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**CORROSION, EROSION AND
OXIDATION OF NEW
CEMENTED CARBIDES**

by

DAVID DONALDSON KERR, B.Eng.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of

Master of Engineering (Mechanical)

Department of Mechanical and Aeronautical Engineering

Carleton University

Ottawa, Ontario

April, 1989

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**The undersigned recommend to the Faculty of Graduate Studies
and Research acceptance of the thesis**

"CORROSION, EROSION AND OXIDATION OF NEW CEMENTED CARBIDES"

**submitted by David D. Kerr, B.Eng.
in partial fulfilment of the requirements for the degree of
Master of Engineering (Mechanical)**

A handwritten signature in dark ink, appearing to read "L. de Halluin", is written over a horizontal line.

Thesis Supervisor

A handwritten signature in dark ink is written over a horizontal line.

Chair, Department of Mechanical and Aeronautical Engineering

Carleton University

May, 1989.

ABSTRACT

Traditional cemented carbides made of Tungsten Carbide (WC) with a Cobalt (Co) binder are not particularly resistant to corrosion by aqueous media. New cemented carbides have been fabricated with various binder compositions, comprising the systems: WC-Ni, WC-Ni-Cr, WC-Ni-Al and WC-Ni-Cr-Al, each with a binder content of 10% by weight. The performance of these new alloys in various environments has been compared to that of a commercially available WC-Co grade with the same binder content.

The corrosion of these materials has been investigated by polarization methods and weight loss immersion tests in 2N H₂SO₄ and 0.5N NaCl media. The resistance of these materials to erosion corrosion, erosion by solid particle impact and to high temperature thermal oxidation has been investigated. Significant improvements were obtained with the new materials to corrosive attack by these media and to the erosive corrosive slurry. Slight improvements to thermal oxidation and erosion resistance were also obtained.

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LIST OF SYMBOLS

<u>Symbol</u>	<u>Description</u>
A	Initial surface area (cm ²)
b _a	Anodic Tafel slope (mV)
b _c	Cathodic Tafel slope (mV)
D	Density (g/cm ³)
dW	Weight loss (g)
E	Electrode potential (mV vs SCE.)
E _{cath}	Cathodic potential (mV vs SCE.)
E _{corr}	Corrosion potential (mV vs SCE.)
E _{init}	Initial corrosion potential (mV vs SCE.)
E _p	Passive potential (mV vs SCE.)
E _{pp}	Peak passive potential (mV vs SCE.)
E.W.	Equivalent weight (g)
G.T.	Gas treated
I	Current density (uA/cm ²)
I _{cc}	Critical current density (uA/cm ²)

I_{corr}	Corrosion current density ($\mu A/cm^2$)
I_p	Passive current density ($\mu A/cm^2$)
M	Molality
N	Normality
N.G.T.	Not gas treated
Q	Activation energy (kCal/mole)
R	Gas constant (1.986 cal/K/mole)
R_e	Erodent flow rate (g/min)
R_p	Polarization resistance (kOhms)
SCE	Saturated Calomel Electrode
T	Absolute temperature (K)
W_e	Weight of erodent consumed (g)
W_f	Final weight (g)
W_i	Initial weight (g)

CHAPTER I

INTRODUCTION

1.1 NATURE OF CEMENTED CARBIDES

Cemented carbides, or Hardmetals, were first used during the First World War in the production of drawing dies. As a result of their special properties their use is now widespread. Cemented carbides have a uniquely useful combination of mechanical, physical, and chemical properties. Their metallurgical characteristics are such that these properties can be substantially modified by alloying and by structure control so that specific grades can be produced for various widely different service conditions.

Most widely used of the cemented carbides is that composed of hard tungsten carbide (WC) particles with a ductile cobalt (Co) binder (WC-Co). Many areas of research have been explored in the past to improve the properties of WC-Co and to lower its production costs. Initially this research was in the area of studying the effect, on the properties, of varying the composition of the alloy⁽¹⁾. It was found that finer WC particles produced a harder alloy while increasing the Co binder content increased the bend strength of the alloy. Composition control, in this manner, has been the prime means of controlling the mechanical properties of cemented carbides.

WC-Co has been alloyed with other carbides and used in applications where a particular property required enhancement. Technological advances have included the development of submicron sized WC particles, which result in higher hardness and compressive strength⁽¹⁾. This technology is very applicable to high wear services associated with low temperatures. Another development that has been made to give better wear and corrosion resistance to WC-Co is the application of coatings consisting of more complex multi-carbide alloys.

Cemented carbides are utilized in a variety of applications ranging from cutting tools and rock drill bits to the materials used in mechanical valve seals, nozzles and ball bearings. Their high hardness and abrasion resistance enable them to out-perform other materials commonly used in such applications.

The recent rapid increase in the price of cobalt has been a significant cause for study of potential replacements for Co in the binder of cemented carbides⁽²⁾. The most promising replacement binder material seems to be Nickel (Ni). The German hardmetal industry successfully used Ni during W.W.II when supplies of Co were limited. It has been found that WC-Ni grades are more resistant to certain corrosive media than are the traditional WC-Co grades⁽⁴⁾. The use of Ni in hardmetals is still largely restricted to laboratories where their properties are being studied. The reason for this is

that properties such as high hardness and strength are not as easily attained as with the WC-Co grades.

The greatest advantage that cemented carbides have over new ceramic products are their superior fracture toughness and higher resistance to thermal shock. In order to compete with the new wave of ceramic technology these properties and any others possible with new hardmetal grades must be exploited to their full potential.

1.2 FABRICATION OF CEMENTED CARBIDES

The production of hardmetals incorporates typical powder metallurgy (PM) techniques and may be summarized by the following processes:

1. Blending of high grade powders of carburized tungsten and powdered binder metal or metals.
2. Comminution of these powders with the use of a ball mill or by other means. This ensures that each carbide particle is coated with fine particles of the binder.
3. Introduction of a pressing lubricant, usually a wax, to improve the pouring and compacting properties of the powder.
4. Pressing of the powder into the desired shape. This step gives the resulting compact enough strength (green strength) to enable it to undergo the remaining processes.

5. Pre-sintering to remove the pressing lubricant. The compact may then be machined if desired.
6. Sintering at a temperature slightly above the eutectic point of the system, to achieve a density as high as possible.

Various new methods have been introduced to the production process in an effort to improve the properties of hardmetals. To achieve higher and more uniform densities, the Hot Isostatic Pressing (HIP) technique has found great success⁽⁵⁾.

Sintering conditions were found to have a noticeable effect on the structure of the produced cemented carbides⁽⁶⁾. Optimal temperatures and durations were the subject of extensive research. A better understanding of the effects that impurities have on the properties as well as the effects of carbon content in the binder, and other reactions between the products and the atmosphere during sintering was obtained⁽⁷⁾. New methods to counter these problems consist largely of introducing atmosphere control during the sintering process⁽⁸⁾.

The atmosphere during sintering can be either a high vacuum or gas may be introduced at specified flow rates. An inert gas such as argon is used for most of the sintering cycle to ensure that no oxygen (O_2) is available for any undesired oxidation of the sintered specimens. A characteristic result of pre-sintering PM products, in flowing

H₂, is a de-carburization of the sintered compact. To maintain a stoichiometric carbon balance it is necessary to introduce a gas treatment (G.T.) phase during the sintering cycle. This is accomplished by introducing a mixture of methane (CH₄) and hydrogen (H₂) gas into the sintering furnace for a certain duration while the temperature is held at a point below the final sintering temperature. This offsets any de-carburization that may have occurred. The carbon content of hardmetals has an effect on a wide range of their physical and mechanical properties including density, level of porosity, and hardness. For the purpose of this study, specimens which did not undergo a gas treatment cycle are designated N.G.T.

1.3 PURPOSE OF THE PRESENT STUDY

The purpose of this research was to develop cemented carbides with enhanced resistance to corrosion, erosion, and oxidation. Therefore several new grades of cemented carbides were fabricated, comprising the following systems: WC-Ni, WC-Ni-Cr, WC-Ni-Al, and WC-Ni-Cr-Al. These new grades, along with a commercially available WC-Co grade, have been evaluated in experiments. The exact nature of the grades and manner of testing is discussed in subsequent chapters. The aim of this study is to be able to identify systems which may be more

suitable, in applications involving aggressive environments or high temperatures, than the standard WC-Co grade. These aggressive environments are found in mining, petroleum, metal finishing, and pulp and paper industries.

1.4 ALLOY COMPOSITION AND PROPERTIES

Each of the cemented carbide systems that have been fabricated contain 90% WC by weight, the particles initially having a mean grain size of 4.7 μm . The binder components make up the remaining 10% by weight. The binder composition of the various grades is listed in Table 1. The binder elements were introduced into the alloy make-up batches in the form of pure Ni, Cr_3C_2 , and AlN. Pure tungsten powder was also introduced, where required.

The physical and mechanical properties that were determined for the various grades are the porosity level, microstructural features, density, and hardness. These properties were determined using the following ISO Standards:

ISO Standard 4505: Hardmetals - Metallographic determination of porosity and uncombined carbon (1st ed., 1978).

ISO Standard 4499: Hardmetals - Metallographic determination of microstructure (1st ed., 1978).

ISO Standard 3369: Impermeable sintered metal materials and hardmetals - Determination of density (1st ed., 1975).

ISO Standard 3878: Hardmetals - Vickers hardness test (2nd ed., 1983).

The properties of the various grades are tabulated in Table 2. These include the density, hardness (from the Vickers 30 kg test), and the core porosity levels for the major types of specimens of each alloy, whether the specimens were G.T. or N.G.T., the sintering temperature and duration, and the values for those grades that were hipped. Table 1 also indicates the porosity levels for the alloys but only in qualitative generalization.

Table 1 Alloy Binder Composition

Alloy Designation	Abbr. Name	Binder Components % by wt. of the binder				Porosity Level
		% Co	% Ni	% Cr	% Al	
G10	G10	100.0	---	---	---	low
G10Ni	10Ni	---	100.0	---	---	low
G10Ni1Cr	1Cr	---	99.0	1.0	---	low
G10Ni10Cr	10Cr	---	90.0	10.0	---	low
G10Ni20Cr	20Cr	---	80.0	20.0	---	med.
G10Ni50Cr	50Cr	---	50.0	50.0	---	high
G10Ni2Al	2Al	---	98.0	---	2.0	low
G10Ni5Al	5Al	---	95.0	---	5.0	low
G10Ni10Al	10Al	---	90.0	---	10.0	med.
G10Ni16Al	16Al	---	84.0	---	16.0	high
G10Ni10Cr2Al	10Cr2Al	---	90.0	9.8	0.2	low
G10Ni10Cr5Al	10Cr5Al	---	90.0	9.0	1.0	med.

Table 2 Alloy Properties

ALLOY	SINT. TEMP. (°C)	SINT. TIME (min)	DENSITY (g/cm ³)	HARDNESS (Hv30)	ISO POROSITY		
					A	B	C
G10 G.T.	1430	30	14.55	1160	00	02	02
10Ni G.T.	1520	30	14.63	1060	00	02	00
LT	1440	30	14.67	1050	00	< 02	00
N.G.T. LT	1520	30	14.71	1020	00	< 02	00
	1480	30	14.67	1070	00	02	00
1Cr G.T.	1520	30	14.63	1110	00	02	00
LT	1440	30	14.64	1120	02	00	00
N.G.T. LT	1520	30	14.66	1150	00	< 04	00
	1480	30	14.67	1140	00	02	00
10Cr G.T.	1520	30	14.53	1310	06	00	00
LT	1440	30	14.41	1170	08	00	00
N.G.T. LT	1520	30	14.56	1320	06	00	00
	1480	30	14.50	1230	06-08	00	00
20Cr G.T.	1520	30	14.18	1300	08	00	00
LT	1440	30	13.66	1210	08	02	00
HX1	1480	30	14.92	1250	06-08	00	00
N.G.T. LT	1520	30	14.33	1380	08	00	00
	1480	30	14.23	1350	08	00	00
50Cr G.T.	1520	30	12.43	1500	>> 08	00	00
HX1	1480	30	13.0	1500	>> 08	00	00

N.B.:

G.T.: Gas treated (stoichiometric carbon balance)

N.G.T.: Not gas treated (under carburized)

LT: Low sintering temperature; HX1: HIP batch X1

Table 2 Alloy Properties (continued)

ALLOY	SINT. TEMP. (°C)	SINT. TIME (min)	DENSITY (g/cm ³)	HARDNESS (Hv30)	ISO POROSITY		
					A	B	C
2Al G.T.	1440	60	14.57	1080	02	00	00
N.G.T.	1400	90	14.51	1460	04	02	00
5Al G.T.	1440	60	14.5	1240	02	00	02
10Al G.T.	1440	60	14.25	1220	06	00	02
N.G.T.	1400	90	14.20	1220	08	00	00
16Al G.T.	1440	60	13.47	1200	> 08	04-06	00
HX1	1440	60	13.6	1320	06-08	04	00
N.G.T.	1400	90	12.95	1010	>> 08	00	00
10Cr- 2Al G.T.							
HX1	1480	30	14.5	1320	< 02	00	00
N.G.T.	1440	60	14.18	1190	> 08	00	00
10Cr- 5Al G.T.							
HX1	1480	30	13.6	1310	06-08	00	00
N.G.T.	1440	60	13.26	1000	> 08	00	00

N.B.:

G.T.: Gas treated (stoichiometric carbon balance)

N.G.T.: Not gas treated (under carburized)

LT: Low sintering temperature; HX1: HIP batch X1

1.4.1 Microstructure

The final sintered structure of these alloys is fairly uniform. They are however composite materials with two distinct and separate phases or regions in their overall structure.

The more predominant phase is the WC, making up approximately 90% of the alloys by weight, or roughly 80% by volume. The binder phase is more complex as it is in fact an amalgamation of all the elements introduced into the alloy make-up batches. During the sintering process some dissolution of the WC into the binder occurs. The carbon content in the binder is also dependent on the sintering conditions and the gas treatment cycle used during sintering. The binder phase is then an alloy of the following elements: Ni or Co, W, C, plus Cr and/or Al where applicable.

Separate phases may also exist within the binder. An example of this may be seen in the case of high Cr bearing grades where some Cr may exist as a separate carbide phase. In those grades with high carbon content there exists occasionally some separate uncombined carbon. This often results in porosity of ISO type C. There is also occasionally some migration of the binder elements to the surface of the compacts during sintering. There was evidence of this in the case of the high Cr bearing grades, where Cr rich regions existed on the as sintered surface. The result of this is

that the surface morphology of these materials may be slightly different from that found in the core regions.

Another stage of the production of these grades, milling of the powders, also greatly affects the resulting microstructure of the grades. Milling of the powders ensures that the different powders are thoroughly mixed and distributed as evenly as possible. During milling the WC grains are coated with the binder material which aids the sintering process. The WC grains however tend to be crushed during this stage of processing, the result being a finer mean grain size and greater variation in grain size than is desirable. During sintering of the pressed compacts there is typically some grain growth associated with the WC phase. This grain growth may be limited by shorter sintering durations at higher temperatures or by the addition of a grain growth inhibitor. Several elements are effective in this task, Chromium being one of them.

The result on the microstructure, of these variables in the production, of these grades is that there exists some variation in key microstructural parameters. These parameters are:

1. WC grain size
2. Binder content
3. Binder morphology

Since the materials tested in the present study are still in development or initial production applications, their proprietary nature precludes a detailed description of their final composition, microstructure or the methods of processing utilized. Such a detailed description is also beyond the scope of this study.

The microstructure typical of the grades is shown in Plates 1 and 2. These micrographs reveal the microstructure of gas-treated specimens, each sintered at high temperature, of the 10Ni and 10Cr alloys respectively (each at 1500 times magnification). In each case the WC phase may be seen as the large angular dark regions. The binder phase makes up the balance of the structure, surrounding the WC particles.

Plate 1. Micrograph of 10Ni, gas-treated, sintered at 1520 °C, (1500 X).

Plate 2. Micrograph of 10Cr, gas-treated, sintered at 1520 °C, (1500 X).

CHAPTER II

THEORY

2.1 CORROSION

2.1.1 Introduction

The American Society for Testing and Materials (ASTM)⁽⁹⁾ defines corrosion as being the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties.

In a corroding system, two co-existing electrochemical reactions are present:

where M is the corroding metal and Z is usually a species in solution. The electrochemical corrosion of a metal may be expressed in terms of the electromotive force (emf) of the corrosion cells that make up the corrosion process. The electrode corrosion potential is equal to the potential at which the rate of oxidation of M is equal to the rate of reduction of Z^+ , as shown in Figure 1. Oxidation occurs at the anode while reduction occurs at the cathode on the metals surface. The measurable net current, the difference between the oxidation and reduction currents, at this point is equal to zero because the current flow is balanced. The current

Figure 1 Relationship between overvoltage and current for a corroding electrode system consisting of two co-existing electrochemical reactions⁽¹⁰⁾.

value depicted in Figure 1 at this point, i_{corr} , is a theoretical value of current resulting from the corrosion reaction. When the corrosion potential is moved from this potential (overvoltage) one of the mixed couple systems will either be further oxidized or further reduced. At more noble (higher) electrode potentials (anodic polarization) M is further oxidised while Z^+ is reduced, the result being a measurable positive net flow of current through the system. The reaction is reversed by inducing cathodic polarization.

Stern⁽¹¹⁾ reviews the relationship between the anodic and cathodic processes that occur, and the effect of various factors, in a corroding system. These factors that affect the corrosion mechanism are primarily related to the nature of the polarization which occurs, whether activation or concentration polarization. These forms of polarization affect the cathodic processes, that is the reduction of the species in solution, Z^+ . Activation polarization is related to the activation energy required to reduce this species and is dependent on the nature and concentration of the species, surface roughness, geometry and composition of the metal, temperature of the solution, and the presence of reducible impurities in solution, such as O_2 . Concentration polarization is a change in potential due to a change in the rate of diffusion, of the reducing species, to the cathode surface. The factors that affect the degree of concentration polarization that occurs are the velocity of the solution adjacent to the cathode

surface and the concentration of the reducing species in solution.

The effect of these forms of polarization are that the reduction / oxidation of the species Z' shifts to a higher or lower potential and the corresponding intersection (Figure 1) with the redox of M occurs at a different potential, resulting in a change in magnitude of i_{corr} .

This reaction between the cells of a corroding system may be illustrated by considering the reactions that occur separately. The reactions in a cobalt - water system will be considered.

Figure 2 illustrates the reactions occurring between cobalt (Co) and water (H_2O). In this case, referring to equations 2.1, the metal (M) is Co and the species in solution (Z') is the cation H^+ .

The Co is oxidised to oxidation state II, while H^+ is reduced to form H_2 (hydrogen gas evolution). These reactions occur at the anode and cathode, respectively. The common reactions that may occur at the anode are⁽¹²⁾:

where n = oxidation state II or III.

The common reactions that may occur at the cathode are:

Figure 2 Electrochemical corrosion process occurring for a Cobalt - Water system.

Each of these reactions is accompanied by a negative change in free energy. Some of these products are soluble and go into solution to form ions. Others remain on the surface of the metal as a film, which may deter further corrosion. The development of surface products may polarize the electrode and will result in a change in the electrode potential and the current density may be reduced, i.e. the corrosion rate decreases. The mechanism whereby protective films develop is called passivation.

