CHAPTER – I

INTRODUCTION

1.1 GENERAL INTRODUCTION

Corrosion is defined as the undesirable deterioration of materials, usually metals or alloys by electrochemical or chemical reaction with its environment that adversely affects those properties of metals or alloys that are to be preserved [1]. International Union of Pure and Applied Chemistry (IUPAC) defines corrosion as "an irreversible interfacial reaction of materials (metals, ceramics or polymers) with its environment which results in consumption of the materials" [2,3]. This is a broad definition of corrosion and clarifies the fact that corrosion is not restricted to metals or alloys only, but also to almost any other materials used for engineering purposes.

Corrosion is an inevitable process. As new engineering materials are developed, they need to have improved corrosion properties. The lack of corrosion-resistant properties of the engineering materials will be the cause of wastage of much money, labor as well as deterioration in the quality of such materials in a short time. Therefore, the works of engineering become unreliable without testimony of corrosion properties of the materials. Early in the past, engineers did not take into consideration the importance of corrosion science during the initial designing of the materials with the thought that the problems arising from corrosion could be avoided by additional surface treatments. Whenever novel materials are developed, their industrial applications depend on the corrosion behavior over extended periods of service. The corrosion problems should be considered at an appropriate stage of the materials development. Hence, corrosion research is also a part of engineering. In general, two things are to be significantly taken into mind before the engineering materials are subjected for application. Firstly, under what conditions it is used and secondly, how it is processed. Now a days, the corrosion scientists have to play significant role to develop such engineering materials.

Corrosion problems are such that they are faced in all branches of industries. There is a challenge to corrosion scientists to investigate adequate corrosion control techniques and mechanism through which a better understanding can be made. The damage caused by the corrosion is not prevented totally. Still the cost of materials is led by the corrosion loss. It is believed that the cost of corrosion is about 3-4% of the Gross National Products (GNP) of the most industrialized countries [4]. Moreover, it is assumed that about 40% of this GNP loss can be avoided by improving corrosion properties of engineering materials. It has been reported that the US and India lost more than $276 billion and IRs 800 billions, respectively, per annum on account of corrosion. Substantial portion of this could be saved if proper corrosion management system was adopted [5].

Different techniques were developed in the past to prevent deterioration of the engineering materials by corrosion. It is generally accepted that measures of corrosion protection by passivity were discovered in the early of the 18th century when the miraculous observation was reported that iron corrodes heavily in dilute aqueous solutions of nitric acid, but remains inert or passive as platinum metal in concentrated nitric acid solutions. Corrosion science received extra impetus with the beginning of the 20th century when stainless steels were widely used [2]. Corrosion problems appeared with widespread uses of steels with high tensile strengths and of steel enforced concrete. However, corrosion problems are encountered in all branches of industries. Corrosion scientists and engineers, therefore, strive to develop new materials with enhanced corrosion resistance properties. Technologists generally ignore the corrosion scenario during the initial stages of design hoping to check it later by additional surface treatments. However, in most cases it is wiser to take into account the corrosion resistance properties at an early stage of materials development. The applicability of any novel materials for industrial purposes and developmental areas is ultimately determined by their long term corrosion resistance in its environment.

In corrosion studies, the surface phenomenon plays a vital role. The surface reaction of interest include anodic dissolution (a fundamental corrosion reaction in which metal ions pass from surface to the solution), passivation (the formation of a thin layer of few nanometers of oxyhydroxide or hydroxide or salt on the metallic surface that protects metal surface against further dissolution or corrosion), and passivity breakdown (localized ruptures of the passive film) leading to localized corrosion and so on [2,6]. Understanding these surface phenomena is very important to find remedies to corrosion problems which are extremely costly. Furthermore, degradation of industrial materials can cause the shutdown of the entire processing system with subsequent loss of productivity, system reputation and money. In fact, the universal presence of corrosion makes it an ardent topic for the modern age.

