that precipitation is a process involving more than one stage. The initial stage of precipitation at lower ageing temperatures, is believed to involve a cluster of atoms coherent with the matrix. At a later stage of the ageing process, it would be expected that these clusters would break away from the matrix lattice to form distinct particles with their own crystal structure and a definite interface.

The general kinetic behaviour of the precipitation process is in agreement with that expected on thermodynamic grounds, same as in Al-Cu alloys. From Figs. 37, 41, 45 it appears, generally that the rate of ageing increased markedly with increasing temperature while peak hardness decreases. Two stage hardening takes place at low ageing temperatures and is associated with high maximum hardness, while single stage hardening occurs at higher ageing temperature. The hardness of the nickel+chromium carbide composite deposits is higher than the hardness of electroless nickel deposits. The difference in the hardness between electroless and composite deposits is shown in Table VIII. The average hardness difference is 105 Hv for nickel+chromium carbide composite.

It has been shown by Cahoon et al (159) that

$$\sigma_0 = \frac{VHN}{3} (0.1)^{n-2}$$

where σ_0 = flow stress, n = Meyer Index.

Taking the value for n = 2, i.e. the material is assumed to be fully work hardened, the difference in flow stress due to the particles is equal to $\frac{105}{3} = 35$ kg/mm^2.

However taking n = 2.5, i.e. assuming the matrix is fully annealed, the flow stress difference = $\frac{105(0.1)^{0.5}}{3}$ = 11 kg/mm^2. This latter value is in excellent agreement with the increase of flow stress measured in the cobalt alloys containing varying amounts of 2 μm tungsten carbide particles prepared by a powder metallurgy method(160). The increase of flow stress of a cobalt alloy when it contains 27% Wc particles by volume is 11 kg/mm^2 as calculated from Figure 64. Thus the hardness of the composite material is produced by two mechanisms, the precipitation hardening effects similar to those described for aluminium-copper alloys and the dispersion hardening mechanism just described.

5.4 Metallography

The parallel striations present in the as plated nickel-phosphorus system,(caused by variations in degree of etching), are characteristic of periodic variations of composition (presumably P) rather than alternate lamellae of different phases. These striations remained in similar positions when the specimen was reground, polished and etched. This indicates that striations are due to gross phosphorus effect rather than to changes on a local scale. Phosphorus content fluctuations are likely to have been caused by variations in plating conditions during lengthy plating trials. Changes in pH have been suggested as a cause although bath temperatures and impurity content could also lead to alteration of the amount of P deposited, as it has been suggested by Gutzeit (27), Lee (78), Goldenstein et al (98) and Johnson and Ogburn (161).

It is interesting to note that the banded structure is not present in the composite material. The dispersion of the carbide particles in the deposit is interesting as the distance between the particles in the deposit is uniform. As the developing surface is being bombarded randomly by the particles there is an over-riding factor which controls the particle incorporation: the nature of this is unknown.

The surface topography of the composite deposits of cobalt indicated the reasons for increased porosity. The particles lead to cavities within the surface which become plated over and are not filled up. There is much less porosity in nickel+chromium carbide composites as compared to cobalt composites.