These anodic reactions for Co are dependant on the electrode potential and/or the ion activity in solution, which in the case of water is measured by pH. With knowledge of which reactions are occurring and the potential and pH values at which they occur, a Pourbaix diagram may be constructed, an example of which is given for the Co - H₂O system in Figure 3. This diagram provides a thermodynamic basis for the study of corrosion reactions and it allows for prediction, for a certain set of equilibria, of whether a metal will corrode or passivate. Figure 4 illustrates the theoretical domains of corrosion, immunity and passivation of Co. The use of such diagrams and the theory behind them is described by Pourbaix elsewhere^[13].

Figure 3 Potential pH equilibrium diagram for the system cobalt - water, at 25 °C^[12].

Figure 4 Theoretical domains of corrosion, immunity and passivation of cobalt, at 25 °C^[12].

2.1.2 Alloying for Corrosion Resistance

Traditional materials used in structural and other engineering applications have always suffered from the effects of their environment. Improved design and use of a metal can improve its performance in a particular application to a degree but inevitably the need for a more resistant material arises.

Alloying a metal with other metals or elements has been a popular method for enhancing particular properties of materials for numerous applications. The need for corrosion resistance in structural materials has led to the creation of a wide variety of alloys. Amongst these alloys are the stainless steels and other families of specialty steels designed for use in particular applications or environments.

Uhlig and Revie⁽¹⁴⁾ discuss the creation of such alloys as well as a wide variety of non-ferrous alloys and their respective merits. In an effort to improve the resistance of a metal to attack by corrosive media several approaches can be taken. A particular combination of elements may result in an alloy that is essentially inert in a given environment. The tendency of a metal to passivate in a particular medium can be improved through alloying with more noble elements. Heat-treatment techniques may also be employed to exploit a superior phase of the alloy.

2.1.3 Galvanic Corrosion

Galvanic corrosion occurs between two dissimilar metals which are immersed in a corrosive media and are connected electrically. A difference in the electrode potentials of the two metals results in the establishment of a cell. The more resistant (or noble) metal becomes the cathode while the less resistant metal assumes the role of the anode. This generally results in an increased rate of attack experienced by the less resistant metal.

The phenomenon of galvanic coupling is widely exploited for its beneficial nature. The ability to store and convert chemical to electrical energy forms the basis of operation of batteries. A material to be used in service may also be cathodically protected by electrically connecting a sacrificial anode to it. The result of this is that the protected metal becomes virtually immune to the surrounding media. Anodic protection consists of anodically polarizing a material to a higher potential and into its passive region. The protection of metals by this means is discussed by Uhlig and Revie⁽¹⁴⁾.

The driving force behind galvanic corrosion is the dissimilarity in the emf of each of the coupled metals in a particular medium. The resulting current flow between them is determined by the surface area of the cathode or anode that is exposed to the corrosive medium. The current density that

is produced at the surface of the oxidizing anode will be greatly increased if the surface area of the cathode is much larger than that of the anode. It is more desirable to keep this ratio of cathodic to anodic surface areas as low as possible.

2.1.4 Corrosion Testing

There are several methods whereby the actual performance of a material may be tested and the corrosion resistance of a material in a given environment may be measured. The traditional means of measuring corrosion rates consists of immersing a material to be tested in the desired medium for a planned duration. The products of the corrosion process may be removed from the material after the test and the weight loss of metal due to corrosive attack can be determined. The corrosion rate is then expressed in terms of weight loss per unit area per unit time or it may be expressed in terms of penetration per unit time. The obvious shortcoming of these weight loss immersion tests is that they provide very little information on how a metal is corroding.

The study of how materials corrode and how to prevent corrosion from occurring has been made much easier with the advent of methods and tools to study electrochemical corrosion, namely the potentiostat. The potentiostat is a tool that corrosion scientists use to study the behaviour of

a corroding material. It is especially useful for making rapid corrosion rate measurements. These techniques may be used to accurately measure very low corrosion rates, which are difficult to measure with conventional weight loss techniques. Electrochemical corrosion rates may also be measured for large structures that cannot be visually inspected or subjected to weight loss measurements.

A potentiostat may be used to polarize an electrode (a specimen) in an electrochemical cell, that is the potential of the electrode may be controlled, and the resulting current produced from the corrosion reactions can be recorded. This technique permits a quantitative analysis of the active - passive character of a material in a particular environment. Potentiodynamic polarization techniques, in which the applied potential of the specimen is varied at a preset rate, permit the characterization of several valuable features of a particular material. These are:

1. The ability of a material to spontaneously passivate in a particular medium.
2. The potential region over which the specimen remains passive.
3. The corrosion rate of the material in the passive region as well as in other regions.

Once the behaviour of a particular material immersed in a particular medium is known, the corrosion rate of that

material may be regulated in service by maintaining a certain potential on the material, to keep it in a passive state.

2.1.5 A Review of Potentiostat Techniques

The electrochemical corrosion of a metal may be expressed in terms of the electromotive force (emf) of the corrosion cells that make up the corrosion process. The emf of a cell is measured by opposing it with a known emf until no current is flowing through the cell, a condition that is measurable through the use of a galvanometer connected in series with the cell. The applied emf is measured with a potentiometer. The operation of potentiometers is described in detail by Greene⁽¹⁵⁾ and by Uhlig and Revie⁽¹⁶⁾.

The potentiometer is an integral component in the application of the potentiostat to electrochemical corrosion studies. Figure 5 schematically illustrates the wiring diagram of the apparatus used for potentiostatic and potentiodynamic anodic polarization measurements. The potentiostat automatically maintains the desired potential between the working electrode (the specimen) and the reference electrodes by passing the appropriate current between the working and counter electrodes. The use of a variety of potentiostat designs are described in the literature and their applications to corrosion studies are discussed by various authors^(15,17,18,19).

The incorporation of microcomputers in recent electrochemical corrosion investigative techniques has been a useful addition in terms of controlling the experiments and for recording data. Tipton⁽²⁰⁾ discusses the advantages of using such techniques.

The data obtained from potentiodynamic anodic polarization measurements is traditionally plotted as shown in figures 6-8. Figure 6 reveals the hypothetical active - passive anodic behaviour of a metal, as measured by this technique. Figure 7, commonly referred to as a Tafel plot, illustrates the hypothetical behaviour in the active region. Analysis of this plot permits a study of the Tafel (or active) region also shown in figure 6. Figure 8 is a hypothetical linear polarization plot, which again is a study of a small region of the overall behaviour, specifically the region near the open circuit potential of the test specimen.

The means for extracting information from these tests (and plots) is based largely on electrode kinetic theory developed by Stern and Geary⁽¹⁹⁾. Their analysis of the shape of polarization curves, particularly in the Tafel region, for corroding systems reveals the relation between the corrosion rate and the polarization resistance and Tafel slopes. The equations used to analyze the data from this study, based on this electrode kinetic theory, are presented later in Chapter 5. A brief explanation of the terms and relations represented by these plots follows.

Figure 5 Schematic potentiostatic anodic polarization wiring diagram⁽¹⁶⁾.

Figure 6 Hypothetical cathodic and anodic polarization plots for a passive anode⁽²¹⁾.

Figure 7 Hypothetical cathodic and anodic polarization diagram⁽²¹⁾.

Figure 8 Hypothetical linear polarization plot⁽²¹⁾.

Figures 6 and 7 are plots of electrode potential, E , versus Log current density (C.D.), i . Absolute values of i are plotted in the cathodic region, i.e. at potentials below E_{corr} . The corrosion rate is determined from the values of the anodic and cathodic Tafel slopes, and the corrosion current density value at the intersection of the extrapolated Tafel slopes (i_{corr}) which occurs at the open circuit potential (E_{corr}). The corrosion rate may also be determined from the polarization resistance value, R_p , which is the slope of a plot of polarization versus current density (figure 8) measured in the vicinity of E_{corr} .

The effect of various experimental factors in the measurement of corrosion behaviour by these methods are discussed in detail by Greene and Leonard⁽²²⁾. These variables are:

1. The scan rate: The rate at which the potential is increased affects the recorded current density values. Higher scan rates generally result in polarization curves that are shifted to higher current density values.
2. Potential step size: The incremental size by which the potential is increased has only a slight effect on the polarization curves. Current densities tend to decrease with increasing step size.
3. Cathodic pre-treatment: Holding the potential of the test specimen at a potential below E_{corr} for a duration before the scan results in an increased critical current density (i_{cc}),

but does not affect the magnitude of E_{ms} or i_p . Lower cathodic potentials and/or longer durations of pre-treatment further increase i_{sc} values.

Their conclusion of the effect of cathodic pre-treatments are that they should be used only if they reflect the actual system under study. Scan rates should be kept as slow as possible to better reflect features in the passive region which might otherwise be obscured by high scan rates.

2.1.5.1 Potentiostatic Measurements

Potentiostatic tests provide a means of studying the decrease in the corrosion current density, over time, produced by a corroding metal while it is held at a constant potential. This test may be performed on specimens polarised into a specific region of their active - passive behaviour. For example the kinetics of passive film growth may be studied by polarizing a metal into the passive region and analyzing the decay of the produced anodic current.

2.2 EROSION / CORROSION

2.2.1 Introduction

The ASTM⁽²²⁾ defines erosion corrosion as being a conjoint action involving corrosion and erosion in the presence of a corrosive substance. The combined nature of erosion and corrosion processes that occur necessitate an examination of the erosion mechanism alone. Erosion is defined⁽²³⁾ as the progressive loss of original material from a solid surface due to mechanical interaction between that surface and a fluid, a multicomponent fluid, or impinging liquid or solid particles.

Fontana⁽²⁴⁾ presents an excellent discussion of the effects that erosion corrosion has on materials used in a variety of applications as well as the reasons for the superior resistance that some metals have to this form of attack. The corrosion rate of certain metals in specific environments may decrease due to the development of a passive film on the metals surface, as discussed earlier. A metal subjected to erosion corrosion may have this protective film either damaged or removed from its surface entirely. This wear mechanism has the effect of increasing the damage experienced by the corroding metal as it may be continually exposed to fresh attack by the environment.

Those metals that are more resistant to erosion corrosion typically have a tenacious passive film that is resistant to wear or this protective film may develop at a sufficiently rapid rate to offset the rate at which it is removed from the metal surface.

The erosive action that leads to increased attack may be due solely to flow of the corroding liquid, such as flow through pipes, valves, nozzles, pumps, etc., or it may be due to abrasive particles carried in solution, such as a slurry, flowing through these components. The primary factors that affect the severity of attack by erosion corrosion are⁽³⁴⁾:

1. Velocity: the velocity of a corroding fluid, particularly if it is carrying solid particles, has a direct effect on the rate at which a material will experience attack.
2. Turbulence: turbulent flow of the corrosive medium results in greater agitation of the liquid at the metal surface than is the case for laminar flow. The level of agitation of the fluid affects how intimate the contact between the metal and its environment is and how aggressive the resulting corrosion attack will be.
3. Impingement: the flow of a corrosive fluid along a metal may not lead to excessive attack until it is forced to change direction, say within the confines of a piping system, or impinges directly on a metal surface. Likewise a fluid carrying erodent particles (a slurry) will be more damaging at higher angles of impingement.
4. The nature of the metal or alloy: such factors as the chemical composition, corrosion resistance, hardness and metallurgical history of a metal or alloy will affect its resistance to erosion corrosion.

While the hardness of an alloy is a good criterion for resistance to mechanical erosion it does not necessarily mean that a hard alloy will be more resistant to erosion corrosion. If the alloy is inert in the corrosive medium then its resistance will depend on its resistance to mechanical erosion. The resistance of more active metals, that resist corrosion through the development of a passive film, will depend largely on how tenacious and resistant to erosion the protective layer is. Those active metals that show little tendency to passivate in a specific medium will be expected to have even less resistance to the additionally aggressive nature of an erosive - corrosive environment.

The present study examines the results of testing cemented carbides in an erosive - corrosive slurry. As a related area to the erosion corrosion performance of these alloys the mechanism of mechanical erosion by solid particle impact has also been investigated.

2.2.2 A Review of Erosion by Solid Particle Impact

The study of solid particle erosion of materials typically consists of subjecting a materials surface to a jet of gas or liquid which carries eroding particles. The impact of these particles on the target material results in a removal of the metals surface by either a ductile or brittle mechanism

of erosion. The primary factors that affect the damage a target material will sustain from erosion are:

1. Properties of the target material: properties such as the hardness, fracture toughness, and microstructural features such as alloy homogeneity and porosity.
2. Properties of the erodent: properties such as the eroding particle size, shape and hardness.
3. Experimental parameters: variables such as the erodent velocity, the angle of impact, and the erodent concentration (the ratio of mass of particles per unit volume of combined erodent and fluid).

Pennefather⁽²⁸⁾ gives an excellent review of how each of the fore mentioned parameters affect the erosion of materials and discusses the mechanisms behind the two common modes, either ductile or brittle, of material removal. Ductile erosion is associated with plastic deformation of the target material and is characterized by higher rates of erosion at low angles of attack (30°) than at angles normal to the material surface (90°). Brittle erosion is often the mechanism by which harder materials erode. This mode is associated with elastic - plastic deformation of the target materials surface leading to the nucleation of cracks which propagate under continued impact and result in the removal of the surface material. This mode of erosion is characterized by higher rates of erosion at high angles of attack than at low impact angles.

2.3 THERMAL OXIDATION

The ASTM⁽¹⁾ defines oxidation as being the corrosion of a metal that is exposed to an oxidising gas at elevated temperatures. At high temperatures water is not stable in the liquid phase and the corrosion that occurs between a metal and its environment occurs by direct chemical combination. The oxidation of a metal usually results in development of a film of solid metal oxide on the surface. This film acts as an interface between the metal and its environment and allows reduction of the oxidising atmosphere and oxidation of the metal to occur simultaneously. An example of the oxidation of a metal, M, in air is shown below:

At the metal / film interface:

At the film / air interface: (2.4)

The reaction in the film is:

where n = oxidation state of the metal.

This reaction resembles the anodic and cathodic reactions of electrochemical corrosion and in fact behaves in a similar fashion. The primary difference is that the cations (O^{2-}) exist in a solid ionic film rather than in an aqueous

solution. Kofstad⁽²⁶⁾ describes the factors that affect the oxidation reaction of a metal as being:

1. Pre-treatment and surface condition of the metal: The growth of an oxide film occurs outward from the metal surface. The surface condition and features of the metal will affect the rate of growth of the oxide.
2. Temperature: The energy required in formation of the surface oxide is supplied by the environment. The rate of the oxidation reaction is dependant on the ambient temperature.
3. Gas composition and pressure: The fraction of the environment that is involved in the oxidation reaction versus the environment as a whole affects the rate of reaction. For example: the oxidising component of air is O_2 , the fraction of O_2 (the partial pressure) that may be in contact with the metal surface, or available for reaction, will determine the rate of the oxidation reaction.

The oxidation reaction of a metal in air proceeds by diffusion of O^{2-} to the metal surface and through the oxide film, once a film exists. The factors mentioned earlier affect the ease with which this diffusion occurs and how much diffusion will occur. The formation of an oxide film may affect the rate at which O^{2-} is able to diffuse to the metal surface. Those metals that have high resistance to thermal oxidation generally form an oxide film that acts as a barrier to further oxidation. This protective film significantly

reduces the rate at which O^{2-} is able to diffuse to the metal surface, thus limiting further oxidation of the metal. Such resistance is characterized by reducing oxidation rates with continued exposure to the oxidising environment.

As seen in the examination of electrochemical corrosion, the tendency of a various metals to react depends on the properties of the metal. The oxidation reaction for various metals may also be expressed in terms of the emf of the reaction cells. Those metals that have a higher oxidation potential than others will require a higher temperature before the reaction will occur. Metals may then be alloyed with other more resistant elements to improve the thermal oxidation resistance.

CHAPTER III

A REVIEW OF PREVIOUS STUDIES ON CEMENTED CARBIDES

3.1 CORROSION OF CEMENTED CARBIDES

3.1.1 Studies Performed by Potentiostat Techniques

The number of electrochemical corrosion studies that have been performed on cemented carbides by potentiostat techniques is extremely limited, however the prospect of applying these methods in an effort to select superior grades for different corrosive environments has recently gained significant interest within the hardmetal industry.

The most recent study was performed by Almond and Roebuck⁽²⁷⁾. They have examined the electrochemical corrosion of a few WC-Co and WC-Co-Cr grades, with varying binder content (6 & 11 wt.%) and varying WC grain size, in a 3.5% NaCl solution (0.6N NaCl). While the authors did not discuss their methods of testing or quote specific results, such as corrosion rates, they do make a few observations. The results of potentiodynamic anodic polarization tests of these grades revealed that the grades with lower binder content were less resistant to attack by simulate sea water. The same results were observed for the finer grained grades. The best performance was therefore observed in the grades with larger

WC grains and high binder content. The addition of Cr₃C₂ to the WC-Co grades lowers the current density values plotted in the polarization curves.

These findings are fairly consistent with the notion that it is primarily the binder phase that corrodes, while the WC grains are largely inert in this medium. The ratio of the exposed surface area of the WC phase to the whole surface of cemented carbides does increase as the binder content is decreased. The effect of the galvanic coupling of these two phases leads to higher corrosion rates of the binder as this ratio is increased. An increasing WC grain size should also increase this ratio and lead to higher corrosion rates but in the case of this study the authors have stated that the reverse has occurred.

Another recent study of value was performed by Scheers⁽²⁸⁾ on the electrochemical corrosion of four commercially available WC-Co grades, one of which (G10) is similar to that used as the reference WC-Co grade in the present study. Cemented carbides with varying binder content and WC grain size were tested by potentiodynamic anodic polarization methods in 2N H₂SO₄ and 6N HCl, at room temperature (25 °C) and at 80 °C. The results of testing in the sulfuric acid medium revealed a corrosion rate increase of one to two orders of magnitude with the increase in temperature, for most of the grades tested.

The effect, on the corrosion resistance, of varying the binder content was the same as mentioned earlier. However a decrease in WC grain size did result in a decreased corrosion rate. From the results obtained in this study it is apparent that variations in the binder content have a more pronounced effect on the corrosion resistance than does a changing WC grain size, for tests in hot 2N H_2SO_4 . Testing in room temperature sulfuric acid reveals that these two compositional parameters have roughly equal influence on the corrosion resistance of the various grades. There was no passivation observed in the behavior of any of these WC-Co grades. Some of the results of this study will be compared to those obtained in the present study at a later stage.

In an earlier study, Voorhies⁽²⁹⁾ examined the electrochemical corrosion of dry pressed WC powder compacts in 2N H_2SO_4 and in 2M H_3PO_4 . The surface area of these compacts was assumed to be the surface area of the WC powder per unit mass. Through anodic and cathodic polarization tests the behavior of WC is analyzed in the active region. The study also includes an analysis of current density decay versus time data recorded from potentiostatic tests. While this study did not analyze the corrosion of cemented carbides it has examined the behavior of a significant component of these alloys, the WC phase.

Ghandehari⁽³⁰⁾ examined the anodic behavior of a WC-6%Co cemented carbide in phosphoric acid solutions. In another

study⁽³¹⁾, with other authors, he examined the anodic dissolution of the binder phase (W-Co) from WC-6%Co alloys, by phosphoric acid. This was performed by electrochemical corrosion techniques applied to a particulate bed electrode system. By studying the corrosion of crushed cemented carbides, the authors improved the process of selectively leaching the binder from the alloy while leaving the WC phase largely unattacked. This technique is widely used in the hardmetal industry for recycling cemented carbides.

3.1.2 Studies Performed by Weight Loss Immersion Techniques

Weight loss immersion corrosion techniques, as mentioned earlier, provide little qualitative information on the corrosion of materials but they are a simple and effective means of determining the corrosion rate of a material in a particular environment. This technique has been used amongst the hardmetal industry for studying the corrosion resistance of various cemented carbide grades. Those studies which were performed with the aim of improving the corrosion resistance of WC based cemented carbides by experimenting with replacement binder metals will be examined.