1.2 ELECTROCHEMICAL THEORY OF CORROSION

Modern corrosion science stems from the local cell theory proposed by U. R. Evans and mixed potential theory by C. Wagner and W. Traud. These two marvelous theories are combined into the electrochemical theory of corrosion. According to the electrochemical theory of corrosion, the anodic current of metal dissolution (an electrochemical anodic oxidation) must be balanced with cathodic current on the metals. The cathodic reaction is the reduction of oxygen dissolved in the solution or / and the reduction of proton, that is, hydrogen evolution. The magnitude of the current of anodic and cathodic reactions must be equal. However, the direction is reversed in corrosion process. The model is known as a local cell model of corrosion in which the anodic and cathodic reactions take place on the same metal surface with a current of the same magnitude. The anodic and cathodic sites usually change location by time to time. Occasionally, the sites are fixed. Therefore, the corrosion of metallic substances is an electrochemical reaction and is explained by the local cell model in which both anodic and cathodic reactions simultaneously occur at individual anodic and cathodic sites. Since the anodic and cathodic reactions originate in different redox reactions, the corrosion potential (that is, the open circuit corrosion potential under the corrosion) is explained by the mixed potential theory. The mixed corrosion potential cannot be determined from thermodynamic equilibrium potential, but from a balance of electrochemical kinetics. Therefore, mixed potential theory is a versatile tool to have better understanding of corrosion of metallic substances (that is, metals or alloys) which are immersed in an electrolyte [7]. The mixed potential theory is composed of two hypotheses- (a) any electrochemical reaction may be divided into two or more oxidation and reduction partial reactions, and (b) the total rate of oxidation must be equal to the total rate of reduction. This is illustrated by the figure 1, for the case of a metal, M, immersed in an acidic electrolyte.

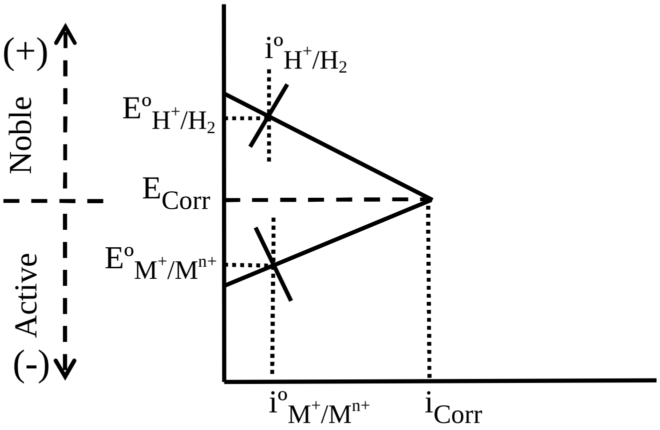

Figure 1: Schematic Evans diagram showing corrosion potential E_{corr} or open circuit corrosion potential (OCP) and corrosion current i_{corr}.

On the other hand, Professor Norio Sato of Japan proposed that the corrosion process involves not only electrochemical oxidation-reduction reactions but is also accompanied by acid-base reactions [8]. According to

Prof. Sato, anodic metal dissolution commences with the ionization of metal atoms on the surface and the metal ions hence produced on the surface are transferred into aqueous solution to form hydrated metal ions or metal ion complexes associated with anions as shown in the figure 2. The ionization of surface metal atoms is an electrochemical oxidation, whereas the hydration or complexation of metal ions is a chemical process that belongs to the Lewis acid-base reaction.

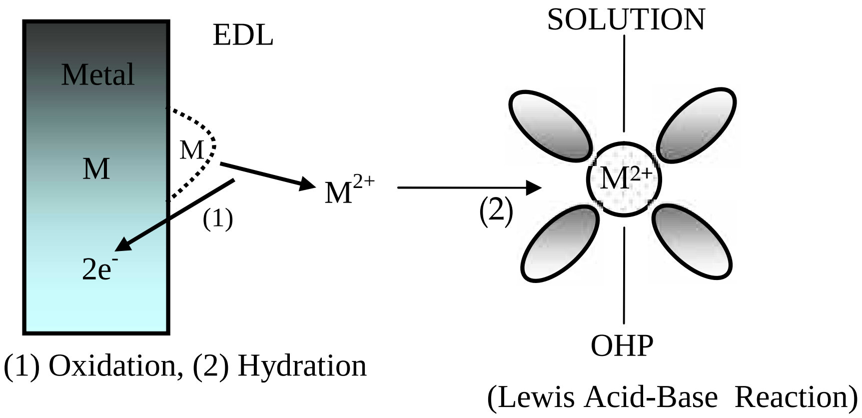

Figure 2: Anodic metal dissolution comprising of metal atom ionization (oxidation) and metal ion hydration (Lewis acid-base reaction)[8].