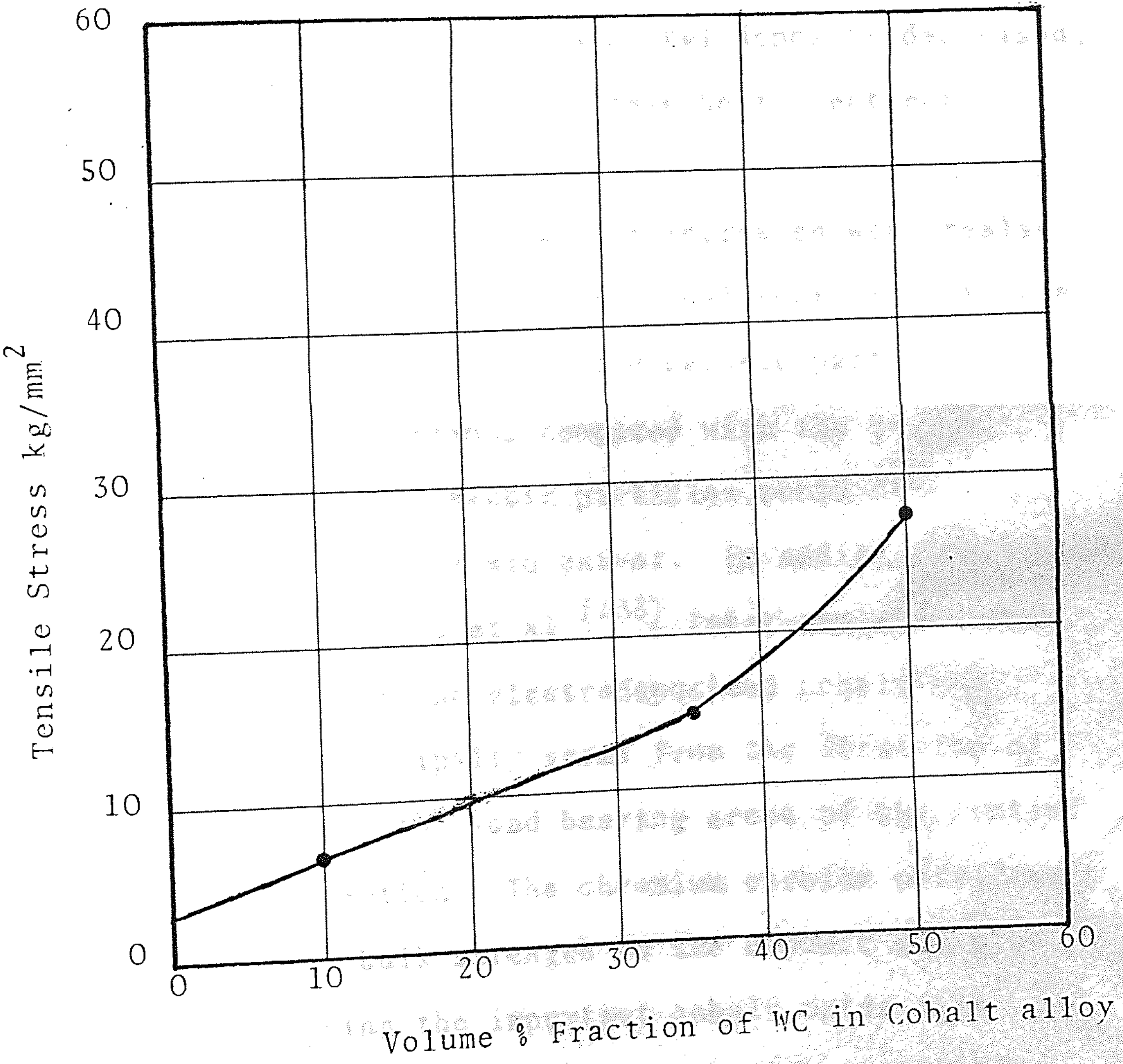
Table VIII

Difference in hardness of electroless nickel composite and electroless nickel after various heat treatments

Heat Treatment	HARDNESS (Hv)		ΔHV
	Electroless nickel	Electroless nickel composite	
As deposited	515	645	130
Fully hardened	1155	1225	70
Over-aged (Heated at 800°C for 50 hours in vacuum)	100	220	120

Average hardness difference 105 Hv

FIGURE 64 RELATIONSHIP BETWEEN VOLUME FRACTION OF WC PARTICLES AND FLOW STRESS IN COBALT ALLOY(160)



5.5 Wear Rate and Coefficient of Friction

The results of the pin and disc work indicated that generally, the wear rate decreased with the increasing hardness of electroless and composite deposits. The wear rate of electroless nickel+chromium carbide is the same as that of hard chromium, the hardness of both being similar at 1100 Hv. These results are in agreement with those obtained by Weightmann and Feldstein (80), Parker (81) and Randin et al (100). All these workers had also found that the wear rate of electroless nickel deposits decreased, when hardness is increased by suitable heat treatment.

Kedward (109) has suggested that the increased wear resistance of electrodeposited composite cobalt-ceramic particle deposits is due probably to the hard ceramic particles having better wear resistance compared with the softer substrate, and that the ceramic particles would dispersion harden the matrix to a certain extent. In addition to these suggestions, Kedward et al (135) later explained that the wear resistance of the electrodeposited cobalt composite coating principally stems from the formation of cobalt oxide glaze on the load bearing areas of the contact during interfacial motion. The chromium carbide particles impart significant bulk strength to the deposit and play a major part in keying the important cobalt oxide film to the plating surface. The wear mechanism inevitably involves a metal to metal situation in the early stages of interfacial contact with a small amount of mild adhesive wear which generates debris, the cobalt content of which oxidises quickly. At the high temperatures, due to frictional heating an oxide film develops and rapidly becomes compacted on the surface and finally glazes on the load bearing regions. After the formation of glaze, wear rate decreases and high wear resistance will be maintained providing there is no violent uprating of interfacial action. The formation of the glaze is temperature dependent and 300°C is considered to be the lowest ambient temperature at which it forms readily. The glaze develops more rapidly at higher ambient temperatures and the initial metallic wear-phase is reduced; as temperatures of operation rise wear resistance improves. The high wear rate of the deposits at room temperature and lower temperature reflects the degree of difficulty in forming the glaze, or even the complete inability for the glaze to occur at all. In either event, the oxidised debris remains only loosely adherent, abrades and is largely swept away continuously during relative interface motion.