The most recent study was performed by Kny and Schmid⁽³²⁾, of Plansee, who examined the corrosion of WC-9%Co, WC-9%Ni, WC-8.5%Ni-0.5%Cr, WC-10%Co-4%Cr and other grades, with fine WC grain size, in a variety of media at room

temperature and at 100 °C. Ground specimens with a surface area of 9 cm² were immersed in solutions for periods of 20 days without stirring.

In 2N H₂SO₄ at both room temperature and 100 °C the resistance of these grades was found to improve significantly with replacement of the Co binder by Ni. Further corrosion resistance was attained by adding Cr to the Ni binder. The Co-Cr grade did not perform as well as the straight Ni grade.

The results of testing these grades in 0.5N NaCl at room temperature reveal that the Ni binder performs slightly better than the Co grade and the addition of Cr to Ni greatly increases the resistance to attack by this medium. The Co-Cr grade also performed quite well in NaCl.

Another recent study was that performed by the Boart Research Centre (BRC)⁽¹³⁾ on the corrosion resistance of a variety of commercially available WC-Co grades and a few experimental WC-Ni-Cr grades that are similar to those tested in the present study. The grades tested include a WC-Co grade similar to the reference grade in the present study, G10Co, and G10Ni8Cr, G10Ni12Cr, and a fine grained WC-8.5%Ni-0.5%Cr grade similar to that mentioned earlier. Specimens of these grades with a surface area of 9.5 cm² were ground and immersed in a variety of media for a period of 20 days. The results of testing in 2N H₂SO₄ and 0.5N NaCl at room temperature and boiling revealed that the corrosion resistance of these grades was improved by the replacement of Co by a Ni-Cr binder in

both media and for both temperatures. The measured weight losses that occurred from immersion in the NaCl media were very low and were claimed to be within the experimental accuracy.

An earlier study was performed by Ekemar et al.⁽³⁴⁾, of Sandvik, on WC-Co, WC-Ni, WC-(Ni-Co) and WC-(Ni-Co-Cr) grades, all with a binder content of 24% by volume. The authors omit the exact composition of the grades and a few details of the techniques used. They tested these grades in buffered solutions covering a pH range from 1 to 11 for a period of 10 days at 26 °C. They reported that the Ni and Ni-Co grades were slightly more resistant than the Co grades in neutral and acidic solutions and that the Cr additions further improve the resistance, particularly in a slightly acidic medium.

3.2 EROSION OF CEMENTED CARBIDES BY SOLID PARTICLE IMPACT

There have been several recent studies on the erosive wear of cemented carbides by solid particle impact. Keshavan and Jee⁽³⁵⁾ have studied the erosion of commercially available WC-Co grades at high velocity with both silica and alumina. The exact composition of the grades is omitted but the authors tested a range of WC grain size from submicron to 3 μm and a binder content ranging from 6 to 16 % by weight. The erosion rates were found to decrease for increasing WC grain size

and/or decreasing binder content. These parameters affect the hardness of cemented carbides. The authors compared the erosion resistance to the hardness and found that the erosion rates did decrease with increasing hardness of the grades tested.

Pennefather⁽²⁸⁾ studied the solid particle erosion of a variety of commercially available WC-Co grades, one of which is similar to the reference grade tested in the present study (G10). The tested grades comprised a wide variety of binder contents and WC grain sizes. The effect on the erosion of these grades, by various sized particles of SiC erodent (30, 50 and 100 microns) was studied at numerous angles of attack ranging from 15° to 90°, at a velocity of 40 m/s. Several relationships between the erosion resistance of the tested grades and their microstructural features were established.

The modes of material removal were determined to be either cobalt extrusion, brittle fracture of the WC grains, or ductile cutting of the cobalt matrix. These individual modes were observed to be prevalent for alloys with binder contents of: less than 10% by weight, contents of 10%, and high binder contents over 10%, respectively. The erosion of these grades varied within the combined ductile and brittle mechanisms of erosion. At high angles of attack with large SiC erodent particles the brittle mechanism of erosion predominated. The erosion rate was found to increase with increasing WC grain size. At high angles of attack with large

erodent the highest erosion rates were observed for a binder content of 10%, lower binder contents resulted in lower erosion rates, while contents increasing above 10% were generally also more resistant up to a certain binder content.

The erosion resistance of the various grades was generally observed to increase with increasing hardness of the grades. The macroscopic fracture toughness, of the grades, did not appear to affect the erosion resistance of the grades but it is believed that the microscopic toughness of the binder phase does have an effect.

Ball and Paterson⁽³⁶⁾ have studied the erosion of cemented carbides by different methods. The low velocity erosion of various WC-Co grades was studied by subjecting the specimens to a stream of air carrying 100 μm SiC particles at 40 m/s with an impact angle of 45°. While specific information on the composition of the grades is omitted, it is stated that the grades tested had binder contents ranging from 6 to 25% by weight, for WC grain sizes of 2 and 5 microns. The variation in erosion rates for these grades followed the trends discussed earlier. The change in erosion rates of the grades tested is only slight, as the binder content changes or as the WC grain size changes.

The erosion by high velocity air (approximately 340 m/s) carrying coal ash particles with an angle of impact of 45° was also studied. The results of these tests reveal that the harder materials are more resistant. The best performance

among the cemented carbides is seen with fine grained, low binder content grades.

The erosion of a variety of materials was also examined by high speed particle erosion in a liquid carrier, water. Water carrying 100 ppm by weight silica (mean particle size of 8 μm) at a velocity of 250 m/s, was delivered through a test cell. The test cell consisted of a conical valve and seat, where the materials under investigation were used as the valve material. The volume loss of the valve material was recorded after successive time intervals. The materials tested in this way include a couple of WC-Ni cemented carbides.

The authors report that the Ni grades (WC-5%Ni and WC-9%Ni, WC grain size of 2 μm) reveal reduced rates of erosive attack over time and the best performance of the materials tested. The two WC-Co grades tested (WC-6%Co and WC-11%Co, WC grain size of 2 μm) showed a relatively rapid and constant rate of erosion. The authors suggest that this superior performance by the Ni grades is due to a corrosive aspect of the test and the superior corrosion resistance of Ni in water.

Wright et al.^[37] have tested ceramic materials and a range of WC-Co grades, with WC grain sizes between 1 and 1.5 μm and binder volume fractions between 5 and 37%. These grades were subjected to erosion by a slurry made of an oxidation-resistant grade of machine oil carrying silica (SiO_2) particles, with a mean size of between 10 and 15 μm , at a

velocity ranging up to 140 m/s with various angles of impingement. The results of this study reveal that the erosion rates of the WC-Co grades increase with increasing binder content for the range of velocities tested, at impact angles greater than 20°. The erosion rates of these grades was also seen to decrease with increasing hardness of the cemented carbides.

Seger and Maroofian⁽³⁸⁾ have examined the erosion resistance of a variety of materials including several WC-Co grades and a WC-Ni grade. This study was performed with a modified sandblasting cabinet whereby the specimens were simply exposed to attack by a known weight of sand (SiO₂) carried by high velocity air at an angle of 30°. The results of this study show that the WC-Ni grade has only marginally superior erosion resistance than the comparable WC-Co grade, with 6% binder and WC grain size of 2 µm. The trends amongst the WC-Co grades tested showed that low binder contents and/or fine WC grain size is beneficial to erosion resistance.

Levy et al.⁽³⁹⁾ have examined the erosion behavior of a variety of materials including a couple of commercially available WC-Co-Cr grades. The technique used for this study consisted of eroding the specimens with 200 µm SiC particles carried in an air stream at 30 m/s at impingement angles of 30, 60 and 90°. The results of this study show that the cemented carbides erode in a brittle manner and that the

erosion resistance, of the materials tested, increased with finer grain size and lower levels of porosity.

3.3 EROSION CORROSION OF CEMENTED CARBIDES

The number of erosion corrosion studies that have been performed on cemented carbides is extremely limited. One study⁽³⁶⁾, as previously mentioned, attributed the higher resistance of WC-Ni grades, to erosion by water borne erodent, to the corrosive aspect of the test.

A recent study by Kny and Schmid⁽³⁷⁾, discussed earlier, also examined the resistance of cemented carbides to attack by a corrosive - erosive slurry of artificial sea water and SiO₂ sand (80 - 200 μ m grain size) at a speed of 70 m/min. The results of these tests show that the erosion corrosion resistance significantly improves with the replacement of Co by Ni in grades with 9% binder by weight. Further improvements were made with the addition of Cr to the Ni binder.

3.4 THERMAL OXIDATION OF CEMENTED CARBIDES

Nishigaki et al.⁽⁴⁰⁾ performed thermal oxidation tests on alloys with a binder content of approximately 30% by weight,

the composition being WC-27%(Co+Ni)-0.9%Cr-(0-1.5%)Al. Their studies concluded that there was a significant improvement in the oxidation resistance as the Co was replaced with Ni. A further improvement was also attained with the addition of Al to the binder. The authors attributed the improved resistance to the formation of a protective surface layer. The distribution of the binder elements, through the oxide film, was analyzed by Electron Micro Probe Analysis (EPMA). The increased concentration of Al, Cr and W near the inner oxide surface was evident, while the concentration of Ni and Co was higher towards the surface of the oxide film.

In another study performed by Oakes⁽⁴¹⁾ hardmetals with a binder content of 10% by weight were tested. The grades tested comprised the following systems: WC-Co, WC-Co-Ni, WC-Co-Ni-Cr and WC-Co-Ni-Cr-Mo. The replacement of almost 1/2 of the Co in the binder with Ni did not result in an improvement in the oxidation resistance. The addition of 0.5% Cr to the Co-Ni binder did prove beneficial.

Ekemar et al.⁽³⁴⁾ report that the incubation time before oxidation occurs is greater for a WC-Ni grade than for a WC-Co grade. The authors omit the composition of the grades tested but their results of testing with a thermal analyzer show that up to a temperature of 700 °C, their Ni bonded grade is superior to the Co grade. At temperatures above 700 °C the incubation time is negligible.

A study by Almond and Roebuck⁽⁴²⁾ on ultra-fine grained WC-Co grades (grain size less than 1 μm) show that the thermal oxidation of grades with both 6 and 10% binder, tested at 600 °C, is lower with the addition of 0.5% Cr₃C₂ to the Co binder than with other grain growth inhibitors such as VC.

CHAPTER IV

EXPERIMENTAL APPARATUS AND PROCEDURE

4.1 POTENTIOSTAT / GALVANOSTAT EXPERIMENTS

4.1.1 Experimental Apparatus

The apparatus has been constructed following the guidelines stated in the standard practice for such tests, the ASTM Standard Reference G5-82⁽¹⁴⁾. The set-up of the apparatus is shown schematically in Figure 9. The principal components are:

- EG&G Princeton Applied Research Potentiostat / Galvanostat Model 173.
- EG&G Princeton Applied Research Model 276 Interface.
- EG&G Princeton Applied Research Model 332 SoftCorr Corrosion Software, Version 2.1
- Apple IIe Computer
- Epson RX-80 Printer
- Test cell comprising reference electrodes, Luggin probe
  - salt bridge, gas inlet/outlet tubes, and a thermometer.
- Working electrode holder
- Doerr Stedi-Drive speed control unit
- Applied Motors 1/4 hp. electric motor

Figure 9 Schematic diagram of potentiostat / galvanostat experimental apparatus.

Figure 10 Schematic diagram of the test cell.

The potentiostat / galvanostat may function in several ways depending on which type of experiment is to be performed. For the purpose of conducting potentiodynamic anodic polarization scans of a specimen the potentiostat / galvanostat applies a potential to the specimen, increasing from an initial potential to a final potential at a controlled rate of increment. The current produced by the corrosion of the specimen is measured and recorded versus the applied potential. For the purpose of conducting potentiostatic measurements the test specimen is held at an applied potential and the resulting current is measured and recorded versus time for the duration of the experiment.

The SoftCorr software is a menu driven package which permits selection of the test type and specification of all of the experimental input parameters. Through the use of the interface it allows the user to control virtually all of the operational aspects of the potentiostat / galvanostat. The software permits acquisition of all the experimental data and incorporates post processing programs for graphical presentation of the data and numerical analysis of the data to yield results from the experiments.

The test cell contains the solution in which the specimens are being evaluated. It is constructed, as shown in Figure 10, to permit the following items to be immersed in the solution: the test (or working) electrode, a counter

electrode (made of platinum), a reference electrode, a gas inlet tube, and a thermometer.

The working electrode is the specimen to be tested and is held in an insulated holder which permits an electrical connection between the test specimen and the potentiostat. The holder (and specimen) is rotated by the motor at a speed of 200 rpm. This allows corrosion products to be carried away from the surface of the specimen, while causing only moderate agitation of the solution within the test cell.

The reference electrode used in these tests is a saturated calomel electrode (SCE), a reference against which all potentials are measured. The SCE is incorporated within a Luggin capillary probe which contains a salt bridge allowing an electrical connection between the bulk solution and the SCE, whilst keeping the two separate. The tip of this probe is positioned in close proximity to the specimen surface.

The gas inlet tube and outlet vent allow for de-aeration of the test solution by purging with N_2 .

4.1.2 Experimental Procedure

Several types of tests were performed using this apparatus. The two primary ones were Potentiodynamic Anodic Polarization and Potentiostatic measurements. The procedures for conducting these tests followed the standard practice for

each test as laid out in the ASTM Standard Reference G5-82⁽¹⁴⁾. The important procedural variables are listed below:

1. Scan Rate for Potentiodynamic Polarization Scans was 1 mV/s (3.6 V/hr) and the step size was 2 mV.
2. The initial potential applied to the specimens was 250 mV below the freely corroding potential, E_{corr} . The scans were continued up to a final potential of 1600 mV vs. SCE. There was no cathodic pre-conditioning of the specimens.
3. Potentials for Potentiostatic tests were determined from the potentiodynamic scan results at 3 points: E_{cath} , E_p , and E_{pp} . The duration of the Potentiostatic tests was 20 minutes.
4. The test solutions were 2N H_2SO_4 (pH = 0.5) and 0.5N NaCl (pH = 7.5). The volume of test solution used was 600 ml for each test. The solutions were prepared from reagent grade chemicals and doubly distilled water.

The preparation of the specimens consisted of mounting the cylindrical specimens in lucite then grinding off approximately 2 mm of the specimen surface to expose the core structure. The lucite mount was then drilled through to the rear surface of the specimen and threads were tapped for connection, both mechanical and electrical, to the holder. The specimen surface was then successively polished to a final polish with 1 μ m diamond paste, within 1 hour of the test.

Immediately prior to testing the specimens were cleaned with methanol in an ultrasonic bath, rinsed and dried.

Prior to testing the test solutions were de-aerated by purging with N₂ for a period of 30 minutes. The purging then continued throughout the test duration. The specimens were then immersed in the test cell and allowed to stand for a period of approximately 20 minutes prior to commencing the tests.

The minor deviations from the standard practice involved in this procedure were the use of N₂ for purging the O₂ from the test solution rather than the recommended H₂. This is however a common practice and is not a significant deviation. Another minor deviation was made in terms of the specimen size. The geometry and size of the specimens used was determined by what shape and size was available with the PM techniques used during fabrication of the specimens. Limitations also existed in terms of how compatible the specimens were with the existing experimental apparatus, ie. the working electrode holder. The specimen surface area used was much smaller than that suggested. The volume of test solution was also less than that recommended, but was deemed an acceptable deviation.

The major deviations from the standard practice, involved in this procedure, were made for the reduction in the duration required to perform each test that they permitted. These deviations are listed as follows:

1. The temperature of the test solution was not held at the recommended value of 30 °C but was instead variable, ie. dependant on the ambient room temperature. The solution temperature was measured for each test and was found not to deviate too greatly. The average temperature over all the tests was approximately 25 +/- 3 °C.

2. The specimens were immersed for a period of only 20 minutes, rather than the recommended period of 60 minutes, prior to commencing the tests. The purpose of this conditioning period is to allow the specimen to reach a steady state of corrosion and for the freely corroding potential (E_{corr}) of the specimen to settle to a steady value. An investigation of what occurs during this period was made through use of E_{corr} vs. Time testing at the freely corroding potential. This type of experiment measures and records the potential of the test specimen (vs SCE) against time for the duration of the test. It was observed that the value of E_{corr} (for these specimens) settles to a steady value within 10 to 15 minutes. Therefore the duration of 20 minutes for conditioning the specimens was deemed to be sufficient.

4.2 IMMERSION CORROSION EXPERIMENTS

4.2.1 Experimental Apparatus

The apparatus used in the immersion corrosion tests is shown schematically in Figure 11. The components used in these tests are standard laboratory equipment and are described as follows:

- 500 ml Erlenmeyer flasks
- 1000 ml Erlenmeyer flasks with reflux condensers
- Hot plates
- Supporting frame
- Fume cabinet

4.2.2 Experimental Procedure

The procedures for conducting these tests followed the standard practice as described by the ASTM Standard Reference G31-72⁽⁴³⁾. The volume of solution used in all tests was 500 ml. The media tested were: Stagnant 2N H₂SO₄ for a duration of 250 hrs.; Stagnant 0.5N NaCl for a duration of 500 hrs.; and Boiling 2N H₂SO₄ for a duration of 48 hrs., in the hot immersion corrosion tests. Doubly distilled water was added regularly to the flasks during the tests to correct for any evaporation of the test solution that may have occurred.

Figure 11 Schematic diagram of weight loss immersion corrosion apparatus.

Immediately prior to immersion the specimens were cleaned with methanol in an ultrasonic bath and dried. After the tests the specimens were scrubbed with a hard brush before being cleaned and dried again. Those specimens with excessive levels of porosity were kept in a desiccator for a few days to ensure that they were as dry as possible. An attempt at cleaning the corrosion products from the surface of the specimens was made as per ASTM standard G1-81⁽⁴⁴⁾. This procedure consisted of immersing the specimens in 6N HCl in an ultrasonic bath for short durations. This practice had no measurable effect on any of the specimens except the reference grade G10. The weight loss experienced by the cobalt grade was determined to be due to further corrosive attack of the Co binder and not the desired cleaning of surface products. This practice was therefore discontinued. The specimens were weighed before and after each test on a balance that recorded to 0.1 mg.

The specimen geometry used was in the form of rectangular blocks, as discussed further on. Ideally the specimen geometry should have been cylindrical to limit the occurrence of edge effects. Limitations in the pressing techniques involved in fabricating the specimens preclude the use of long cylindrical specimens, with sufficient surface area, in these tests.

The preparation of specimens consisted of sandblasting the specimen surface prior to testing. This surface

preparation was a rapid means of removing the as sintered surface of specimens, which typically comprises a different concentration of the various binder elements than would be present in the core region of a specimen. It was also an effective means of removing corrosion products from the surface of previously tested specimens. While this method did not accomplish the high surface finish that accompanies the traditional methods of surface polishing, which in the case of large cemented carbide specimens is an extremely time consuming operation, it did afford a relatively uniform finish and revealed the exposed phases of the structure in their respective proportions.

The ends of the specimens tested in these experiments were masked where the alloy and specimen designations were inscribed in the specimen surface.

4.3 EROSION EXPERIMENTS

4.3.1 Experimental Apparatus

The erosion testing apparatus was designed and constructed by the Centre for Energy Studies, Technical University of Nova Scotia. A schematic diagram of the apparatus is shown in Figure 12. Its principal components are:

Figure 12 Schematic diagram of solid particle impact erosion apparatus.