Corrosion of metals or alloys, no doubt, is an electrochemical reaction occurring on metals due to the influence of environment. The corrosion behavior of various metals can be compared by polarization measurements [9]. Some typical examples of the polarization curves are shown in the figure 3.

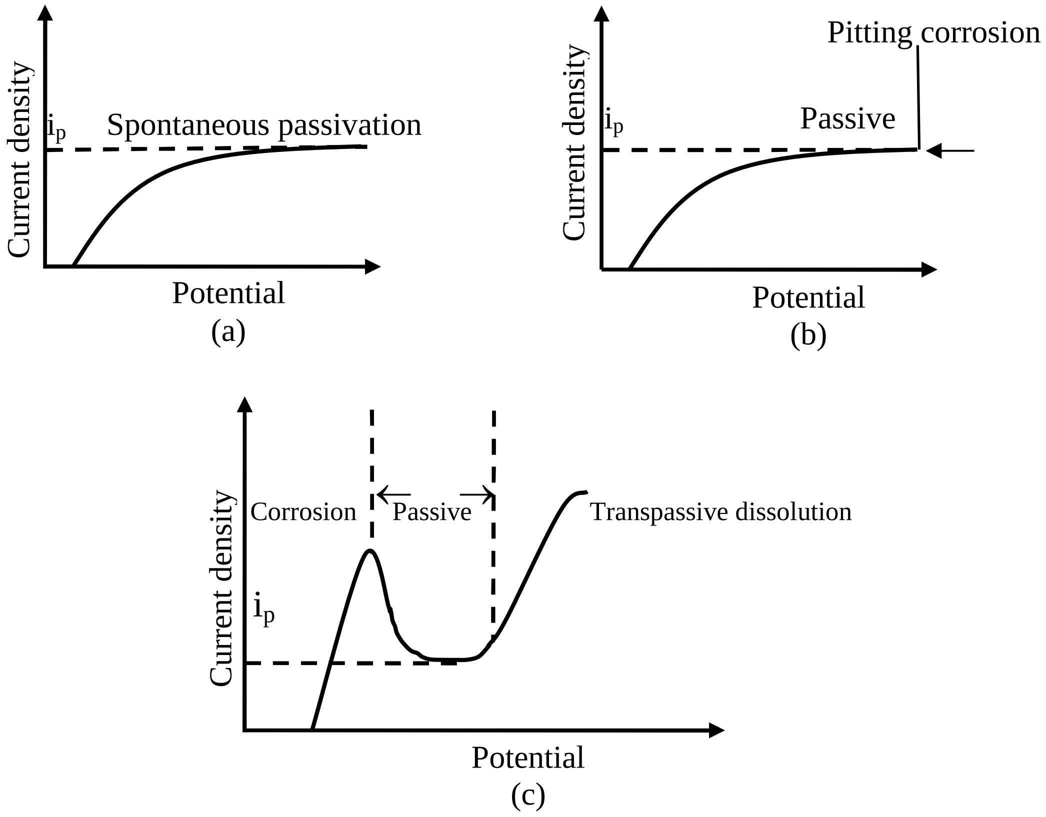

Figure 3: Polarization curves showing (a) spontaneous passivation, (b) pitting corrosion and (c) active-passive and transpassive dissolution.

Furthermore, the dissolution reaction of a metallic substance or an alloy (M) can be expressed as:

$$M \longrightarrow M^{n+} + ne^{-} \tag{1}$$

The corrosion of a metal involves oxidation reaction that happens at anode. The rate at which metal undergoes dissolution reaction can be measured in terms of anodic current density, (i_a), which is given by the following equation.

$$i_a = i^0_a \exp \alpha (E - E_m) \quad (2)$$

where, i^0_a is the equilibrium exchange current density at anode, α is a constant value for the reaction (1), E is the measured potential of the anodic reaction and E_m is the equilibrium potential of the anodic reaction.