Kedward (109) further attributed some of the wear characteristics of the electrodeposited cobalt+chromium carbide system on the surface enrichment of the hard carbide to produce an M_3C_7 type compound by heat treating for 4 hours at 1000°C in vacuum. In an experiment to compare this effect using the electroless cobalt+chromium carbide system, an electroless cobalt+chromium composite was heat treated at 1000°C for 4 hours in vacuum. After this heat treatment, the deposit had melted and no particles could be seen on microscopic examination. It is evident that the melting point of cobalt-phosphorus alloy produced by electroless deposition is less than 1000°C. These explanations of Kedward's can probably be applied to electroless cobalt and cobalt+chromium carbide composite deposits, but are not applicable to electroless nickel deposits where the formation of glaze is not reported at all.

5.6 Corrosion Resistance

Panels plated with electroless nickel coatings and electroless nickel+chromium carbide composite deposits were assessed by appearance of the deposits after the completion of the salt spray test and outdoor exposure for six months. It appears that electroless nickel deposits have fewer stains after the test than the composite coating. The corrosion resistance of the electroless nickel deposit decreased with heat treatment up to 400°C for 1 hour, but after heat treatment at 600°C for 1 hour, it improved. Similarly the resistance of electroless nickel+chromium carbide composites to salt spray was reduced by heat treatment up to 400°C for 1 hour but slightly improved when heated to 600°C for 1 hour. This is in agreement with the findings of Andrew and Heron (93). After outdoor exposure electroless nickel+chromium carbide composite deposits had less stains than electroless nickel deposits only.

Electroless nickel and nickel+chromium carbide have less noble corrosion potential than the corrosion potential obtained for electroless nickel+chromium deposits, this is in agreement with the results obtained by Parker (154).

5.7 Forging Test

Generally, the wear volume of the dies coated with electroless and composite deposits decreases with increasing deposit hardness. The wear volume of the dies coated with electroless cobalt+chromium carbide deposits 1.33 x 10^{-3} cm^3 (heat treated to maximum hardness) and electroless nickel+chromium carbide deposits 1.35 x $10^{-3}cm^3$ (heat treated to maximum hardness is about half the wear volume for the dies coated with 125 μm and 250 μm Tribomet deposits, as reported by Still (157). This improvement in the wear resistance of the electroless carbide composite deposits of cobalt and nickel is due probably to the hardening of the electroless composite deposits due to the combined precipitation hardening and dispersion hardening mechanism. Table IX gives the results of the wear of different deposits on die surfaces as obtained by Still (157). He has explained the high wear volume of the Tribomet coatings, on the presence of severe cracking in the Tribomet deposits. The better wear resistance of electroless nickel and cobalt+chromium carbide composite deposits, may also be due to the formation of an oxide film on the deposits and the lack of adherent scale. The small amount of scaling that did occur was confined to the centre of the bottom die and could be detached easily from the die surface with the fingernail. This scale was not formed as a result of oxidation of the alloy, but was probably due to scale flaking from the billets and then being impacted onto the die surface. This characteristic of having little scale is very useful from the practical considerations as the retention of the smooth surface will give the forging a good quality surface and help to prevent the sticking of forgings in the die cavity. The same argument can be used in favour of electroless carbide composites of nickel and cobalt against multi-layer deposits of 90 μm of 83% Co/17% Ni with a top overcoat of 10 μm chromium. The electro-deposited alloy deposits being soft and ductile prevents the cracking of the underlying steel, but the top coating of chromium reduces the wear of the electrodeposited alloy deposits, but still these were scaled heavily making the surface rough, thus reducing their efficiency for use as coatings for protecting die surfaces during forging process.

Electroless nickel+chromium composite deposits (heat treated to maximum hardness of 1650 Hv) is the only exception among the deposits tested, having a higher wear volume than the softer nickel+chromium carbide composite deposits. They also have more scale on their surface and this scale was quite firmly adherent to the surface and can only be removed by electrolytic treatment, unlike the scale formed on the nickel or cobalt+chromium carbide deposits. This scale may probably be formed due to the oxidation of the alloy coating as spread all over the surface. This anomalous behaviour can possibly be explained by the following:

1. Wear, in certain situations, may be dictated by a soft microconstituent only and the Vicker's hardness will not identify microconstituents.