- A Sylco Powder Feeder, Mark IX, Serial 600
- An Applied Test Systems Inc. Tube Furnace, Series 3110
- A GTE Sylvania Serpentine Gas Heater, Series 1
- An IBM PC Computer and Epson MX-80 Printer
- A Tecmar Lab Master Data Acquisition Board

The essential operations performed by the apparatus may be summarized as follows. A stream of nitrogen gas (N_2) carries a specified amount of erodent, metered out by the powder feeder, to the test chamber. A second stream of (N_2) combines with the first stream and accelerates the erodent carrying gas to a desired velocity. The velocity is measured by the rotating disk method. The angle of impingement was adjusted on the specimen holders within the test chamber, prior to testing. A positioning mechanism places the specimens under the discharge nozzle for a desired duration. The functions of the apparatus are controlled by the IBM PC computer through use of the Tecmar data acquisition and control system.

4.3.2 Experimental Procedure

The procedures for conducting these tests followed the standard practice as described by the ASTM Standard Reference G76-83⁽⁴⁵⁾. The erodent used in these tests was Silicon Carbide

(SiC) (grain size: 180 microns) which was discharged from the powder feeder at a rate of 12 grams per minute. The test velocity used was 30 metres per second and the duration of the tests was 15 minutes. Two angles of attack were used in the testing, 90 and 30 degrees. The specimens were located at a distance of 10.0 mm from the end of the nozzle. The nozzle used in these tests had an inner diameter of 4.0 mm and a length of 50.0 mm. The eroded surface area on the specimens was roughly 80 mm². This resulted in a particle flux at the specimen surface of approximately 2.5 mg/mm²/s. All of the tests were performed at room temperature. The specimen surface tested was as sintered. Fresh erodent was used for each test. The specimens were weighed on an analytical balance before and after each test. The specimens were cleaned of any adhering erodent with a soft brush.

4.4 EROSION CORROSION EXPERIMENTS

4.4.1 Experimental Apparatus

The erosion corrosion testing apparatus was designed and constructed by the Engineering Performance Section, in the Metals Technology Laboratories of Energy, Mines and Resources Canada. A schematic diagram of the apparatus is shown in

Figure 13, the specimen holder is shown in Figure 14. Its principal components are:

- A Sandpiper Pump, Model SB 1 1/2 - A, Type SN-3-CI
- A Mansfield Tranquilizer, Model TA2, Type N-1-CI
- A Test Chamber and a supporting framework structure
- A Ratiotrol Speed Control
- Boston Electric Motor (1/2 hp)

The essential operations performed by the apparatus may be summarized as follows. The slurry used consists of 2N H₂SO₄ with 20% solids (60 μ m SiC) by weight. The slurry is pumped into the top of the test chamber and extracted from the bottom. The test specimens are positioned on the circumference of a disk which rotates in the slurry. Excessive swirl of the slurry is prevented by the use of baffles in the test chamber.

4.4.2 Experimental Procedure

The test specimens were moved through the slurry at a speed of 5 m/s for durations of 48, 24, and 12 hours. The slurry composition was 12 litres of water, 700 ml of concentrated H₂SO₄ (S.G.=1.98), and 4 kg of 60 micron SiC particles. The temperature of the slurry was elevated above

Figure 13 Schematic diagram of erosion corrosion apparatus.

Figure 14 Diagram of erosion corrosion test specimen holder.

room temperature by mechanical losses transferred to the solution, and was generally observed to be 30 ± 5 °C.

The specimen preparation was the same as discussed earlier for the immersion corrosion test procedure. The surface of the test specimens, where they were clamped by the specimen holder, was masked. The remaining surface area exposed to the slurry was equal to approximately 14 cm². The nature of the test suggests that only a fraction of this area is attacked by the erosive action of the slurry. For the purpose of calculating corrosion rates resulting from this test only half of the unmasked surface area is said to be exposed, ie. approximately 7 cm².

One successful test run constituted all 12 alloys, in groups of 4, subjected to the experiment once and then again in reverse order. Subsequent tests were performed on new specimens with a fresh slurry. The Specimens were weighed before and after each test and the resulting weight loss was converted into a corrosion rate of microns per year ($\mu\text{m/y}$). The harsh nature of the experiment resulted in many equipment failures and unsuccessful test runs initially. In an effort to improve the frequency of successful runs the test duration was reduced from the initial periods of 48 to 24 hrs., and ultimately to 12 hrs. The attack experienced by the specimens was severe enough to produce easily measurable weight losses, even over this short duration.

4.5 THERMAL OXIDATION EXPERIMENTS

4.5.1 Experimental Apparatus

The experimental apparatus used in these tests consisted of:

- A Lindberg Hevi-Duty Tube Furnace, Type 54253-N
- A Thermocouple and Temperature Gauge

A schematic diagram of the test apparatus set-up is shown in Figure 15. The specimens were placed on a stainless steel (318) tray which in turn was placed in one end of the pre-heated furnace. The Specimens were exposed to Oxygen due to the natural convection flow of air through the furnace tube.

4.5.2 Experimental Procedure

The experiments were performed at temperatures of 700 °C and 900 °C for durations of 1 hr. as well as tests at 700 °C for 10 hrs.. The tests were repeated with the specimens in different positions as there existed slight variations in temperature and O₂ availability, depending on their position in the furnace.

Specimen preparation consisted of sandblasting the surface of the specimens, as discussed earlier.

Figure 15 Schematic diagram of thermal oxidation apparatus.

The specimen surface area said to be exposed in these tests does not include the bottom surface of the specimens which, being in contact with the tray, was observed to experience negligible oxidation.

4.6 SPECIMEN DIMENSIONS AND SURFACE PREPARATIONS

Table (3) lists the typical dimensions of the specimens used in each of the tests, height (H), width (W), and length (L), as well as the surface area exposed and the surface condition. In certain cases specimens were masked, reducing the surface area. The surface area quoted is as masked.

Table 3. Specimen Dimensions and Surface Conditions

Experiment Type	Typical Specimen Dimensions (cm)			Typ. Area Exposed (cm ²)	Surface Condition
	H	W	L		
Pot./Galv.	1.0	0.8d.	CYL	0.5	Polished (1 μ m)
Immersion	1.4	1.0	4.3	20.0	Sand blasted
Erosion	0.4	1.4	2.5	2.0	As sintered
Eros./Corr.	1.4	1.0	4.3	7.0	Sand blasted
Oxidation	0.4	1.4	2.5	7.0	Sand blasted

CHAPTER V

DATA ANALYSIS

5.1 POTENTIOSTAT / GALVANOSTAT EXPERIMENTS

5.1.1 Potentiodynamic Anodic Polarization Measurements

The data obtained in these experiments are analyzed primarily through use of computer methods. The Princeton Applied Research Model 332 SoftCorr (vers 2.1) corrosion software permits the user to run the experiments and both collect and analyze the data. Two programs are available for analysis of the data obtained from the potentiodynamic anodic polarization measurements, PARCalc and Polarization Resistance Analysis. The following description of these programs is based on the information detailed in the software operating manual⁽⁴⁶⁾.

PARCalc is a data-processing program used to calculate Tafel constants, corrosion current, and the corrosion rate from the data. It uses a chi-squared minimization technique to calculate the values of the Tafel constants, corrosion potential, and corrosion current representing the experimental data that best fit the equation for Stearn and Geary kinetics:

$$I(E) = I_{\text{corr}} * (10^{(E-E_{\text{corr}})/b_a} - 10^{-(E-E_{\text{corr}})/b_c}) \quad (5.1)$$

The chi-squared minimization technique may be represented by:

$$X^2 = (1/(N-4)) \sum_{j=1}^{j=N} [I_j - f(E_j, E(I=0), b_a, b_c, I_{corr})]^2 / S_j^2 \quad (5.2)$$

where: N = number of data points

I_j = the j-th current measurement, made at E_j

S_j = the estimated standard deviation of the j-th current measurement

b_a, b_c = the anodic and cathodic Tafel constants

I_{corr} = the corrosion current ($\mu A/cm^2$)

$E(I=0)$ = the potential at which the measured current is zero during the experiment

f = the function to fit (Eqn 5.1) evaluated at E_j

PARCalc makes initial estimates, for the desired values, based on current-potential data. From the initial estimates an iterative process continues until $X^2 < 0.1$, or the change in $X^2 < 5\%$ between iterations.

The Polarization Resistance Analysis (PRA) program selects those data points lying within $\pm 10mV$ of $E(I=0)$. The calculations performed on these selected data are:

1. Polarization Resistance (R_p)

$$R_p \text{ (k}\Omega\text{)} = E \text{ (mV)} / I \text{ (}\mu A\text{)} \quad (5.3)$$

= slope of the PRA plot of E vs. I

2. Corrosion Current (I_{corr})

$$I_{corr} (\mu A/cm^2) = (b_a * b_c) / (2.3(b_a + b_c) * A * R) \quad (5.4)$$

where: A = the specimen surface area in cm^2

3. Corrosion Rate (Corr Rate)

$$Corr Rate = (C * I_{corr} * E.W.) / D \quad (5.5)$$

where C is a constant and may be:

$$C = 33.0 * 10^{-3} \text{ for units of } \mu m/y \text{ (microns/year)}$$

$$C = 0.904 * 10^{-3} * D \text{ for units of mdd (mg/dm}^2\text{/day)}$$

where: $E.W.$ = the equivalent weight in grams

D = is the specimen density in g/cm^3

The test conditions for these experiments are tabulated in Appendix I, as are the results of the PARCalc and PRA analyses. The raw data are also appended in graphical form.

Figure 16(a-d) shows an example of the different plots that are produced by the analysis of a single test of this type. These examples (a-d) are respectively: a, the initial plot of E vs $\log(I)$; b, a secondary plot of the data showing both the active and passive regions of the scan; c, a plot of the active (or Tafel) region of the data used in the PARCalc analysis; d, a plot of E vs I of the data used in the Polarization Resistance Analysis. Only the plots of the type shown in Figure 16b are appended.

Figure 16 Typical plots resulting from a potentiodynamic anodic polarization measurement, a, initial plot; b, second plot showing active - passive behaviour; c, active region; d, polarization resistance plot.

5.1.2 Potentiostatic Measurements

The potentiostatic measurements of these alloys result in data which may be plotted in the form of plots of I ($\mu\text{A}/\text{cm}^2$) vs. Time (sec.) and reveal the decay in corrosion current density over time for tests where passivation is occurring. A plot of $\text{Log}(I)$ vs. $\text{Log}(\text{Time})$ reveals a straight line. From the slope of this line a measurement of how rapidly a specimen passivates may be made. Comparing the rate of passivation for the various alloys indicates which grades have a stronger tendency to passivate.

The data obtained from these tests have been plotted in this way and a simple curve fitting routine was employed to determine the intercept and slope of these plots. These simple curve fits having the form of:

$$y = b - (m * x)$$

where b is the intercept, or the initial value of $\text{Log } I$, and m is the slope, or the rate of decay in the current density values.

The test conditions for the potentiostatic tests are tabulated in Appendix I. The raw data are also appended in graphical form.

5.2 IMMERSION CORROSION EXPERIMENTS

The experimental data obtained from these tests are tabulated in Appendix II. The data for one test consists of: test duration (T), surface area (A), initial weight, final weight, weight loss (dW), and the corrosion rate in units of $\mu\text{m/y}$ and mdd.

The corrosion rate is calculated as follows⁽⁴⁾:

$$\text{Corr. Rate} = (C * dW)/(D * A * T) \quad (5.6)$$

where C is a constant and may be:

$$C = 8.76 * 10^7 \text{ for units of } \mu\text{m/y}$$

$$C = 2.40 * 10^4 * D \text{ for units of mdd (mg/dm}^2\text{/day)}$$

where: D = the specimen density in g/cm^3 ,

dW = weight loss in g,

A = exposed surface area in cm^2 ,

T = duration of exposure in hours.

5.3 EROSION EXPERIMENTS

The experimental data for these tests are tabulated in Appendix III. The data for one test consists of: test angle, duration (T), erodent flow rate (R_e), total weight of erodent used (W_e), initial weight of the specimen (W_i), final weight

of the specimen (W_0), weight loss (dW), and the calculated erosion rates in both weight loss ($g/g * 10^{-4}$) and volume loss ($cm^3/g * 10^{-4}$).

The erosion rate is calculated as follows, first the total erodent weight used is calculated:

$$W_0 (g) = R_0 (g/min) * T (min) \quad (5.7)$$

$$\text{Weight loss, } dW (g) = W_0 (g) - W_1 (g) \quad (5.8)$$

The erosion rate is given by:

$$\text{Eros. Rate} = dW / W_0 \quad (\text{in units of } g/g) \quad (5.9)$$

Dividing by the specimen density yields an erosion rate in units of cm^3/g .

The 90° tests yield results that are accurate enough to permit a comparison between the 90° results for different grades. The 30° test results are not as accurate due to the small size of the specimens tested. In this position the target area of the erodent would occasionally not correspond fully with the specimen face.

5.4 EROSION CORROSION EXPERIMENTS

The experimental data from these tests are tabulated in Appendix IV. These data tables are in the same format as those discussed earlier in Section 5.2. The corrosion rate is calculated as shown in Equation (5.6).

5.5 THERMAL OXIDATION EXPERIMENTS

The experimental data obtained from these tests are tabulated in Appendix V. The data for one test consists of: test temperature, test duration, initial surface area, initial weight, final weight, weight gain, and the oxidation rate. The oxidation rate is calculated from the weight gain per surface area and is expressed in units of mg/cm^2 .

The temperature dependance of oxidation rate constants for the thermal oxidation mechanism obeys the Arrhenius-type equation⁽²⁶⁾:

$$k = k_0 \exp(-Q/RT) \quad (5.10)$$

where: Q = activation energy in cal/mole

R = gas constant (1.986 cal/K/mole)

T = absolute Temperature (K)

k_0 = pre-exponential factor, independent of temp

k = oxidation weight gain in mg/cm^2

This behavior permits the calculation of the activation energy values for thermal oxidation of the various alloys tested at 700 and 900 °C, letting $k_0 = 1$ for the purpose of comparison:

$$Q = ((\text{Log}_{10}(k_2) - \text{Log}_{10}(k_1)) / (1/T_2 - 1/T_1)) * 2.303 * R \quad (5.11)$$

where: k_1 = the oxidation rate at temperature T_1 .

k_2 = the oxidation rate at temperature T_2 .

T_1 = 973 K (700 °C)

T_2 = 1173 K (900 °C)

5.6 POST EXPERIMENTAL ANALYTICAL INVESTIGATIONS

5.6.1 Chemical Analysis

Specimens of the solutions used in the immersion corrosion tests were submitted for chemical analysis. This analysis identifies the elements which were involved in the corrosion reaction and remain in solution. The Atomic Adsorption Analysis (AAA) technique was used to determine the quantity of Co, Ni, Cr, and Al which passed into solution from the specimens. The results are reported as weight per unit volume of solution [g/l]. The determination of Tungsten (W)

content was performed by the Inductively Coupled Plasma (ICP) technique. The results of this analysis are reported in parts per million [ppm], which may also be expressed in units of mg/l.

The results of these analyses are tabulated in Appendix VI. Included in the tables are the original weight loss values experienced in the corresponding immersion corrosion tests.

5.6.2 Electron Micro Probe Analysis (EPMA)

EPMA was used to analyze the concentrations of elements, through cross sections, in the oxide layers of the thermally oxidized specimens. The diffusion of elements, combined with oxygen, away from the metal substrate and through the oxide layer reveals the role each element plays in the mechanism of the thermal oxidation of these alloys. Cross sections of the specimens to be analyzed were prepared, an example is shown in Plate 3. The results of these analyses are included in Appendix VII.

Visual observations were made of those specimens used in the potentiostat / galvanostat experiments. An attempt at EPMA of the corroded surfaces provided very little information. The preferential attack of the binder, which occurs, resulted in a surface that was too uneven to be accurately analyzed by EPMA.

CHAPTER VI

RESULTS AND DISCUSSION

6.1 POTENTIOSTAT / GALVANOSTAT EXPERIMENTS

6.1.1 Experiments Performed in 2N H₂SO₄

6.1.1.1 Potentiodynamic Anodic Polarization Measurements

The results of testing in 2N H₂SO₄ revealed that all of the new grades, except for 50Cr, perform better than the standard cobalt grade G10. The Co bearing alloy tests resulted in a corrosion rate one to two orders of magnitude greater than the new alloys, except for those with high levels of porosity. The Co grade exhibited negligible tendency to passivate.

The corrosion rates obtained by PARCalc analysis for high-temperature sintered specimens are plotted in Figure 17, for both G.T., N.G.T., and hipped specimens. Examination of the results for the new grades shows that the undercarburized Ni and Ni-Cr specimens are the most resistant to corrosion. The Ni-Al alloys were less resistant to the H₂SO₄ medium. The Ni-Cr-Al grades also performed quite well, particularly the grade with small additions of Al to the binder. The largest improvement in the new alloys occurs by substituting Ni for Co.

2

OF/DE

2

MICRO

Figure 17 Results of potentiodynamic anodic polarization scans conducted in 2N H_2SO_4 , Log corrosion rate ($\mu\text{m}/\text{y}$) for various grades tested, G.T., N.G.T., and hipped specimens.

The porosity level of these alloys (listed in Table 2) has a great effect on their performance in corrosive media in a test such as this. The corrosion current produced is dependent on the surface area exposed to the solution. A higher surface area produces a higher current resulting in an increased corrosion rate. An extremely porous alloy such as 50Cr, with its sponge-like structure, does in fact soak up the media and presents to the media a surface area many times greater than assumed. The resulting high corrosion rates are then predominantly attributable to this phenomenon.

Polarization effects may also be another contributing factor to the high corrosion rates experienced by porous specimens. As the aqueous medium penetrates, through the porous structure below the surface, there will exist slight variations in the concentration of H^+ in contact with the specimen. As this species is reduced in the cathodic processes of corrosion there will be a drop in the availability of H^+ below the surface. This would lead to some degree of unfavourable concentration polarization whereby the surface becomes more cathodic with respect to the underlying structure, thus increasing the corrosive attack.

The alloys subject to this occurrence are those with high levels of Cr or Al additions such as 20Cr, 50Cr, and 16Al. Specimens of these grades that had been further processed by Hot Isostatic Pressing (HIP) were subjected to testing. These hipped specimens, with reduced porosity, showed a significant

improvement in corrosion rates compared with their as sintered counterparts. The hiped 50Cr grade remained extremely porous and had correspondingly poor corrosion resistance.

Upon examination of the full results of these tests, tabulated in Appendix I, several trends are evident. The first is that the corrosion potential (E_{corr}), of the various grades examined, closely matches the electrode potential (E_{init}) measured prior to commencement of the tests. This indicates that the specimens had reached a steady state prior to testing and that the initial cathodic current experienced by the specimens did not affect their surface composition or polarize the specimens. The values of E_{corr} for the various grades vary slightly, the most noble being the straight Ni bonded alloy.

Another trend may be seen in the values of the Tafel slopes for the various grades. Both the cathodic and anodic slopes are fairly consistent amongst the alloys and range around the value of 100 mV per decade of current density rise. The exception to this being the porous high Cr grades. The peak passive potential values (E_{pp}) and the passive potential values (E_p), measured at the lowest current density values in the passive region, are all fairly uniform amongst the various grades. The values for the tested grades range around 0 mV and 400 mV vs SCE, respectively. The current density values at these potentials are known as the critical current density (i_{cc}) and the passive current density (i_p). A comparison of

the drop that occurs in these values for each grade offers a qualitative indication of the extent to which each grade develops a passive film.