TABLE IX Wear volume of different deposits/die steel

Type of Deposit or Die Steel	Mean Wear Volume $10^{-3}cm^3$
Electem No. 5 die steel	4.37
100% nickel deposit	2.28
100% cobalt deposit	15.38
Micro-cracked chromium deposit	0.59
Decorative chromium deposit	0.31
Hard chromium deposit	0.20
Brush plated Co-W	2.04
90 μm 83% Co/17% Ni + 10 μm chromium (micro-cracked)	0.70
90 μm 83% Co/17% Ni + 10 μm chromium (hard)	0.45
125 μm Tribomet deposit	4.08
250 μm Tribomet deposit	3.00
5% chromium steel	0.90
3% Ni, 3% Mo steel	0.33
Cobalt+Molybdenum deposit	0.52
Cobalt+Tungsten deposit	0.67
5% Cr, 2% W steel	2.04

2. The higher hardness of the nickel+chromium layers, compared with the nickel+chromium carbide composite deposit (850 Hv as deposited, 1650 Hv fully hardened, 645 Hv as deposited and 1225 Hv

fully hardened), for Ni+Cr and Ni+Cr_2C_3 respectively, may be explained by the following. In the as deposited condition there is 40% of chromium particles in the nickel matrix compared with 27% Cr_2C_3. As shown previously the hardness of the composite increases with increasing particle concentration. After heat treatment the very high hardness of the Ni+Cr deposit is possibly due to the hardening effects of the precipitates of chromium phosphides(162), in addition to the nickel phosphide and the remaining chromium particles. It is also possible that there is a small degree of solution hardening of the nickel matrix by chromium dissolving in it (163). It is also possible, further hardening could result from the formation of α-phase at 400-500°C (164). The high wear volume of the nickel+chromium layer is possibly due to the flaking of the deposit.

5.8 Possible Application

Since the results obtained from simulated industrial die forgings are encouraging, that electroless nickel+ chromium carbide and cobalt+chromium carbide deposits (both heat treated to maximum hardness) reduces the wear of the die surface by 75% approximately and their surfaces remain smooth after the test. Thus these deposits appear to have a good chance of providing wear resistance in many industrial applications, therefore they are likely to be useful for commercial application. Already a number of industrial applications have been reported, in which a similar electroless nickel+silicon carbide composite deposit has been claimed to reduce wear in service.

5.8.1. Tool for moulding glass filled resins

Nickel+silicon carbide composite deposits can withstand low stress abrasion in the plastics industry. It is reported that nickel+silicon carbide composite works well in applications where it is abraded by a glass filled resin (150,151,152, 165). A set of moulds used in the manufacture of glass reinforced thermoset plastic last for 10,000 parts, but after coating with 50 μm thick electroless nickel+silicon carbide composite it has produced 450,000 parts and is still in service. The process is also practical for very large plastic mouldings. A 37 μm coating was applied to a large compression mould weighing 3500 Kg. The mould produces a reinforced plastic front end piece for an automobile in a Ford motor car plant in Germany.

5.8.2. Forging applications

A drop forge insert used to forge connecting rods. The operation involved placing a bar, at 1280°C, on the die and sinking it with a 1800 Kg hammer. Typically, a die is scrapped after 15 shifts. One with hard chromium plating lasted less than one shift, while one with a nickel+silicon carbide coating was still intact after 15 shifts (165).

5.8.3. Foundry applications

The wear resistance of co-deposited silicon carbide particles, coupled with lubricity of electroless nickel matrix resists abrasive wear and helps release unbroken sand cores from core boxes (152,154,165).

In Germany co-deposits have been successfully applied to epoxy plastic patterns. Sand blown into the mould form, followed by compaction would erode away the rounded and angular edges of the patterns after 2,000 moulds were made. After the composite coating was applied, more than 25,000 impressions were made prior to wear damage.

5.8.4. Metal forming application

In drawing and forming sheet metal the problem of pick-up and galling is common. A number of dies plated with a composite coating radically improved performance. For example, an automotive door hinge die under optimum conditions required an average of one hour repair time for each 3,000 parts produced. The die, when coated with 37 µm of electroless nickel+ silicon carbide composite ran 400,000 hits before pick-up or galling. The material formed is 5.2 mm thick carbon steel.