The reference Co grade exhibits negligible passivation. The G.T. Ni and Ni-Cr grades exhibited the largest drop in current density values, in the order of two magnitudes, indicating the development of a passive film. The active to passive transition of the N.G.T. grades revealed a slightly smaller reduction, between one and two orders of magnitude, in current density. The Ni-Al grades possessed similar behaviour between the G.T. and N.G.T. specimens, and revealed a drop of between one and two orders of magnitude. The Ni-Cr-Al grades revealed a good tendency to passivate, particularly the 10Cr2Al grade which showed a reduction between i_{∞} and i_p of two orders of magnitude.

The beneficial results of replacing the Co as the binder material are clearly indicated by these experiments. The lower corrosion rates and the ease of passivation that these new grades are imbued with are due largely to the properties of their respective binders. There is however a galvanic aspect to the corrosion of these materials that may be responsible for some of the improvement in corrosion resistance.

As was mentioned earlier the effect of galvanic coupling between two materials will lead to accelerated attack of the more active (or anodic) metal. Unfortunately in the case of

cemented carbides the binder phase assumes the role of the anode while the more noble WC phase acts as the cathode. This leads to the occurrence of localized galvanic cells at the exposed interfaces between the WC and binder phases. The disadvantage in this coupling is increased due to the disparity in the cathodic and anodic surface areas in contact with the solution. The surface of one of these grades has a ratio of cathodic to anodic surface area (A_{WC}/A_{binder}) of roughly 4 to 1. As the corrosion process proceeds the anodic fraction (the binder) is attacked, leaving the WC unattacked. This selective removal of the exposed binder results in a gradually increasing ratio of area.

The effect that an increasing ratio has is shown in Figure 18. As the ratio A_{WC}/A_{binder} increases, the intersection of the reduction of WC and the oxidation of the binder occurs at higher potential and current density values. This results in a higher electrode potential (E_{corr}) and a higher value of corrosion current density (I_{corr}), and therefore increasing corrosion rates as the corrosion process proceeds. The result of this is that the corrosion of the binder in cemented carbides accelerates with time unless an oxide film develops that will impede further corrosion.

E_{corr} values may be monitored over time accurately and the results of such testing indicated an initial period of rapid decrease while the corrosion process stabilizes. The values

Figure 18 Theoretical effect of varying cathode to anode area ratio (A_{WC}/A_{Bin}) on corrosion behaviour of WC alloys.

Figure 19 E_{corr} vs Time test results for G.T. 10Ni conducted in 2N H_2SO_4 .

of E_{corr} then gradually increased with time. An example of this behaviour is shown in Figure 19.

The corrosion rates calculated in these experiments are based solely on an analysis of the data from the active region of the potentiodynamic scans. Within this range of electrode potentials, approximately 250 mV below and above E_{corr} , the current density values or the degree of attack is not too high. The ratio $A_{\text{WC}}/A_{\text{binder}}$ remains fairly constant in this region. This mild degree of attack allows for examination of the effect of varying two of the microstructural parameters of these cemented carbides, that is the WC grain size and the binder content. Obviously such a comparison can only be performed on grades which share the same basic composition, such as WC-Co grades.

Changing these parameters influences the ratio $A_{\text{WC}}/A_{\text{binder}}$ and results in varying degrees of galvanic corrosion. This ratio decreases as the binder content is increased leading to lower corrosion rates. This ratio is also decreased with decreasing WC grain size. The results of a study by Scheers⁽²⁰⁾, mentioned previously in Chapter III, on WC-Co grades reflect this phenomenon for testing in both 2N H₂SO₄ and 6N HCl at room temperature and at 80 °C.

While the binder content does not vary significantly between the various grades tested, the WC grain size is known to decrease as the Cr additions are increased. From the previous discussion it is clear that, aside from the

resistance of the binder itself, one would expect an improvement in corrosion rates as the C⁻ content is increased. This improvement has not occurred however. The reasons for this are the increasing levels of porosity, and the corrosion resistance of the binder material in each alloy itself. The possibility of another galvanic reaction within the binder itself would explain the observed trends.

The binder phase of the Ni-Cr grades is meant optimally to be a homogeneous alloy of the constituent elements. The Cr is added to these grades in the form of Cr₃C₂. The resulting microstructure does unfortunately contain a certain degree of non-uniformity in the amalgamation of Cr with the binder. Chromium rich regions are present, as are separate uncombined carbides of chromium. This separate carbide phase is in the form of very fine particles dispersed throughout the binder. The presence of this carbide is increased with increasing Cr content and with increasing carbon content. It then follows that the quantity of carbide present would be reduced in the N.G.T. specimens of a particular grade, as compared to the G.T. specimens which have a higher carbon content.

This separate carbide phase, being more noble than the surrounding binder, would act as a cathode and result in a separate galvanic reaction with the surrounding binder. This would result in increased corrosion of the binder in these grades. This does in fact occur as shown by the results of

these tests. The corrosion rates experienced by the Ni-Cr grades did increase as the Cr content was increased. The low Cr grades also performed better with lower contents of carbon, that is the N.G.T. grades were superior to the G.T. grades.

It is difficult to quantitatively measure the behaviour of the separate phases that make up these materials. The exact composition of the binder is not known due to the dissolution of WC into it that occurs during sintering, and no easy means exists of reproducing it without the WC. The powdered WC is equally difficult to accurately test as the surface area of contact that exists between a specimen and an aqueous medium is difficult to ascertain. Testing of WC specimens was attempted using dry pressed, sintered WC compacts. These specimens are designated as WCD in the appendix. The high porosity levels resulted in very high values of recorded current density and the computed corrosion rate. The electrode potential (E_{corr}) was determined to be -294 mV vs. SCE. This falls within the range of values measured for the various alloys. The accuracy of this result is questionable however.

6.1.1.2 Potentiostatic Measurements

Potentiostatic measurements were performed in 2N H_2SO_4 at three regions of the potentiodynamic polarization behaviour observed for these alloys. The potentials chosen were E_{cath} ,

E_p , and E_s , corresponding respectively to points midway along the cathodic Tafel slope, the primary passive potential at which the current density reaches a critical value (i_{cs}) before passivation occurs, and the potential value in the middle of the passive region where the current density value (i_p) reaches a minimum.

The logarithmic plots of the decay in measured current density over time, $\log(I)$ vs $\log(T)$, for these tests reveal a straight line. From these plots the initial current density value, the intercept (b), and the rate of decay, the slope (m), have been measured. The results of the testing performed at cathodic potentials proved to be inconclusive as there was a tremendous amount of scatter in the measured data and for the most part there was no evident change in the recorded current density values over time.

The results of testing at E_{pp} clearly reveal the decay in current density and the plotted data fit a straight line quite accurately. The results of these tests are presented in Figure 20. G10 has the highest initial current density value and the lowest rate of decay. This result indicates the severity of attack experienced by the Co grade and reveals that the oxide film that develops does so slowly. The trends apparent amongst the new alloys are that the straight Ni grade has a faster rate of decay and that as Cr is added the current density values and the rate of decay decrease, particularly for the N.G.T. specimens. The Ni-Al grades all perform

Figure 20 Results of potentiostatic tests conducted in 2N H_2SO_4 at the peak passive potential (E_p) for various alloys.

Figure 21 Results of potentiostatic tests conducted in 2N H_2SO_4 at the passive potential (E_p) for various alloys.

similarly with fairly high initial current density values and moderately high rates of decay, both of which increase slightly as the Al content increases. The Ni-Cr-Al grades both perform quite well again with moderate initial current density values and rates of decay that both increase as the Al content is increased.

The results of testing at potentials in the passive region of each alloys behaviour are plotted in Figure 21. The reference Co grade (G10) exhibited current density values two to three orders of magnitude larger than the new grades. The 10Ni specimens once again showed the highest rate of oxide film formation. Additions of Cr resulted in lower current density but poorer rates of decay, with the exception of the G.T. 10Cr grade which had a high initial value but decayed rapidly. The Ni-Al grades showed increasing current density values and rates of decay as the content of Al was increased. The Ni-Cr-Al grades had very low current density values and rates of decay which also increased as the Al content increased.

These potentiostatic tests have indicated that the substitution of Co with Ni as the binder material greatly reduces the severity of attack by 2N H_2SO_4 . The current density values produced by the corrosion reaction are lower and they decay with time more rapidly, as the oxide film develops.

6.1.2 Experiments performed in 0.5N NaCl

The results of potentiodynamic anodic polarization testing of the alloys performed in the 0.5N NaCl medium are plotted in Figure 22. These tests resulted in very low corrosion rates for all of the alloys. All of the values are of the same order of magnitude, except the 50Cr and 10Al grades. The most corrosion resistant alloy system is the Ni-Cr system, except for the very porous 50Cr grade. The addition of Cr to the binder results in lower corrosion rates. The carbon level of these grades has the opposite effect on their resistance in this medium, compared to the tests in acid. The G.T. specimens with their higher carbon content prove to be more resistant. The 10Cr2Al grade once again had the best resistance. The Ni-Al grades did not perform well, having corrosion rates higher than that for the reference Co alloy, G10. The poor performance of those alloys with high porosity levels is evident. The reasons for this are as discussed for the tests conducted in 2N H₂SO₄. As with previous tests hiping improved the resistance of those alloys with high levels of porosity. No significant tendency to passivate was observed in any of the grades tested.

Examination of the complete data tabulated in Appendix I reveals several differences in the behaviour of these grades as opposed to their behaviour in the acidic medium. The first difference is the disparity between E_{init} and E_{corr} values. The

Alloy

Figure 22 Results of potentiodynamic anodic polarization scans conducted in 0.5N NaCl, Log corrosion rate ($\mu\text{m}/\text{y}$) for various grades tested, G.T., N.G.T., and hipped specimens.

new grades all have much lower E_{corr} values than the initial corrosion potential prior to testing. The values of E_{corr} are also much lower than those for the acidic medium. The Tafel slopes also reveal significant fluctuations, and disparities between the cathodic and anodic values. The Ni-Cr grades have similarly high values except for the 50Cr grade. The Ni-Al grades all revealed anodic Tafel slopes larger than their respective cathodic slopes.

The disparity in electrode potential values is certainly a contributing factor to the non-uniformity in the Tafel slopes, for each grade taken separately. The reason for this behaviour lies in the effect of the galvanic coupling, as described earlier. This effect is more apparent in 0.5N NaCl due to the higher disparity between the corrosion potentials of the separate phases. Testing a sintered WC compact revealed an electrode corrosion potential (E_{corr}) substantially higher, at -86 mV vs SCE, than the values for the composite specimens. As with the comparable test described for the acidic medium, the accuracy of this value is questionable due to the extremely high porosity level of these WCD compacts.

The underlying cause for the anomalous behaviour of these grades in the cathodic region of their scans is due to polarization of the specimen surface that occurs, decreasing the electrode potential values. This behaviour may be explained by considering the effects of coupling in the active region as shown in Figure 23. This plot of E vs $\text{Log}(I)$ shows

Figure 23 Active behaviour of WC composites as observed by potentiodynamic scans in 0.5N NaCl.

the galvanic coupling of the WC phase, from point (1), and the binder phase, point (2). The redox coupling would hypothetically occur at the intersection point (3). This condition exists initially and the value E_{init} , measured before commencement of the test, corresponds with this point.

The potentiodynamic scan proceeds by passing the appropriate cathodic current through the specimen to bring it to a potential of 250 mV below the value measured initially (E_{init}) and proceeds to scan in the noble direction. Once the potential surpasses the value of E_{bin} the binder phase itself oxidizes and the measured current density passes from a cathodic current to an anodic one, at point (4). The resulting interpolation of the measured behaviour yields point (5) and the corresponding values of E_{corr} and I_{corr} are obtained. The decrease in electrode potential and increase in the corrosion current density are due to this behaviour, as are the increase in the anodic Tafel slopes and the decrease in the cathodic Tafel slopes.

The involvement of the Cl^- ion in this process is associated with the oxidation of the binder in this active region and throughout the scan. The attack of the binders in the various alloys by this ion is detrimental as it causes the anodic polarization which results in the previously discussed anomalous behaviour. Uhlig and Revie⁽¹⁴⁾ state that the Cl^- ion breaks down passivity or prevents its formation in Cr, Ni, and Co alloys and that a normally passive metal will instead

continue to dissolve at high rates both in the active and passive potential ranges. This is consistent with the observed behaviour of these alloys.

Potentiostatic measurements were attempted on a couple of grades that revealed some apparent transition from an active to a passive state, such as the straight Ni grade. These measurements were inconclusive as the current density values did not alter significantly with time and revealed a high degree of scatter amongst the recorded data.

6.2 IMMERSION CORROSION EXPERIMENTS

6.2.1 Room Temperature Tests in 2N H₂SO₄

Room temperature immersion weight loss tests were conducted in two media, 2N H₂SO₄ and 0.5N NaCl. The results of testing in the acid media will be discussed first. The results of these tests are plotted in Figure 24, being averages of results from test series: 2, 4, and 6a.

The results reveal that the new grades are more resistant to corrosive attack by the 2N H₂SO₄ than the traditional Co grade. The resistance of the Ni bonded grade is improved with additions of Cr, a result found in similar tests performed by other authors^[32,33]. In particular the under carburized (N.G.T.) specimens perform very well. This is in agreement

Figure 24 Results of weight loss immersion corrosion testing conducted in stagnant 2N H_2SO_4 at room temperature for 250 hours.

with the results of the potentiodynamic testing, as discussed earlier. Increasing Cr content improves the corrosion resistance up to 20% Cr, the 50Cr grade, once again, is less resistant due to its high level of porosity.

The sixth series of tests in which the specimens, after being immersed for a period of 250 hrs., were re-immersed in the same solution for an additional duration of 250 hrs. experienced reduced rates of attack in the second immersion. The results for this test are plotted in Figure 25. This behaviour is consistent with the process of passivation which occurs continuously over time. The only exceptions to this trend are the grades with high porosity levels (20Cr, 50Cr, and 16Al), in which the longer duration permits the acidic media to further penetrate the porous structure of the specimens.

A calculation of the percent reduction in corrosion rates of the second immersion compared to the initial immersion reveals the ability of the alloys to passivate. The results of this analysis are shown in Figure 26. The Co grade shows the lowest decrease in weight loss while the under carburized Cr bearing grades have the highest reduction in rate of attack. This result coupled with their low corrosion rates gives the Ni-Cr alloys the best performance among the grades tested.

There are several differences between the results obtained by this method of testing compared to those obtained

Figure 25 Results of sequential weight loss immersion corrosion testing conducted in stagnant 2N H_2SO_4 at room temperature for periods of 250 hours.

Figure 26 Percent reduction in corrosion rates between first and second sequential immersions, conducted in stagnant 2N H_2SO_4 at room temperature.

by the potentiodynamic polarization scans. These differences are due primarily to the fact that each method of testing is quite different. The weight loss immersion corrosion tests reveal the weight loss over a long duration and the degree of attack that occurs is much greater.

The environment is different between the two test methods. The test solution for these experiments, not being de-aerated, has a higher concentration of O_2 , which will increase the anodic corrosion processes resulting in further oxidation of the binder. The solution is also stagnant and has insignificant agitation compared to the conditions used in the polarization scans. This reduction in solution velocity leads to a reduction in the cathodic processes. Less reduction of the WC phase results in a lower corrosion rate experienced by the binder.

The primary differences observed in the results of these tests are that the corrosion rates are more uniform amongst the new grades and that increasing the additions of Cr to the binder result in decreasing weight losses.

With time, those grades that show a tendency to passivate will do so and experience gradually decreasing weight losses. This process occurs over time as the attack of the binder proceeds. This penetration of the binder will proceed to a certain depth, gradually reducing as an oxide film develops. The attack of the binder phase in these alloys is more clearly

illustrated if we again consider the behaviour of one class of these grades, namely the WC-Co alloys.

The galvanic effect discussed earlier, based on the examination of commercially available WC-Co grades by other authors, revealed the influence of varying the ratio A_{WC}/A_{binder} on the corrosion rates. The result of testing by polarization scans⁽²⁸⁾ revealed that a decreasing ratio was beneficial, as discussed earlier. The results of another study⁽³¹⁾ in which these same WC-Co grades were tested by weight loss immersion methods indicated that varying this ratio had the opposite effect. As the binder content was increased the weight loss, or corrosion rate, increased.

The explanation for this behaviour is simply that the degree of penetration of the binder that occurs over long duration is influenced by the geometry of the microstructure. The penetration rate may be lower initially for a particular grade but will proceed to a greater depth for grades with more widely spaced WC grains, as found in higher binder content grades. Among WC-Co grades, with varying binder content and WC grain size, the actual depth of penetration might not vary too greatly but the volume of binder lost will increase as the binder content is increased. It is the volume lost to corrosion that increases with a decreasing ratio of A_{WC}/A_{binder} .

The grades tested in this study only have a slightly varying ratio of A_{WC}/A_{binder} as the WC grain size varies, as discussed previously. The fact that their resistance improves

as this ratio decreases, for increasing Cr content, reveals the beneficial improvement that Cr additions have on the resistance of the binder itself to attack by this environment over long durations.

The results of chemical analysis performed on solution samples after testing are tabulated in Appendix VI. There is good agreement between the measured weight loss experienced by the specimens and the summation of the determined concentration of the various elements. In each case the fraction of W (F_w) was determined to be very low. The presence of this W in solution is due to the fact that the binder comprises a certain fraction of W. The percent fractions of W, Cr, and Al, out of the summation of binder elements have been calculated and are also tabulated.

The percent fraction of W varies depending on how much dissolution of it into the binder occurs during sintering, and how much comes away during corrosion. The percent fraction of Al that is reported in this manner matches very closely the overall composition fractions. The results for Cr do not compare as closely to the original composition fractions. As the Cr additions were increased the fraction reported by chemical analysis does not increase proportionally. This indicates that not all of the Cr is being attacked in the high Cr grades. This finding lends further support to the theory of a galvanic reaction between a finely dispersed chromium carbide phase, within the binder phase, and the surrounding

binder. The fraction of Cr that forms a carbide would not be expected to go into solution.

6.2.2 Room Temperature Tests in 0.5N NaCl

The results of room temperature immersion testing in 0.5N NaCl are plotted in Figure 27. These results are averages from test series 3 and 7a. The weight losses in all tests were very low in value. The new alloys show a significant improvement in resistance to the NaCl media compared to the standard Co grade. The gas treated Ni and Ni-Cr grades perform better than their N.G.T. counterparts in this media, unlike the tests in the acidic media. This was also observed in the results of potentiodynamic testing, as discussed previously. There is no significant difference between the corrosion rates of the new grades other than the low Cr content G.T. specimens which show the best performance.

The highly porous grades, such as 50Cr, occasionally recorded a weight gain in these tests. This was due to the very low weight losses being overshadowed by residue from the solution which could not be completely removed from the specimens. A sequential test series was also performed in this media. The corrosion rates, which are appended, were again seen to reduce between the first and second immersions.

The results from this method of testing were again seen to vary from those determined by polarization scans. The

Figure 27 Results of weight loss immersion corrosion testing conducted in stagnant 0.5N NaCl at room temperature for 500 hours.

reasons for these variations are the same as discussed for this type of testing performed in the acidic media. The weight losses experienced, over a long duration, by the new grades are more uniform and are all less than that of the reference grade G10.

The chemical analysis of solution samples resulted in very low concentrations of the elements. The concentrations of Cr and Al were often too low to be measured. There was often a significant degree of disparity between the experimentally recorded weight losses and the combined reportings of chemical analysis, the latter being the lesser of the two. This is due in part to the experimental inaccuracies inherent in the measurement of such low weight losses and concentrations. The visual observations made of the specimens and test solutions, that are appended, suggest another explanation for this disparity. One observed phenomenon was the formation of a precipitate (ppt.) in the test solutions for certain grades. The chemical analysis will not have detected the elements that have combined in this way, and dropped out of solution. Localized corrosion was also observed in the case of certain grades, which if severe enough could theoretically result in the loss of WC grains from the surface. These inert grains would not be detected by chemical analysis either.