5.8.5. Machining and finishing tools

Such tools are used for microfinishing of screw threads, ball grinding grooves and other profile sections. In these cases the requirements as to accuracy are so exacting for profiled diamond tools that they cannot be met by the conventional electroplating process. Electroless nickel composite (151) deposits containing diamond particles can be used. The diamond particles employed in this application are of a mean diameter of 6, 9 or 12 µm. The composite deposits can also be applied to reamers used for highly abrasive aluminium alloys, to contact surfaces of honing heads and to broaching tools for graphite.

5.8.6. Corrosion

Corrosive wear in metals manifests itself in two different forms. First the material actually enters a solution or dissolves, second corrosion is intergranular; with the latter there is little or no material lost, but metallic grains or crystals in a material literally become dissociated due to corroded areas at their boundaries. The subsequent loss in strength, hardness, and resistance to other forms of wear is substantial if not catastrophic. Resistance of the electroless nickel+silicon carbide composite coatings (152,165) to this type of wear is typically identical to that of an electroless nickel coating. But if abrasion is involved, it is advantageous to apply this composite. For example, in the moulding of glass or talc filled polyvinylchloride, hydrochloric acid is formed. If chromium is used to plate the mould, it would be a catastrophe as HCl would immediately dissolve chromium. Electroless nickel deposit not only provides the matrix for bonding the carbide particle, which will be resistant to the hydrochloric acid, but it will also help in preventing intergranular corrosion.

6. CONCLUSIONS

6.1. Electroless nickel and cobalt carbide composite deposits containing 27% by volume of carbide (chromium, tungsten, titanium) particles have been produced. Similarly, nickel and cobalt composite deposits containing 40% and 30% by volume of chromium particles have also been produced.

6.2. The volume of the carbide particles co-depositing with the nickel and cobalt composite deposit is independent of the amount of the carbide particles added to the electroless plating solutions in the range 10g - 200g/l.

6.3. After heat treatment, the maximum hardness of nickel+chromium carbide in 1225 Hv, it is 6% more than the maximum hardness of nickel (1155 Hv) obtained after heat treatment. Also the maximum hardness of nickel+chromium composite deposit is 1650 Hv, which is 30% more than electroless nickel deposit. Similarly, the maximum hardness values after heat treating of cobalt+chromium carbide and cobalt+chromium deposits are 1405 Hv and 1440 Hv respectively, which are 8% and 10% high than maximum hardness values of cobalt obtained after heat treatment.

6.4. The wear rate and coefficient of friction of nickel and cobalt and their carbide composite deposits decreases with an increase in the hardness of the deposits. The wear rate of the pins coated with electroless deposits was 4 times better than the wear rate of the uncoated pin, whereas the wear rate of the pins coated with carbide composite deposits were 5 times better than uncoated pins.

6.5. The wear volume of the forging dies was reduced when they were coated with nickel and cobalt carbide composite deposits (heat treated to maximum hardness) and there was little scale on the deposits after forging. There was a reduction of 50-70% in the wear of the die surfaces when coated with electroless nickel+chromium carbide (heat treated) and cobalt+chromium carbide composite deposits (heat treated) as compared to uncoated die surface.

6.6. Although nickel+chromium deposits are harder than nickel+chromium carbide deposits, their performance during forging tests was rather disappointing. Their wear rate was greater than for the carbide composites, and more scale adhered to their surface. Their high hardness was achieved by a different mechanism from that involved in the case of the carbide composites.

7. SUGGESTIONS FOR FURTHER WORK

1. Composite deposits based on electroless Ni/B baths should be investigated because electroless nickel-boron deposits have higher hardness and a higher softening temperature than nickel-phosphorus deposits.

2. The effect of the particle size and shape on the properties of the composite electroless deposits should be investigated,so that the effect of size and shape on porosity in the composite deposits can be investigated.

3. Transmission and scanning electron microscopy of the nickel and cobalt composites containing chromium particles should be undertaken, both as deposited and after heat treatment, to investigate the structure.

4. Hot hardness of the composite deposits of nickel and cobalt should be investigated, since some applications of these deposits are at elevated temperature.

5. A commercially viable acid bath should be investigated to produce sound electroless cobalt and its composite deposits, since porosity is too high although present deposits have performed quite well in the wear tests.

6. Since heat treated nickel+chromium carbide and cobalt+chromium carbide have performed in such an encouraging manner on experimental dies, the next stage in the work should involve the plating and evaluation of the industrial dies. This will necessitate the operation of a much larger bath than that employed in the present work. The transfer from the 1-4 litre scale to a pilot scale, will involve a number of problems such as routine control of the plating solutions, maintenance of the constant properties of the deposits and availability of an efficient agitation system. The latter will itself require a subsidiary investigation on the effect of agitation systems on particle dispersion in the deposit. The operation of a large bath for extended periods of time may possibly lead to difficulties caused by the oxidation of hypophosphite to phosphite, or build up of the Fe^{+++} ions from the substrate. The properties of the deposits therefore would require further study to observe changes which may occur as solution ages.