6.2.3 High Temperature Tests

The results of the weight loss immersion tests performed in boiling 2N H₂SO₄ are plotted in Figure 28. The results clearly illustrate the deleterious effect of porosity, as seen in the high corrosion rates obtained for the high Cr and high Al content grades. Excluding the results of the 50Cr and 16Al grades, the increased resistance of the new alloys compared to the Co alloy (G10) is significant. The N.G.T. specimens are superior to the G.T. specimens tested. This was also the case in room temperature testing in this media, both by weight loss and potentiodynamic measurements, as discussed earlier. The 10Ni and 1Cr grades are the most resistant to attack by the hot acid, particularly the under-carburized specimens of these alloys.

The increased temperature of this test had a tremendous effect on the severity of attack of these grades. The corrosion rates for these grades have increased at least two orders of magnitude compared to the values obtained in the room temperature weight loss tests. This increase is primarily due to the high degree of activation polarization that occurs. The increased supply of ambient energy eases the reduction of the cation H⁺ thus accelerating the cathodic processes and increasing the electrode potential. The anodic processes, the oxidation of the binder, occurs at the

Figure 28 Results of weight loss immersion corrosion testing conducted in boiling 2N H₂SO₄ for 48 hours.

corresponding higher potential and corrosion current values, leading to the observed increase in corrosion rates.

During the 48 hr. duration tests the specimens of the G10, and high Al content grades repeatedly failed. The observed mode of failure was that the corners and edges of the specimens fractured off in successive layers. Kny and Schmid⁽³²⁾, in similar tests, also report the occasional breakage of their specimens. It is known that internal tensile stresses are created in the binder upon cooling from the sintering temperature due to the disparity between coefficients of thermal expansion of the two phases, the binder having a higher coefficient than the WC phase. It is probable that the severe corrosion of these susceptible grades leads to enough removal of the binder material so as to cause the fracture across the edges (at 45 degrees). This behaviour alone, besides the high corrosion rate, is enough to make the Co grade very unsuitable for use in this environment.

6.3 EROSION EXPERIMENTS

The results of the erosion testing are plotted in Figure 29. The results of this testing reveal that the erosion resistance of the gas treated (G.T.) specimens of the new alloys is slightly superior to the standard Co grade. The resistance increases with greater amounts of Cr and Al

Figure 29 Results of erosion of G.T. specimens by 180 μ m SiC at 30 m/s, for 90° and 30° angles of impingement.

Figure 30 A comparison of erosion rates with vickers hardness values for G.T. specimens.

additions to the Ni binder, except in the case of the G.T. 10Cr grade which does not follow the observed trends.

The erosion resistance of the new alloys would appear to vary somewhat with their hardness, a phenomenon also reported in studies of WC-Co grades by others^(25,28,27). The hardness increases with increasing additions of Cr and Al and the erosion resistance increases likewise, as shown in Figure 30. The high porosity of the 50Cr grade results in poorer resistance than would be expected, of this the hardest of the alloys. In this case, what occurs most likely is that, the sponge like structure leads to a crumbling of the poorly supported surface of the specimens.

The erosion rates in all cases were lower for the 30° attack angle than for the 90° tests. This signifies that the erosion process is occurring in a brittle manner. Studies by Ball and Patterson⁽³⁶⁾ and by Pennefather⁽³⁵⁾ on WC-Co hardmetals both show that the erosion mechanism that occurs is dependant on binder content. Those grades with low binder content (less than 10% by weight) erode by a mechanism controlled by the brittle WC phase. At higher binder contents the mechanism of erosion is controlled by features of the binder phase, namely in a more ductile manner.

The alloys tested in this study, all having a binder content of 10% by weight, may not have a sufficient binder content to fully examine the benefits of the varying binder compositions. The Ni-Al grades show the best resistance to

erosion in this study while not being the hardest of the alloys tested. The 30° angle of attack results are close to those of the 90° tests suggesting that a more ductile mechanism of erosion is occurring. The respective merits of these binder materials might have been more pronounced in grades with higher binder contents.

6.4 EROSION CORROSION EXPERIMENTS

The results of the erosion corrosion testing are plotted in Figure 31. The standard Co grade performs very poorly in this experiment. There is a very large improvement with the substitution of Ni for Co in the binder. Incremental improvements occur as Cr is added to the binder to the limit of 20%, i.e. 20Cr. The under carburized grades are less resistant than their gas treated counterparts despite their superior performance in corrosion tests. The resistance of the 50Cr grade is hindered by its high level of porosity. The Ni-Al grades are fairly resistant except at high levels of Al addition where again the high porosity interferes.

The Co and high Al grade specimens consistently failed in tests of long duration (48 hrs.) but measurements were obtainable for shorter tests (24 and 12 hrs.). The mode of failure in these cases was a fracture across the edges due to the considerable corrosive attack which took place. This

Figure 31 Results of erosion corrosion testing in a slurry of 2N H₂SO₄ and 60 um SiC, velocity = 5 m/s, duration = 12 hours.

phenomenon was also observed in the high temperature immersion corrosion testing of these grades. This failure did not occur in room temperature immersion testing in the acidic media but occurs in this case due, most likely, to the raised temperature of the slurry ($30 \pm 5^\circ\text{C}$) and the added aggressiveness of the turbulent environment.

There was a great deal of variation in the results from test to test in these experiments for the new grades. The most likely explanation for this variation is that the specimens were losing very small amounts of material from their edges, as described previously. The failures in these cases were not easily observed. The one exception to these variations was seen in the G10 grade for which the 12 hour tests resulted in very consistent rates of attack.

The nature of this test may be said to be a combination of the processes which occur separately in the dry erosion and in the immersion corrosion experiments. The large improvement of the new alloys over the standard Co grade is largely due to their superior resistance to corrosive media, as revealed in the corrosion experiments.

The dry erosion results do not show such a significant improvement in the new grades; however, the erosive action of the slurry in the erosion corrosion tests does play a significant role. Its interaction with the corrosion process may best be illustrated in considering the passive films which develop on the surface of specimens and resist further

corrosive attack. The films produced on the surface of some grades will be less tenacious, and more easily removed by the eroding particles, than those developed on the surface of other grades. This phenomenon was most observable in the case of the conventional WC-Co hardmetal which exhibited negligible tendency to passivate. The erosive action taking place is continually removing the corrosion products from the specimen surface and revealing fresh material to be attacked anew by the corrosive media. This action leads to the resulting high weight losses experienced by the Co grade in this experiment.

Another example of this action occurring is in the case of the under carburized specimens of the 10Ni, 1Cr, and 10Cr grades. They are less resistant than their gas treated counterparts despite having lower corrosion rates in the corrosion tests. The potentiodynamic polarization scans of these grades revealed that the drop in corrosion current from peak to passive values is one order of magnitude less for the undercarburized specimens than for those with a stoichiometric carbon balance, as discussed previously. This decreased tendency to passivate resulted in increased attack in the erosion corrosion tests. The G.T. specimens which passivated more readily proved to be more resistant to this harsh environment.

6.5 THERMAL OXIDATION EXPERIMENTS

The results of the thermal oxidation tests for G.T. grades are plotted in Figure 32. The effect of an increase in temperature on the oxidation rates of the alloys is pronounced. There was no measurable weight gain in tests conducted at 500 °C for 2 hrs. The tests conducted at 700 °C show that all of the new grades are slightly superior to the standard Co grade. Increasing the Cr content of the binder is beneficial, as shown by the low oxidation rate of the 50Cr grade. Increasing the Al content also proved to be beneficial. There was no discernable trend distinguishing the performance of G.T. versus N.G.T. specimens.

The activation energies for thermal oxidation for G.T. specimens of each alloy, calculated from the 700 °C and 900 °C results, are plotted in Figure 33. The resultant activation energies are very dependent on the performance at 700 °C and reflect the trends seen in the results of the 700 °C tests, as discussed earlier.

Examples of typical oxidation specimens are shown in Plate 3. The specimens shown are G.T. grades from tests conducted at 700 °C for a duration of 10 hours. The sequence of specimens shown entails the as-sintered state, an oxidized specimen, another showing the cross section through the specimen, and finally a specimen that has been prepared for

Figure 32 Results of thermal oxidation of G.T. specimens, conducted at 700 °C and 900 °C.

Figure 33 Activation energies for thermal oxidation of G.T. specimens.

Plate 3 Typical thermal oxidation specimens (2 X), clockwise from top right: 10Cr, as sintered; 10Cr, oxidized; 10Ni, cross section; 20Cr, mounted and polished for EPMA.

EPMA. The growth of oxide film on these specimens was very regular, as may be seen in these examples.

In the case of each grade, the long duration tests (10 hrs.) at 700 °C result in the same oxidation rates as the 1 hour tests. The implication that there is no reduction in oxidation over a period of time may be better understood by considering the nature of the reactions occurring. Unlike the corrosion processes examined earlier where the binder is the subject of attack and the WC phase is largely inert, the opposite occurs in the case of thermal oxidation. It is the WC phase that is very reactive in the presence of O₂ at high temperature. The tungsten carbide breaks down and the tungsten is oxidized as shown by the reaction below:

The elements of the binder are also oxidized but not as readily as the tungsten. When the binder content of the alloy is sufficient it may restrain the oxidation of the WC by the production of oxides of the binder elements which will form a protective film and inhibit further inward migration of O₂.

The oxide films that developed in the 10 hour test at 700 °C for G.T. specimens of three grades, 10Ni, 20Cr and 10Al, were analysed by Electron Probe Micro Analysis (EPMA). The concentration of elements through the metal and oxide film are recorded in charts of intensity versus location and are

contained in Appendix VII. Each of these scans reveal the drop in concentration of the constituent elements at the metal to oxide film interface and the corresponding increase in concentration of oxygen. None of the scans indicate an increase in the concentration of any of the constituent elements through the oxide film. This finding confirms that no protective barrier had developed. This is in agreement with the earlier comparison of results from short and long duration testing.

The results of another study discussed previously indicated that variations in binder composition did not substantially improve the oxidation resistance of alloys with binder contents of 10% by weight⁽⁴¹⁾. Grades tested with binder contents of 30% by weight⁽⁴⁰⁾ did reveal that at this high binder content the composition of the binder did significantly influence the oxidation resistance.

It is clear from these investigations that improvements in the thermal oxidation resistance could be made with the binder compositions used in this study if their content was a higher percentage of the total alloys.

CONCLUSIONS

The new cemented carbides manufactured in the course of this research have proven to be more resistant to corrosive attack by aqueous media than the traditional WC-Co grades. The results of the testing performed in this study indicate several advantages that the alloys comprising the systems WC-Ni, WC-Ni-Cr, WC-Ni-Al, and WC-Ni-Cr-Al each have over the reference WC-Co grade. These advantages may be summarized as follows:

1. Their performance is significantly superior in 2N H₂SO₄, both in terms of corrosion rates and in their tendency to passivate.
2. They exhibited higher resistance to attack by 0.5N NaCl.
3. The new grades that were subjected to an erosive corrosive attack by a slurry of 2N H₂SO₄ and SiC particles proved to be significantly superior than the reference WC-Co grade.
4. The results of high temperature corrosion, i.e. thermal oxidation, indicated slight improvements in the new grades at temperatures of 700 °C, and higher activation energies for thermal oxidation.
5. The new grades also proved to be slightly more resistant to erosion by solid particle impact than the traditional WC-Co grade tested.

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APPENDIX I

Data From Potentiostat / Galvanostat Experiments

A.1.1 Data from Potentiodynamic Anodic Polarization Measurements performed in 2N H₂SO₄

Alloy/Spec-Test No. (Cond.)	E _{in} (mV)	E _{corr} (mV)	E _c (mV)	E _a (mV)	I _{corr} μA/cm ²	Corr. Rate (μm/y)	Corr. Rate (mdd)	E _p k-Ohms	I _{corr} μA/cm ²	Corr. Rate (μm/y)	Corr. Rate (mdd)	E _{pp} (mV)	I _{cc} μA/cm ²	E _p (mV)	I _p μA/cm ²
G10/01-5	-332	-288.7	133.3	73.0	45.80	844	336	0.471	43.56	802.0	320.0	-40.0	52,000	180.0	19,000
10Ni/07-1 (G.T.)	-181	-173.6	120.57	58.48	0.5696	10.16	4.07	30.39	0.56	10.16	4.07	19.0	2,000	425.0	39.4
10Ni/12-1 (N.G.T.)	-213	-225.04	90.41	51.12	0.2110	3.81	1.54	31.16	-0.45	-8.13	-3.28	-30.0	1,340	420.0	98.0
1Cr/06-2 (G.T.)	-223	-243.34	78.19	101.75	0.6780	12.19	4.89	13.93	1.38	24.60	9.86	41.0	1,560	420.0	34.0
1Cr/12-1 (N.G.T.)	-214	-223.98	71.49	62.69	0.2326	4.32	1.73	30.58	0.47	8.38	3.36	0.0	1,500	430.0	260.0
10Cr/06-1 (G.T.)	-217	-208.59	141.17	89.75	2.6866	48.77	19.40	7.52	3.71	57.70	23.00	-15.0	616	400.0	22.0
10Cr/12-1 (N.G.T.)	-250	-260.7	87.13	162.72	1.9321	35.56	14.20	9.51	2.59	47.50	19.00	-30.0	678	420.0	92.0
20Cr/04-2 (G.T.)	-237	-273.71	67.57	117.34	1.1677	21.59	8.39	16.73	1.11	20.80	8.08	-35.0	618	350.0	18.0
20Cr/10-1 (N.G.T.)	-269	-270.5	87.08	99.19	2.5482	46.23	18.20	7.31	2.75	49.50	19.40	-76.0	410	310.0	34.0
20Cr/17-1 (Hipped)	-288	-313.76	64.15	91.92	1.2766	22.86	9.34	12.06	1.36	24.60	10.10	-65.0	710	400.0	50.0
50Cr/01-1 (G.T.)	-280	-280.56	275.78	215.6	3243.1	88,113	30,000	0.0156	3,363	91,390	31,120				
50Cr/03-1 (Hipped)	-244	-321.76	107.46	182.98	437.78	9,152	3,260	0.0654	449	9,400	3,350	110.0	20,400	600.0	10,000
2Al/01-4 (N.G.T.)	-239	-256.54	80.78	122.53	1.3163	23.62	9.39	14.95	1.41	25.70	10.20				
2Al/10-1 (G.T.)	-267	-275.22	94.85	123.08	0.8602	15.75	6.29	23.29	1.00	18.30	7.30	0.0	1,210	450.0	98.0
10Al/09-4 (N.G.T.)	-256	-285.4	71.07	91.14	1.8298	34.04	13.20	8.64	2.01	37.60	14.60				
10Al/16-1 (G.T.)	-267	-269.94	114.45	66.47	0.9615	18.03	7.04	19.18	0.95	17.80	6.95	8.0	910	430.0	22.0
16Al/01-4 (N.G.T.)	-265	-276.28	114.07	112.4	22.875	461.0	163.6	1.3036	18.86	380.2	134.9				
16Al/10-1 (G.T.)	-309	-316.29	94.23	79.48	2.2432	45.47	16.85	8.43	2.22	45.00	16.60	17.0	700	420.0	20.0
16Al/04-2 (Hipped)	-280	-319.49	48.82	78.24	0.1911	3.56	1.32	33.55	0.39	7.62	2.82	20.0	1,170	550.0	186.0
10Cr2Al/01-1 (Hipped)	-288	-305.23	65.45	52.19	0.1688	3.05	1.21	14.75	0.85	15.75	6.26	-70.0	690	350.0	12.8
10Cr5Al/01-1 (Hipped)	-308	-312.06	95.25	83.93	5.0209	93.47	34.83	---	---	---	---	-75.0	2,640	325.0	114.0
WCD/01-1	-232	-294.14	194.3	1098.0	2423.4	36,630	8,030	0.0285	2,512	89,800	19,700				

A.1.2 Data from Potentiodynamic Anodic Polarization Measurements performed in 0.5N NaCl

Alloy/Spec -Test No. (Cond.)	Einit (mv)	Ecorr (mv)	bc (mv)	ba (mv)	Icorr ($\mu\text{A}/\text{cm}^2$)	Corr. Rate ($\mu\text{m}/\text{y}$)	(mdd)	Rp (kOhms)	Rp Icorr ($\mu\text{A}/\text{cm}^2$)	Corr. Rate ($\mu\text{m}/\text{y}$)	(mdd)
G10/01-101	-594	-566.9	261.4	50.8	0.556	10.16	4.05	36.1	0.51	9.40	3.75
10Ni/07-102 (G.T.)	-333	-392.58	155.57	95.21	0.3797	6.86	2.75	---	---	---	
10Ni/12-101 (N.G.T.)	-368	-404.45	301.56	136.68	0.6118	10.92	4.40	69.45	0.59	10.41	4.20
1Cr/06-101 (G.T.)	-377	-469.75	157.35	158.5	0.1059	1.78	0.72	297.34	0.12	2.03	0.81
1Cr/12-101 (N.G.T.)	-431	-480.57	210.48	175.43	0.1903	3.56	1.43	-31.53	-1.03	-18.30	-7.34
10Cr/06-103 (G.T.)	-353	-424.24	234.06	168.49	0.1706	3.03	1.21	213.31	0.20	3.56	1.42
10Cr/12-101 (N.G.T.)	-396	-465.37	220.55	195.06	0.3604	6.86	2.74	111.7	0.40	7.37	2.94
20Cr/10-101 (N.G.T.)	-327	-398.68	168.89	152.06	0.1927	3.30	1.30	233.5	0.15	2.79	1.10
20Cr/17-101 (Hipped)	-545	-597.22	115.35	210.81	0.6170	11.18	4.57	31.33	1.03	18.50	7.56
50Cr/02-101 (G.T.)	-304	-381.72	240.04	368.93	1135.04	24,815	8,450	0.054	1,169	25,580	8,710
50Cr/03-101 (Hipped)	-350	-544.35	40.7	159.73	19.2662	402.6	143.0	0.6022	23.39	489.0	174.0
2Al/10-101 (G.T.)	-421	-612.28	42.13	314.64	1.3978	25.65	10.24	6.88	2.34	43.20	17.25
10Al/16-101 (G.T.)	-405	-581.43	60.2	393.65	2.564	48.26	18.80	9.15	2.48	46.48	18.15
16Al/10-101 (G.T.)	-413	-606.68	35.52	220.87	0.9853	19.56	7.23	13.03	1.02	20.30	7.51
16Al/04-101 (Hipped)	-353	-385.66	470.07	242.26	0.4246	8.38	3.10	102.39	0.68	13.50	5.00
10Cr2Al/01 -101 (Hip)	-346	-516.06	63.16	99.36	0.06329	1.02	0.41	232.84	0.07	1.27	0.50
10Cr5Al/01 -101 (Hip)	-256	-487.99	10.92	89.06	0.5649	10.41	3.88	2.1454	1.97	36.58	13.63
WCD/02-101	33.0	-85.86	118.15	390.28	59.725	2,135	468.0	0.6267	62.90	2,250	492.0

A.1.3 Data from Potentiostatic Measurements performed in 2N H₂SO₄ at peak (E_{pp}) and passive (E_p) potentials.