It is thought that the use of electroless composite deposits may be extended into other types of wear situations, particularly for applications such as coatings for use on other types of die (e.g. zinc/aluminium die casting dies), coatings on piston rings, hard facings for valve seats and coatings for components subjected to sliding wear.

8. ACKNOWLEDGEMENTS

The author wishes to thank Dr. J.K. Dennis (supervisor) and Dr. E. Silverstone for their help and advice. Many thanks are due to the technical staff of the Metallurgy Department of the University of Aston for their advice and assistance and to Mrs. Heather Howell for typing this thesis. The author is also grateful to British Council for paying part of his fees.

9.

APPENDIX

EFFECT OF HEAT TREATMENT (IN AIR) ON THE HARDNESS OF ELECTROLESS NICKEL DEPOSITS

Heat Treatment Time (hours)	Hardness (Hv)				
	Heat Treatment Temperature °C				
	200°	400°	500°	600°	800°
One hour	660(±4)	1005(±5)	910(±9)	540(±16)	475(±9)
Two hours	720(±24)	865(±13)	770(±30)	670(±24)	470(±16)
Five hours	970(±28)	965(±24)	840(±26)	750(±35)	690(±10)
Twelve hours	910(±12)	990(±35)	985(±16)	770(±30)	540(±9)
Twenty four hours	575(±9)	695(±10)	885(±11)	490(±10)	400(±5)
Fifty hours	585(±5)	890(±25)	880(±43)	240(±9)	80(±2)
One hundred hours	435(±7)	570(±7)	315(±9)	200(±5)	-

NOTES

1. As plated Hardness 515 Hv

2. Figures in bracket represent standard deviation of at least six results.

3. Values plotted in Figures 10, 13, 16 and 39

EFFECT OF HEAT TREATMENT (IN AIR) ON THE HARDNESS OF ELECTROLESS NICKEL-CHROMIUM CARBIDE DEPOSITS

Heat Treatment Time (hours)	Hardness (Hv)				
	Heat Treatment Temperature °C				
	200°	400°	500°	600°	800°
One hour	760(±4)	1065(±14)	955(±24)	760(±16)	710(±7)
Two hours	855(±14)	1175(±13)	1010(±20)	860(±13)	670(±36)
Five hours	1175(±13)	1180(±24)	1050(±30)	895(±27)	835(±18)
Twelve hours	1060(±23)	1175(±26)	1195(±36)	980(±68)	760(±30)
Twenty four hours	810(±29)	1010(±20)	1040(±10)	615(±29)	560(±9)
Fifty hours	720(±14)	985(±21)	1040(±10)	565(±9)	245(±6)
One hundred hours	660(±12)	750(±8)	515(±32)	505(±9)	200(±12)

NOTES

1. As plated Hardness 645(± 5)
2. Figures in bracket represent standard deviation of at least six results
3. Chromium carbide particles size range 2-3 μm
4. Concentration of the particles in suspension 10 g/l
5. Values plotted in Figures 11, 14, 17, 40

EFFECT OF HEAT TREATMENT (IN AIR) ON THE HARDNESS OF ELECTROLESS NICKEL-CHROMIUM DEPOSITS

Heat Treatment Time (hours)	Hardness (Hv)				
	Heat Treatment Temperature °C				
	200°	400°	500°	600°	800°
One hour	1160(±24)	1550(±45)	1240(±12)	780(±29)	670(±18)
Two hours	1400(±25)	1600(±15)	1310(±90)	795(±45)	625(±16)
Five hours	1050(±15)	1490(±38)	865(±29)	695(±26)	600(±5)
Twelve hours	1400(±35)	1140)±40)	765(±45)	640(±32)	570(±12)
Twenty four hours	890(±12)	1085(±26)	980)±18)	865(±15)	500(±9)
Fifty hours	850(±17)	1050(±12)	1000(±100)	765(±25)	480(±5)
One hundred hours	760(±2)	870(±10)	625(±43)	325(±2)	-

NOTES

1. As plated Hardness 850 Hv(±10)

2. Figures in bracket represent standard deviation of at least six results

3. Chromium particles size range 10-12 μm

4. Concentration of the particles in suspension 10 g/1

5. Values plotted in Figures 12, 15, 18, 41

EFFECT OF HEAT TREATMENT (IN VACUUM) ON THE HARDNESS OF ELECTROLESS NICKEL DEPOSITS

Heat Treatment Time (hours)	Hardness (Hv)				
	Heat Treatment Temperature °C				
	200°	400°	500°	600°	800°
One hour	600(±5)	1050(±9)	795(±8)	600(±5)	455(±4)
Two hours	685(±9)	1075(±13)	1010(±8)	645(±4)	460(±4)
Five hours	1155(±20)	1150(±20)	990(±36)	660(±16)	630(±15)
Ten hours	590(±10)	1120(±40)	995(±31)	670(±10)	515(±6)
Twenty four hours	775(±27)	870(±17)	975(±36)	685(±11)	440(±4)
Fifty hours	710(±10)				

NOTES

1. As plated Hardness 525 Hv

2. Figures in bracket represent standard deviation of at least six results

3. Values plotted in Figures 19 and 22

EFFECT OF HEAT TREATMENT (IN VACUUM) ON THE HARDNESS OF ELECTROLESS NICKEL-CHROMIUM CARBIDE DEPOSITS

Heat Treatment Time (hours)	Hardness (Hv)				
	Heat Treatment Temperature °C				
	200°	400°	500°	600°	800°
One hour	795(±20)	1095(±29)	1035(±24)	990(±29)	805(±11)
Two hours	805(±16)	1095(±13)	1060(±20)	920(±15)	775(±27)
Five hours	1180(±14)	1185(±40)	1225(±30)	925(±25)	900(±28)
Ten hours	790(±20)	1190(±25)	1085(±38)	910(±24)	850(±28)
Twenty four hours	1010(±13)	1100(±20)	1065(±16)	825(±19)	800(±14)
Fifty hours	960(±10)				

NOTES

1. As plated Hardness 645 Hv (±5)

2. Figures in bracket represent standard deviation of at least six results

3. Chromium carbide particles size range 2-3 μm)

4. Concentration of the particles in suspension 10 g/1

5. Values plotted in Figures 20 and 23

EFFECT OF HEAT TREATMENT (IN VACUUM) ON THE HARDNESS OF ELECTROLESS NICKEL-CHROMIUM DEPOSITS

Heat Treatment Time (hours)	Hardness (Hv)				
	Heat Treatment Temperature °C				
	200°	400°	500°	600°	800°
One hour	1200(±12)	1550(±15)	1320(±15)	1000(±26)	870(±15)
Two hours	1420(±15)	1630(±78)	1375(±15)	1060(±17)	950(±9)
Five hours	1300(±12)	1650(±40)	1550(±30)	950(±38)	690(±18)
Twenty five hours	875(±30)	1215(±32)	880(±48)	850(±22)	390(±3)

NOTES

1. As plated Hardness 850 Hv (±10)

2. Figures in bracket represent standard deviation of at least six results

3. Chromium particles size range 10-12 μm

4. Concentration of particles in suspension 10 g/l

5. Values plotted in Figures 21 and 24

EFFECT OF HEAT TREATMENT (IN VACUUM) ON THE HARDNESS OF ELECTROLESS COBALT-CHROMIUM DEPOSITS

Heat Treatment Time (hours)	Hardness (Hv)				
	Heat Treatment Temperature °C				
	200°	400°	500°	600°	800°
One hour	835(±15)	1245(±12)	1180(±15)	850(±11)	720(±7)
Two hours	1080(±15)	1440(±85)	1050(±12)	805(±7)	715(±10)
Five hours	800(±12)	1265(±45)	910(±25)	880(±18)	590(±12)
Twenty four hours	1150(±33)	825(±12)	745(±6)	710(±5)	330

NOTES

1. As plated Hardness 650 Hv (±8)

2. Figures in bracket represent standard deviation of at least six results

3. Chromium particles size range

4. Contents of chromium particles in suspension 10 g/1

5. Values plotted in Figures 28 ,44.

EFFECT OF HEAT TREATMENT (IN VACUUM) ON THE HARDNESS OF ELECTROLESS COBALT DEPOSITS

Heat Treatment Time (hours)	Hardness (Hv)				
	Heat Treatment Temperature °C				
	200°	400°	500°	600°	800°
One hour	830(±12)	1300(±50)	940(±28)	485(±18)	415(±13)
Two hours	970(±10)	1230(±29)	890(±12)	750(±12)	450(±10)
Five hours	715(±12)	1030(±25)	830(±12)	715(±21)	415(±12)
Twenty four hours	635(±7)	890(±30)	420(±2)	280(±2)	190(±3)