Alloy/Spec (Cond.)	Test No.	E _{pp} (mV)	b	M	Test No.	E _p (mV)	b	M
G10/01 (G.T.)	8	-40.0	3.86	0.16	6	180.0	5.46	0.63
10Ni/07 (G.T.)	4	19.0	3.74	0.56	2	425.0	3.46	1.12
10Ni/12 (N.G.T.)	4	-30.0	3.46	0.55	2	420.0	3.70	1.03
1Cr/06 (G.T.)	5	41.0	3.57	0.53	3	420.0	2.17	0.37
1Cr/12 (N.G.T.)	4	0.0	3.06	0.49	2	430.0	2.83	0.46
10Cr/06 (G.T.)	4	-15.0	3.14	0.50	2	400.0	3.75	1.41
10Cr/12 (N.G.T.)	4	-30.0	2.53	0.32	2	420.0	2.50	0.36
20Cr/04 (G.T.)	5	-35.0	2.48	0.35	3	350.0	2.10	0.32
2Al/10 (G.T.)	4	0.0	3.25	0.41	2	450.0	2.35	0.27
10Al/16 (G.T.)	4	8.0	3.50	0.45	2	430.0	3.27	0.73
16Al/10 (G.T.)	4	17.0	3.53	0.44	2	420.0	3.09	0.60
10Cr2Al/01 (Hipped)	4	-70.0	3.03	0.44	2	350.0	1.98	0.25
10Cr5Al/01 (Hipped)	4	-75.0	3.45	0.55	2	325.0	2.51	0.37

A.1.4 Potentiodynamic anodic polarization scans conducted in 2N H_2SO_4 .

A.1.5 Potentiodynamic anodic polarization scans conducted in 0.5N NaCl.

A.1.6 Data from potentiostatic tests conducted in 2N H₂SO₄.

Log i vs Log t, Data from "G10/01-6"

Log i vs Log t, Data from "G10/01-6"

Log i vs Log t; Data from "10N/07-4"

Log i vs Log t, Data from "10N/07-2"

Log I vs Log t, Data from "10N/12-4"

Log I vs Log t, Data from "10N/12-2"

Log I vs Log t, Data from "1Cr/06-5"

Log I vs Log t, Data from "1Cr/06-3"

Log I vs Log t, Data from "1Cr/12-4"

Log I vs Log t, Data from "1Cr/12-3"

Log I vs Log t, Data from "10Cr/08-4"

Log I vs Log t, Data from "10Cr/08-3"

Log I vs Log t, Data from "10Cr/12-4"

Log I vs Log t, Data from "10Cr/12-2"

Log I vs Log t, Data from "20Cr/04-5"

Log I vs Log t, Data from "20Cr/04-3"

Log i vs Log t , Data from "2A/10-4" Log i vs Log t , Data from "2A/10-3" Log i vs Log t , Data from "10A/10-4" Log i vs Log t , Data from "10A/10-3"

Log I vs Log t, Data from "16Al/10-4"

Log I vs Log t, Data from "16Al/10-2"

Log I vs Log t, Data from "10Cr2Al/01-4"

Log I vs Log t, Data from "10Cr2Al/01-2"

Log I vs Log t, Data from "10Cr5Al01-4"

Log I vs Log t, Data from "10Cr5Al01-2"

APPENDIX II

Data Sheets for Weight Loss Immersion Corrosion Experiments

A.2.1 Test Series Number: 1

Media: 2N H₂SO₄; Room Temp.; Date In:17/07/87; Date Out:
07/08/87; Conditions: De-aerated; Specimen surface
condition: sandblasted and cleaned

Note: After de-aeration with N₂ the flasks were sealed from
the atmosphere.

Alloy	Spec	Durat- ion (Hrs)	Surface Area (sq.cm)	Init. Weight (g)	Final Weight (g)	Weight Loss (g)	Corr. Rate (um/y) [mdd]
G10 G.T.	06	500.00	19.956	79.3659	78.7488	0.6171	(373.4) [148.8]
Comments: seal broken at 200 and 400 hrs.							
10Ni N.G.T.	16	500.00	19.795	79.3818	79.3563	0.0255	(15.2) [6.19]
1Cr N.G.T.	16	500.00	19.740	79.3205	79.3085	0.0120	(7.37) [2.96]
10Cr N.G.T.	16	500.00	19.825	79.2190	79.2030	0.0160	(9.65) [3.84]
20Cr N.G.T.	06	500.00	19.949	78.9306	78.9102	0.0204	(12.4) [4.88]
2Al N.G.T.	02	500.00	19.7634	79.2159	79.2083	0.0076	(4.57) [1.82]
10Al N.G.T.	10	500.00	20.059	78.9007	78.8687	0.0320	(19.8) [7.66]
16Al N.G.T.	02	500.00	20.921	78.8366	78.7149	0.1217	(77.0) [28.0]
Comments: seal broken after 450 hrs							

A.2.2 Test Series Number: 2

Media: 2N H₂SO₄; Room Temp.; Date In:21/08/87; Date Out: 01/09/87; Conditions: Stagnant; Specimen surface condition: sandblasted and cleaned.

Alloy	Spec	Duration (Hrs)	Surface Area (sq.cm)	Init. Weight (g)	Final Weight (g)	Weight Loss (g)	Corr. Rate (um/y) [mdd]
G10 G.T.	06	263.50	19.956	78.4949	78.2893	0.2056	(235.5) [93.8]
10Ni G.T.	12	263.50	19.811	79.4197	79.3643	0.0554	(63.5) [25.5]
N.G.T.	16	263.50	19.795	79.2821	79.2360	0.0461	(52.3) [21.2]
1Cr G.T.	12	263.50	19.858	79.3912	79.3343	0.0569	(65.0) [26.1]
N.G.T.	16	263.50	19.740	79.2790	79.2481	0.0309	(35.6) [14.3]
10Cr G.T.	12	263.50	19.836	79.0914	79.0379	0.0535	(61.7) [24.6]
N.G.T.	16	263.50	19.825	79.1826	79.1514	0.0312	(36.1) [14.3]
20Cr G.T.	02	263.50	20.116	79.0024	78.9789	0.0235	(27.4) [10.6]
N.G.T.	06	263.50	19.949	78.8871	78.8848	0.0023	(2.79) [1.05]
2Al N.G.T.	02	263.50	19.763	79.0832	79.0665	0.0167	(19.3) [7.70]
10Al N.G.T.	10	263.50	20.059	78.5550	78.4883	0.0667	(78.5) [30.3]
16Al N.G.T.	02	263.50	20.921	78.6743	78.5919	0.0824	(98.8) [35.9]

A.2.3 Test Series Number: 3

Media: 0.5N NaCl; Room Temp.; Date In:03/11/87; Date Out: 27/11/87; Conditions: Stagnant; Specimen surface condition: sandblasted and cleaned.

Alloy	Spec	Durat- ion (Hrs)	Surface Area (sq.cm)	Init. Weight (g)	Final Weight (g)	Weight Loss (g)	Corr. Rate (um/y) [mdd]
G10 G.T.	06	572.40	19.956	77.6125	77.5570	0.0555	(29.5) [11.7]
	Obs: Spec.: black with blue streaks						
10Ni G.T.	12	572.40	19.811	79.0648	79.0598	0.0050	(2.54) [1.06]
N.G.T.	16	572.40	19.795	78.9270	78.9186	0.0084	(4.31) (1.78)
1Cr G.T.	12	572.40	19.858	79.0517	79.0465	0.0052	(2.79) [1.10]
	Obs: Spec.: brown spots, yellow streaks						
N.G.T.	16	572.40	19.740	79.0965	79.0884	0.0081	(4.31) [1.73]
10Cr G.T.	12	572.40	19.836	78.8257	78.8219	0.0038	(2.01) [0.80]
	Obs: Spec.: brown spots, yellow streaks						
N.G.T.	16	572.40	19.825	79.0038	78.9947	0.0091	(4.83) [1.92]
20Cr G.T.	02	572.40	20.116	78.9320	78.9255	0.0065	(2.79) [1.09]
	Obs: Spec.: many brown spots, yellow streaks						
	Obs: Soln.: flaky yellow ppt. in soln.						
50Cr G.T.	04	572.40	120.578	78.7868	78.7823	0.0045	(2.46) [0.92]
	Obs: Spec.: many yellow spots; Soln.: lots of yellow ppt.						
2Al G.T.	29	548.90	19.814	79.2323	79.2274	0.0049	(2.79) [1.08]
10Al G.T.	36	548.90	20.085	78.8463	78.8433	0.0030	(1.68) [0.65]
16Al N.G.T.	29	241.20	20.743	78.9686	78.9637	0.0049	(6.35) [2.34]
	Obs: Some white ppt. in soln.						

A.2.4 Test Series Number: 4

Media: 2N H₂SO₄; Room Temp.; Date In: 20/01/88; Date Out: 07/02/88; Conditions: Stagnant; Specimen surface condition: sandblasted and cleaned.

Alloy	Spec	Durat- ion (Hrs)	Surface Area (sq.cm)	Init. Weight (g)	Final Weight (g)	Weight Loss (g)	Corr. Rate (um/y) [mdd]
50Cr G.T.	06	432.50	21.845	78.6823	77.6450	1.0373	(775.0) [264.0]
	Obs: Soln.: dark blue/green colour Comment: result disregarded						
2Al G.T.	27	432.50	19.872	78.6977	78.6142	0.0835	(58.4) [23.3]
	Obs: Soln.: light green						
10Al G.T.	36	432.50	20.032	78.8427	78.7487	0.0940	(66.8) [26.1]
	Obs: Soln.: light green						
16Al G.T.	30	353.60	20.731	78.8894	78.7865	0.1029	(93.2) [34.4]
	Obs: Soln.: medium green						

A.2.5 Test Series Number: 5 Agitated test

Media: 2N H₂SO₄ Date In: 10/02/88 Date Out: 19/02/88
Conditions: Swirling; Specimen surface condition: sandblasted and cleaned

Alloy	Spec	Durat- ion (Hrs)	Surface Area (sq.cm)	Init. Weight (g)	Final Weight (g)	Weight Loss (g)	Corr. Rate (um/y) [mdd]
G10 G.T.	11	214.50	19.961	79.4709	78.7110	0.7599	(1,070) [427.0]
	Obs: Soln.: dark rose colour						
10Ni G.T.	40	214.50	19.892	79.3109	79.1140	0.1969	(277.0) [111.0]
	Obs: Soln.: light blue						

A.2.6 Test Number: 6a (First of two consecutive tests)

Media: 2N H₂SO₄; Room Temp.; Date In:05/05/88; Date Out: 16/05/88; Conditions: Stagnant; Specimen surface condition: sandblasted and cleaned

Alloy	Spec	Duration (Hrs)	Surface Area (sq.cm)	Init. Weight (g)	Final Weight (g)	Weight Loss (g)	Corr. Rate (um/y) [mdd]
G10 G.T.	12	262.00	19.948	79.3236	79.0182	0.3054	(353.0) [141.0]
	Obs: Soln.: rose coloured						
10Ni G.T.	59	262.00	19.324	75.5489	75.4981	0.0508	(60.2) [24.1]
	Obs: Soln.: light blue						
N.G.T.	57	262.00	19.208	75.5079	75.4579	0.0500	(58.7) [23.7]
	Obs: Soln.: light blue						
1Cr G.T.	37	262.00	19.894	79.3664	79.3109	0.0555	(63.8) [25.6]
	Obs: Soln.: light blue						
N.G.T.	35	262.00	19.763	79.2765	79.2403	0.0362	(41.7) [16.7]
	Obs: Soln.: light blue						
10Cr G.T.	37	262.00	19.959	79.4336	79.4307	0.0029	(3.30) [1.31]
	Obs: Soln.: clear						
N.G.T.	35	262.00	19.807	79.1208	79.1164	0.0044	(5.08) [2.02]
	Obs: Soln.: clear						
20Cr G.T.	25	262.00	20.526	79.1262	79.1264	---	---
	Obs: Soln.: clear						
50Cr G.T.	15	262.00	21.133	78.9530	78.9312	0.0218	(25.4) [8.65]
	Obs: Soln.: light blue						
2Al G.T.	33	262.00	19.983	79.1906	79.1307	0.0599	(68.8) [27.5]
	Obs: Soln.: light green						
5Al G.T.	03	262.00	20.089	79.3137	79.2660	0.0477	(55.1) [21.9]
	Obs: Soln.: light green						
10Al G.T.	40	262.00	20.097	78.8899	78.8380	0.0519	(60.7) [23.7]
	Obs: Soln.: light green						
16Al G.T.	33	262.00	20.787	78.9562	78.8669	0.0893	(107.0) [39.5]
	Obs: Soln.: medium green						

A.2.7 Test Number: 6b (Second of two consecutive tests)

Media: 2N H₂SO₄; Room Temp.; Date In:19/05/88; Date Out: 31/05/88; Conditions: Stagnant; Specimen surface conditions: cleaned only; Same soln. as 6a.

Alloy	Spec	Durat- ion (Hrs)	Surface Area (sq.cm)	Init. Weight (g)	Final Weight (g)	Weight Loss (g)	Corr. Rate (um/y) [mdd]
G10 G.T.	12 Obs:	281.50 Soln.:	19.948 rose coloured	79.0182	78.7374	0.2808	(302.0) [120.0]
10Ni G.T.	59 Obs:	281.50 Soln.:	19.324 light blue	75.4981	75.4550	0.0431	(47.5) [19.0]
N.G.T.	57 Obs:	281.50 Soln.:	19.208 light blue	75.4579	75.4278	0.0301	(33.0) [13.3]
1Cr G.T.	37 Obs:	281.50 Soln.:	19.894 light blue	79.3109	79.2703	0.0406	(43.3) [17.4]
N.G.T.	35 Obs:	281.50 Soln.:	19.763 light blue	79.2403	79.2205	0.0198	(21.3) [8.56]
10Cr G.T.	37 Obs:	281.50 Soln.:	19.959 clear	79.4307	79.4297	0.0010	(1.07) [0.43]
N.G.T.	35 Obs:	281.50 Soln.:	19.807 clear	79.1164	79.1148	0.0016	(1.73) [0.69]
20Cr G.T.	25 Obs:	281.50 Soln.:	20.526 clear	79.1264	79.1256	0.0008	(0.86) [0.33]
50Cr G.T.	15 Obs:	281.50 Soln.:	21.133 medium blue	78.9312	78.8298	0.1014	(109.0) [37.1]
2Al G.T.	33 Obs:	281.50 Soln.:	19.983 light green	79.1307	79.0840	0.0467	(50.0) [20.0]
5Al G.T.	03 Obs:	281.50 Soln.:	20.089 light green	79.2660	79.2270	0.0390	(41.9) [16.6]
10Al G.T.	40 Obs:	281.50 Soln.:	20.097 light green	78.8380	78.8157	0.0223	(24.4) [9.53]
16Al G.T.	33 Obs:	281.50 Soln.:	20.787 medium green	78.8669	78.7123	0.1545	(172.0) [63.5]

A.2.8 Test Number: 7a (First of two consecutive tests)

Media: 0.5N NaCl; Room Temp.; Date In:01/06/88; Date Out: 23/06/88; Conditions: Stagnant; Specimen surface condition: sandblasted and cleaned.

Alloy	Spec	Duration (Hrs)	Surface Area (sq.cm)	Init. Weight (g)	Final Weight (g)	Weight Loss (g)	Corr. Rate (um/y) [mdd]
G10 G.T.	14	527.50	19.983	79.5155	79.4937	0.0218	(12.5) [4.98]
	Obs:Spec.:black surface;green ppt. in soln						
10Ni G.T.	60	527.50	19.300	75.5257	75.5220	0.0037	(2.18) [0.87]
N.G.T.	58	527.50	19.232	75.4722	75.4686	0.0036	(2.11) [0.85]
1Cr G.T.	38	527.50	19.958	79.3888	79.3865	0.0023	(1.32) [0.53]
N.G.T.	36	527.50	19.726	79.2306	79.2286	0.0020	(1.14) [0.46]
10Cr G.T.	38	527.50	19.993	79.4278	79.4261	0.0017	(0.97) [0.39]
N.G.T.	36	527.50	19.864	79.0175	79.0162	0.0013	(0.74) [0.29]
20Cr G.T.	26	527.50	20.526	79.0809	79.0748	0.0061	(3.56) [1.38]
	Obs:Spec.:yellow spots;yellow ppt. in soln						
50Cr G.T.	16	527.50	21.541	78.9818	79.0000	---	---
	Obs: Spec.: many yellow spots;lots of yellow ppt.						
2Al G.T.	34	527.50	19.903	79.2195	79.2147	0.0048	(2.80) [1.12]
	Obs:Spec.:yellow spots; white ppt. in soln						
5Al G.T.	04	527.50	20.113	79.3890	79.3853	0.0037	(2.13) [0.85]
10Al G.T.	41	527.50	18.825	70.5683	70.5656	0.0027	(1.68) [0.66]
16Al G.T.	34	527.50	20.768	78.9258	78.9176	0.0082	(4.83) [1.79]
	Obs: Spec.: many yellow spots; white ppt.						

A.2.9 Test Number: 7b (Second of two consecutive tests)

Media: 0.5N NaCl; Room Temp.; Date In:29/06/88; Date Out: 21/07/88; Conditions: Stagnant; Specimen surface conditions: cleaned only; Same soln. as 7a.