NOTES

1. As plated Hardness 600 Hv (±16)

2. Figures in bracket represent standard deviation of at least six results

3. Values plotted in Figures 25 and 42

EFFECT OF HEAT TREATMENT (IN VACUUM) ON THE HARDNESS OF ELECTROLESS COBALT-CHROMIUM CARBIDE DEPOSITS

Heat Treatment Time (hours)	Hardness (Hv)				
	Heat Treatment Temperature °C				
	200°	400°	500°	600°	800°
One hour	905(±23)	1250(±31)	1020(±28)	890(±12)	660(±19)
Two hours	1250(±33)	1340(±34)	1120(±17)	950(±12)	755(±40)
Five hours	980(±9)	1405(±40)	935(±9)	840(±18)	585(±13)
Twenty four hours	835(±19)	925(±43)	840(±7)	670(±19)	650(±2)

NOTES

1. As plated Hardness 800 Hv (±15)

2. Figures in bracket represent standard deviation of at least six results

3. Chromium carbide particles size range 2-3 μm

4. Concentration of the particles in suspension 10 g/1

5. Values plotted in Figures 26, 27, 43

EFFECT OF HEAT TREATMENT (IN AIR) ON THE HARDNESS OF ELECTROLESS COBALT DEPOSITS

Heat Treatment Time (hours)	Hardness (Hv)				
	Heat Treatment Temperature °C				
	200°	400°	500°	600°	800°
One hour	770(±35)	1080(±15)	1020(±50)	675(±18)	350(±12)
Two hours	920(±12)	1220(±12)	590(±10)	550(±20)	330(±7)
Five hours	1235(±70)	990(±25)	570(±10)	545(±21)	325(±7)
Twelve hours	1085(±57)	985(±40)	545(±27)	390(±30)	270(±9)
Twenty four hours	630(±12)	865(±12)	505(±13)	345(±10)	220(±2)
Fifty hours	815(±18)	1005(±17)	715(±15)	630(±12)	NR
One hundred hours	620(±50)	715(±15)	570(±10)	190(±5)	NR

NOTES

1. As plated Hardness 600 Hv (± 16)

2. Figures in bracket represent standard deviation of at least six results

3. Values plotted in Figures 29, 32 and 45

EFFECT OF HEAT TREATMENT (IN AIR) ON THE HARDNESS OF ELECTROLESS COBALT-CHROMIUM CARBIDE DEPOSITS

Heat Treatment Time (hours)	Hardness (Hv)				
	Heat Treatment Temperature °C				
	200°	400°	500°	600°	800°
One hour	925(±70)	1200(±54)	1175(±58)	820(±35)	650(±19)
Two hours	1225(±35)	1350(±25)	815(±25)	695(±18)	500(±23)
Five hours	1190(±70)	1370(±35)	800(±25)	665(±18)	385(±10)
Twelve hours	1195(±47)	1040(±40)	780(±24)	675(±5)	350(±2)
Twenty four hours	840(±14)	1080(±12)	870(±10)	650(±11)	240
Fifty hours	880(±30)	1070(±12)	985(±69)	835(±15)	NR
One hundred hours	795(±14)	895(±10)	670(±19)	260(±5)	NR

NOTES

1. As plated Hardness 800 Hv (± 12)

2. Figures in bracket represent standard deviation of at least six results

3. Chromium carbide particles size range 2-3 μm

4. Concentration of the particles in suspension 10 g/1

5. Values plotted in Figures 30, 33, 34 and 46

TABLE

EFFECT OF HEAT TREATMENT (IN AIR) ON THE HARDNESS OF ELECTROLESS COBALT-CHROMIUM COMPOSITE DEPOSITS

Heat Treatment Time (hours)	Hardness (Hv)				
	Heat Treatment Temperature °C				
	200°	400°	500°	600°	800°
One hour	770(±31)	1110(±55)	1190(±44)	895(±15)	620(±35)
Two hours	920(±22)	1400(±35)	860(±40)	670(±43)	445(±25)
Five hours	1145(±28)	1305(±15)	775(±24)	560(±12)	290(±2)
Twelve hours	1225(±15)	1090(±25)	785(±25)	680(±15)	240(±)
Twenty four hours	850(±12)	985(±15)	715(±10)	615(±20)	NR
Fifty hours	870(±7)	950(±11)	1070(±58)	690(±25)	NR
One hundred hours	660(±7)	900(±5)	850(±20)	235(±-)	NR

NOTES

1. As plated Hardness 650 Hv (± 8)
2. Figures in bracket represent standard deviation of at least six results
3. Chromium particles size range 10-12 μm
4. Concentration of the particles in suspension 10 g/1
5. Values plotted in Figures 31, 35 47

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