Alloy	Spec	Duration (Hrs)	Surface Area (sq.cm)	Init. Weight (g)	Final Weight (g)	Weight Loss (g)	Corr. Rate (um/y) [mdd]
G10 G.T.	14	524.00	19.983	79.4937	79.4894	0.0043	(2.46)
	Obs: Spec.: black surface; Soln: green ppt.						[0.98]
10Ni G.T.	60	524.00	19.300	75.5220	75.5209	0.0011	(0.66)
							[0.26]
N.G.T.	58	524.00	19.232	75.4686	75.4673	0.0013	(0.76)
							[0.31]
1Cr G.T.	38	524.00	19.958	79.3865	79.3859	0.0006	(0.36)
							[0.14]
N.G.T.	36	524.00	19.726	79.2286	79.2286	0.0000	(0.00)
							[0.00]
10Cr G.T.	38	524.00	19.993	79.4261	79.4264	---	---

N.G.T.	36	524.00	19.864	79.0162	79.0160	0.0002	(0.13)
							[0.05]
20Cr G.T.	26	524.00	20.526	79.0748	79.0720	0.0028	(1.60)
	Obs: Spec.: yellow spots; Soln: yellow ppt.						[0.62]
50Cr G.T.	16	524.00	21.541	79.0000	79.0320	---	---
	Obs: Spec.: many yellow spots; lots of yellow ppt.						
2Al G.T.	34	524.00	19.903	79.2147	79.2126	0.0021	(1.22)
	Obs: Spec.: yellow spots; Soln: white ppt.						[0.49]
5Al G.T.	04	524.00	20.113	79.3853	79.3837	0.0016	(0.91)
	Obs: Spec.: yellow spots; Soln: white ppt.						[0.36]
10Al G.T.	41	524.00	18.825	70.5656	70.5646	0.0010	(0.64)
							[0.25]
16Al G.T.	34	524.00	20.768	78.9176	78.9139	0.0037	(2.21)
	Obs: many yellow spots; lots of white ppt.						[0.82]

A.2.10 Test Series Number: 8, Hot Immersion Tests

Media: 2N H₂SO₄; Temp.: 100°C; Conditions: Boiling; Specimen surface condition: sandblasted and cleaned

Alloy	Spec	Durati- on (Hrs)	Surface Area (sq.cm)	Init. Weight (g)	Final Weight (g)	Weight Loss (g)	Corr. Rate (um/y) [mdd]
G10 G.T.	06	48.58	19.915	77.1690	75.4141	1.3549	(8,330)
	Obs: Soln.: dark red; Spec.: very chipped						[3,320]
10Ni G.T.	12	48.00	19.854	78.6790	78.4297	0.2493	(1,570)
	Obs: Soln.: light green						[628.0]
N.G.T.	56	48.00	19.624	78.4942	78.4374	0.0568	(356.0)
	Obs: Soln.: light green						[143.0]
1Cr G.T.	12	48.00	19.832	78.6501	78.4089	0.2412	(1,152)
	Obs: Soln.: light green						[608.0]
N.G.T.	16	48.00	19.663	78.8590	78.7724	0.0866	(549.0)
	Obs: Soln.: light green						[220.0]
10Cr G.T.	24	46.33	19.872	79.1365	78.5180	0.6176	(4,040)
	Obs: Soln.: medium green						[1,610]
N.G.T.	18LT	46.33	19.770	78.6363	78.4335	0.2028	(1,336)
	Obs: Soln.: light green						[532.0]
20Cr G.T.	14	48.00	20.236	79.1030	78.2904	0.8126	(5,160)
	Obs: Soln.: medium green						[2,000]
50Cr G.T.	08	47.50	21.544	78.1390	76.3851	1.7539	(12,090)
	Obs: Soln.: dark green						[4,120]
2Al G.T.	27	49.42	19.895	79.2348	78.8537	0.3811	(2,330)
	Obs: Soln.: light green						[931.0]
10Al G.T.	34	49.42	20.026	78.8940	77.9313	0.9627	(5,990)
	Obs: Soln.: medium green						[2,340]
16Al G.T.	27	48.30	20.780	78.9716	76.4019	2.5697	(16,280)
	Obs: Soln.: dark green; Spec.: very chipped						[6,010]

A.2.11 Test Series Number: 9, Hot Immersion Tests

Media: 2N H₂SO₄; Temp.: 100°C; Conditions: Boiling; Specimen surface condition: sandblasted and cleaned

Alloy	Spec	Duration (Hrs)	Surface Area (sq.cm)	Init. Weight (g)	Final Weight (g)	Weight Loss (g)	Corr. Rate (um/y) [mdd]
G10 G.T.	10	47.67	19.936	79.4701	76.1782	3.2919	(20,900) [8,330]
	Obs:	Soln.:	dark red;	Spec.:	very chipped		
10Ni G.T.	12	48.92	19.832	78.1295	77.9533	0.1762	(1,090) [437.0]
N.G.T.	16	48.92	19.715	78.2513	78.2005	0.0508	(315.0) [127.0]
1Cr G.T.	12	48.50	19.888	78.1241	77.9526	0.1715	(1,070) [428.0]
	Obs:	Soln.:	light green				
N.G.T.	16	48.50	19.695	78.4145	78.3635	0.0510	(320.0) [129.0]
	Obs:	Soln.:	light green				
10Cr G.T.	24	76.00	19.850	78.2832	77.5033	0.7799	(3,120) [1,240]
	Obs:	Soln.:	medium green				
N.G.T.	18LT	76.00	19.793	78.3010	78.1196	0.1814	(726.0) [289.0]
	Obs:	Soln.:	light green				
20Cr G.T.	14	45.00	20.169	78.2769	77.7675	0.5094	(3,450) [1,340]
	Obs:	Soln.:	medium green				
50Cr G.T.	08	45.00	21.532	76.2584	75.3342	0.9242	(6,120) [2,080]
	Obs:	Soln.:	dark green				
2Al G.T.	28	49.42	19.814	79.2842	78.9244	0.3602	(2,210) [883.0]
	Obs:	Soln.:	light green				
10Al G.T.	35	49.42	20.035	78.9014	77.9010	1.0004	(6,220) [2,430]
	Obs:	Soln.:	medium green;	Spec.:	chipped		
16Al G.T.	28	48.30	20.784	78.9836	76.4139	2.5697	(16,280) [6,010]
	Obs:	Soln.:	dark green;	Spec.:	very chipped		

Note: LT signifies low sintering temperature of 1440°C used.

A.2.12 Test Series Number: 10, Hot Immersion Tests

Media: 2N H₂SO₄; Temp.: 100°C; Conditions: Boiling; Specimen surface condition: sandblasted and cleaned

Alloy	Spec	Duration (Hrs)	Surface Area (sq.cm)	Init. Weight (g)	Final Weight (g)	Weight Loss (g)	Corr. Rate (um/y) [mdd]
G10 G.T.	13 Obs:	1.00 Soln.:	19.946 rose coloured	79.4173	79.1561	0.2612	(78,900) [31,400]
16Al G.T.	31 Obs:	1.00 Soln.:	20.784 light green	78.8420	78.7726	0.0694	(22,100) [8,170]
10Ni G.T.	12	46.93	19.743	77.2723	77.1432	0.1291	(836.0) [335.0]
N.G.T.	18LT	43.60	19.736	78.9716	78.8624	0.1092	(706.0) [285.0]
1Cr G.T.	12	46.93	19.778	77.5689	77.4589	0.1100	(711.0) [285.0]
N.G.T.	18LT	43.60	19.708	78.9552	78.8604	0.0948	(620.0) [249.0]

Note: LT signifies low sintering temperature of 1440°C used.

APPENDIX III

Results of Erosion Experiments

A.3.1 Erosion rates for tests conducted at 90 and 30 degrees. Velocity = 30 m/s, Re = 12 g/min, Erodent = 180 um SiC, duration of tests = 15.0 min.

Alloy	Spec No.	Cond.	90 deg (g/g) $\times 10^{-4}$	90 deg (cm ³ /g) $\times 10^{-4}$	30 deg (g/g) $\times 10^{-4}$	30 deg (cm ³ /g) $\times 10^{-4}$
G10	07	G.T.	0.317	0.0212	0.164	0.0113
10Ni	41	G.T.	0.200	0.0136	0.113	0.0077
	20	N.G.T.	0.302	0.0205	0.144	0.0098
1Cr	25	G.T.	0.187	0.0128	0.149	0.0102
	20	N.G.T.	0.297	0.0202	0.150	0.0102
10Cr	10	G.T.	0.283	0.0196	0.133	0.0029
	20	N.G.T.	0.277	0.0190	0.122	0.0084
20Cr	15	G.T.	0.174	0.0120	0.128	0.0088
	10	N.G.T.	0.251	0.0176	0.106	0.0075
50Cr	05	G.T.	0.180	0.0133	0.103	0.0076
2Al	26	G.T.	0.231	0.0158	0.226	0.0150
	06	N.G.T.	0.379	0.0262	0.172	0.0119
10Al	33	G.T.	0.169	0.0119	0.133	0.0094
	14	N.G.T.	0.226	0.0160	0.128	0.0091
16Al	26	G.T.	0.129	0.0098	0.154	0.0116
	06	N.G.T.	0.299	0.0231	0.133	0.0103

APPENDIX IV

Data Sheets for Erosion Corrosion Experiments

A.4.1 Test Series Number: 1

Alloy	Spec	Durat- ion (Hrs)	Surface Area (sq.cm)	Init. Weight (g)	Final Weight (g)	Weight Loss (g)	Corr. Rate (um/y) [mdd]
G10 G.T.	13	12.75	7.174	78.9479	78.8373	0.1106	(7,280) [2,902]
10Ni G.T.	12	12.00	7.040	77.0854	77.0822	0.0032	(227.0) [90.92]
N.G.T.	16	12.00	7.050	77.8297	77.8205	0.0092	(642.6) [261.1]
1Cr G.T.	12	12.00	7.048	77.4112	77.4079	0.0033	(233.7) [93.66]
N.G.T.	16	12.00	7.074	78.0157	78.0046	0.0111	(780.54) [313.93]
10Cr G.T.	12	10.42	7.102	78.5715	78.5699	0.0016	(130.3) [51.94]
N.G.T.	16	10.42	7.163	78.8401	78.8364	0.0037	(297.2) [118.3]
20Cr G.T.	02	10.42	7.273	78.8562	78.8553	0.0009	(73.41) [28.52]
50Cr G.T.	04	10.42	7.389	78.7453	78.7449	0.0004	(33.53) [12.52]
2Al G.T.	29	12.75	7.155	79.2223	79.1918	0.0305	(2,011) [802.7]
10Al G.T.	37	12.75	7.303	78.9327	78.8786	0.0541	(3,580) [1,395]
16Al N.G.T.	31	12.75	7.520	78.7633	78.7125	0.0508	(3,447) [1,272]

A.4.2 Test Series Number: 2

Alloy	Spec	Duration (Hrs)	Surface Area (sq.cm)	Init. Weight (g)	Final Weight (g)	Weight Loss (g)	Corr. Rate ($\mu\text{m/y}$) [mdd]
G10 G.T.	13	12.25	7.174	78.8373	78.7289	0.1084	(7,432) [2,963]
10Ni G.T.	12	7.25	7.040	77.0822	77.0767	0.0055	(645.4) [258.7]
N.G.T.	16	7.25	7.050	77.8205	77.8189	0.0016	(184.9) [75.13]
1Cr G.T.	12	7.25	7.048	77.4079	77.4055	0.0024	(281.4) [112.8]
N.G.T.	16	7.25	7.074	78.0046	78.0026	0.0020	(232.7) [93.58]
10Cr G.T.	12	13.50	7.102	78.5687	78.5649	0.0038	(238.8) [95.18]
N.G.T.	16	13.50	7.163	78.8330	78.8300	0.0030	(187.2) [74.52]
20Cr G.T.	02	13.50	7.273	78.8553	78.8528	0.0025	(157.5) [61.18]
50Cr G.T.	04	13.50	7.389	78.7444	78.7414	0.0030	(193.3) [72.18]
2Al G.T.	29	12.25	7.155	79.1918	79.1899	0.0019	(130.3) [52.01]
10Al G.T.	37	12.25	7.303	78.8786	78.8738	0.0048	(330.7) [128.9]
16Al N.G.T.	31	12.25	7.520	78.7125	78.6709	0.0416	(2,937) [1,084]

APPENDIX V

Data Sheets for Thermal Oxidation Experiments

A.5.1 Results of testing at 700 °C for durations of 1.0 hr.
All weight gain results are in units of mg/cm²/hr.

Alloy	Spec No.	Cond.	Test # 1	Test # 2	Test # 3	Test # 4	Average
G10	07	G.T.	7.60	9.78	8.95	10.86	9.30
10Ni	38	G.T.	6.07	7.77	5.58	8.51	6.98
	20	N.G.T.	3.35	5.99	7.15	8.77	6.32
1Cr	25	G.T.	8.43	5.98	5.82	8.74	7.24
	20	N.G.T.	5.10	6.40	9.43	7.32	7.06
10Cr	10	G.T.	4.03	6.32	8.59	6.28	6.31
	20	N.G.T.	6.82	8.29	9.91	7.51	8.13
20Cr	15	G.T.	6.55	4.73	6.89	4.83	5.75
	10	N.G.T.	7.00	7.13	7.87	5.92	6.98
50Cr	03	G.T.	3.38	1.81	2.79	1.93	2.48
2Al	25	G.T.	8.26	7.76	7.66	5.60	7.32
	06	N.G.T.	9.05	6.96	7.16	5.40	7.14
10Al	32	G.T.	6.48	6.07	4.34	5.37	5.57
	14	N.G.T.	3.69	6.08	3.82	5.22	4.70
16Al	25	G.T.	6.03	4.67	4.05	5.14	4.97
	06	N.G.T.	3.90	5.14	3.47	4.54	4.26

**A.5.2 Results of testing at 900 °C for durations of 1.0 hr.
All weight gain results are in units of mg/cm²/hr.**

Alloy	Spec No.	Cond.	Test # 1	Test # 2	Test # 3	Test # 4	Average
G10	07	G.T.	48.91	19.19	46.26	48.29	40.66
10Ni	38	G.T.	53.07	19.37	52.31	47.10	42.06
	20	N.G.T.	69.94	22.29	50.16	53.20	48.91
1Cr	25	G.T.	21.63	52.59	54.72	48.02	44.24
	20	N.G.T.	69.82	21.15	47.34	51.61	47.48
10Cr	10	G.T.	75.58	31.01	42.00	50.61	49.80
	20	N.G.T.	40.25	34.61	50.70	53.15	44.68
20Cr	15	G.T.	17.62	51.95	40.83	48.00	39.60
	10	N.G.T.	38.28	34.94	70.82	110.78	63.69
50Cr	03	G.T.	18.43	41.96	50.01	76.82	46.81
2Al	25	G.T.	34.13	89.48	63.65	112.04	74.83
	06	N.G.T.	16.94	55.39	69.02	105.51	61.72
10Al	32	G.T.	31.10	78.85	95.16	64.86	67.49
	14	N.G.T.	58.03	18.13	95.50	63.61	58.82
16Al	25	G.T.	60.46	28.03	84.14	59.02	57.91
	06	N.G.T.	52.04	14.18	87.37	58.94	53.13

A.5.3 Results of testing at 700 °C, duration of 10.0 hrs.
All weight gain results are in units of mg/cm²/hr.

Alloy	Spec No.	Cond.	Test # 1
G10	07	G.T.	9.57
10Ni	38	G.T.	6.82
1Cr	25	G.T.	7.13
10Cr	25	G.T.	8.75
20Cr	15	G.T.	7.35
50Cr	05	G.T.	2.33
2Al	25	G.T.	7.36
10Al	32	G.T.	6.06
16Al	25	G.T.	5.42

APPENDIX VI

Data From Chemical Analysis of Solutions

A.6.1 Solutions from Immersion Test Series #1, 2N H₂SO₄

Alloy /Spec	FCo (g/l)	FWi (g/l)	FCr (g/l)	FAl (g/l)	Bel (g/l)	Exp W.L. (g/l)	FCr/Bel (%)	FAl/Bel (%)
G10/06	0.84				0.84	1.234		
10Ni/16		0.032			0.032	0.051		
1Cr/16		0.016	0.0009		0.0169	0.024	5.3	
10Cr/16		0.023	0.002		0.025	0.032	8.0	
20Cr/06		0.028	0.004		0.032	0.0408	12.5	
2Al/02		0.011		<0.001	0.0112	0.0152		1.8
10Al/10		0.048		0.005	0.053	0.064		9.4
16Al/02		0.22		0.031	0.251	0.2434		12.4

A.6.2 Solutions from Immersion Test Series #4, 2N H₂SO₄

Alloy /Spec	FW (mg/l)	FWi (g/l)	FCr (g/l)	FAl (g/l)	Bel (g/l)	Exp W.L. (g/l)	FCr/Bel (%)	FAl/Bel (%)	FW/Bel (%)
50Cr/06	3.1	2.19	0.22		2.4131	2.0750	9.1		0.13
2Al/27	1.1	0.16		0.004	0.1651	0.1670		2.4	0.67
10Al/36	5.5	0.16		0.018	0.1835	0.1880		9.8	3.00
16Al/30	0.6	0.17		0.030	0.2006	0.2058		15.0	0.30

A.6.3 Solutions from Immersion Test Series #6b, 2N H₂SO₄

Alloy /Spec	FW (mg/l)	FCr (g/l)	FWi (g/l)	FCr (g/l)	FAI (g/l)	Bel (g/l)	Exp W.L. (g/l)	FCr/Bel (%)	FAI/Bel (%)	FW/Bel (%)
G10/12	4.2	1.18				1.1842	1.1704			0.355
10Ni/59	5.5		0.20			0.2055	0.1878			2.68
10Ni/57	7.6		0.17			0.1776	0.1602			4.28
1Cr/37	5.5		0.20	0.005		0.2105	0.1922	2.38		2.61
1Cr/35	8.0		0.11	0.003		0.1210	0.1120	2.48		6.61
10Cr/37	0.6		0.007	0.0005		0.0081	0.0078	6.17		7.41
10Cr/35	2.9		0.008	0.0007		0.0116	0.0120	6.03		25.0
20Cr/25	<0.5		0.002	0.0002		0.0022	0.0016	9.09		<22.1
50Cr/15	0.7		0.30	0.035		0.3357	0.2464	10.40		0.209
2Al/33	4.2		0.22		0.004	0.2282	0.2132		1.75	1.84
5Al/03	4.9		0.17		0.008	0.1829	0.1734		4.38	2.68
10Al/40	5.2		0.14		0.011	0.1562	0.1484		7.04	3.33
16Al/33	0.5		0.49		0.0008	0.4913	0.4876		0.16	0.102

A.6.4 Solutions from Immersion Test Series #3, 0.5N NaCl.

Alloy /Spec	FW (mg/l)	PCo (g/l)	FWi (g/l)	PCr (g/l)	FAl (g/l)	Bel (g/l)	Exp W.L. (g/l)	PCr/Bel (%)	FAl/Bel (%)	FW/Bel (%)
G10/06	29.4	0.025				0.0544	0.1110			54
10Ni/12	2.0		0.008			0.010	0.010			20
10Ni/16	3.9		0.004			0.0079	0.0168			49.4
1Cr/12	1.7		0.008	<.0001		0.0097	0.0104	<1.0		17.5
1Cr/16	7.6		0.003	<.0001		0.0106	0.0162	<0.9		71.7
10Cr/12	<0.3		0.007	<.0001		0.007	0.0076	<1.4		<4.3
10Cr/16	7.1		0.002	<.0001		0.0091	0.0182	<1.1		78.0
50Cr/04	<0.3		0.010	<.0001		0.010	0.0090	<1.0		<3.0
2Al/29	1.0		0.007		<0.001	0.008	0.0096		<13.0	12.5
10Al/36	<0.03		<0.3		<0.001	0.003	0.0060		<33.3	<10.0
16Al/29	<0.03		<0.3		<0.001	0.003	0.0098		<33.3	<10.0

A.6.5 Solutions from Immersion Test Series #7b, 0.5N NaCl.

Alloy /Spec	PW (mg/l)	PCo (g/l)	PWi (g/l)	PCr (g/l)	PAI (g/l)	Bel (g/l)	Exp W.L. (g/l)	PCr/Bel (%)	PAI/Bel (%)	PW/Bel (%)
G10/14	<0.3	0.015				0.015	0.0522			<2.0
10Ni/60	0.9		0.008			0.0089	0.0096			10.1
10Ni/58	2		0.008			0.010	0.0098			20.0
1Cr/38	<0.3		0.006	<.0001		0.006	0.0029	<1.7		<5.0
1Cr/36	<0.3		0.003	<.0001		0.003	0.0040	<1.7		<10.0
10Cr/38	<0.3		0.002	<.0001		0.002	0.0034	<5.0		<15.0
10Cr/36	0.4		0.001	<.0001		0.0014	0.0030	<7.1		28.6
20Cr/26	0.3		0.010	0.0003		0.0106	0.0178	2.8		2.8
50Cr/16	<0.3		0.002	<.0001		0.002		<5.0		<15.0
2Al/34	1		0.011		<0.001	0.012	0.0138		<8.3	8.3
5Al/04	1		0.007		<0.001	0.008	0.0106		<12.5	12.5
10Al/41	<0.3		0.005		<0.001	0.005	0.0074		<20.0	<6.0
16Al/34	<0.3		0.006		<0.001	0.006	0.0238		<16.7	<5.0

APPENDIX VII

Results of EPMA of Thermal Oxidation Specimens

A.7.1 Results of electron probe micro analysis of 10Ni (G.T.) after oxidation in air at 700 °C for 10 hours.

A.7.2 Results of electron probe micro analysis of 20Cr (G.T.) after oxidation in air at 700 °C for 10 hours.

A.7.3 Results of electron probe micro analysis of 10Al 172 (G.T.) after oxidation in air at 700 °C for 10 hours.

END

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