The anodic current density (i_a) is generally increased logarithmically with increasing potential. A rise in potential results in the formation of a new corrosion product which is a stable solid product in the corrosive environments and able to cover the metal surface spontaneously as a result the dissolution rate of the metal is substantially decreased with polarisation of the materials. Ultimately, this leads to spontaneous passivation (curve 3.a). In the presence of aggressive ions such as halides in the corrosive medium, pitting corrosion can easily be detected whereby there is a sharp increased in the current density and developed pits on the surface by anodic polarization of the materials (curve 3.b). Anodic polarization of the materials, sometimes, causes transpassive dissolution as a result of the formation of soluble cations, which usually have higher valence than the cations of the same metal forming the passive film (curve 3.c).

Similarly, hydrogen ion and / or dissolved oxygen in the electrolytic solution undergo cathodic reactions on the surface of the material as:

$$2H^{+} + 2e^{-} \longrightarrow H_2 \qquad (3)$$

$$O_2 + 2H_2O + 4e^{-} \longrightarrow 4OH^{-} \qquad (4)$$

The rate of above cathodic reactions rises logarithmically with lowering of potential, E, as given in the equation (5).

$$i_C = i^0_C \exp\left[-\beta\left(E - E^0_C\right)\right] \qquad (5)$$

where, i_C is the cathodic current density, i^0_C is the equilibrium exchange current density at cathode, β is a constant value for the reaction 3 or 4 and E^0_C is the equilibrium potential for the cathodic reaction.

According to the mixed potential theory of corrosion, when a metallic substance is immersed in an electrolytic solution, both anodic and cathodic reactions go hand-in-hand with the same rate at the open circuit corrosion potential [9], that is:

$$i_a = i_c \qquad (6)$$

1.3 HISTORY OF SPUTTER-DEPOSITED METASTABLE METALLIC ALLOYS

It is generally believed that the preparation of alloys having a liquid like atomic arrangement requires ultra-rapid quenching of the alloy melt. Early in 1960s, amorphous and supersaturated solid solutions of metallic alloys prepared by rapid quenching attracted considerable attention from materials science communities, because of their technologically important properties such as physical, chemical, mechanical, magnetic, electronic and catalytic properties [10]. Professor P. Duwez, universally regarded as the father of rapid quenching from the liquid state, reported for the first time in 1960 a new metastable amorphous Au-25Si alloy [11]. After the preparation of the amorphous Au-25Si alloy, Duwez and his coworkers developed a series of new metastable amorphous or nanocrystalline single-phase solid solution by using various techniques like vapor quenching, electrodeposition, mechanical alloying and so on. Among these techniques, the vapor quenching method is one of the widely used methods to prepare a homogeneous mixture of components.

Sputtering is one of the main methods of vapor quenching techniques and used as one of the potential methods for the preparation of varieties of amorphous or nanocrystalline alloys [12]. In recent years, this technique is known to form amorphous or nanocrystalline structures over the widest composition range among the various methods. Therefore, the use of sputtering is quite suitable for tailoring of the corrosion–resistant metastable alloys. Furthermore, even if amorphous alloys are not formed by the sputter deposition technique, the alloys thus prepared are always composed of nanocrystals with very fine grains (that is, less than 20 nm) and sometimes behaves similar to the single-phase amorphous alloys. In particular, sputtering is suitable for forming alloys when the boiling point of one of the alloying component is lower than the melting point of the other alloying components, because sputter deposition does not require melting of alloying components for the alloy formation. For instance, boiling points of chromium (2670°C) and nickel (2900°C), which are far lower than the melting point of tungsten (3420°C). However, successful attempts were reported to prepare single-phase amorphous or nanocrystalline W-Cr [13], W-Ni [14,15] and W-Cr-Ni [16] alloys by using the advantages of sputtering.

Furthermore, sputtering is one of the most important techniques for coatings, and its feasibility for preparing corrosion-resistant amorphous layer on the surface of stainless steel has been reported by Nowak [17] and Anderson et al. [18]. The importance of the sputter deposition method for the coating on stainless steel will be discussed later in the section of literature survey of this thesis.

1.4 STRUCTURE AND CORROSION BEHAVIOR OF METASTABLE ALLOYS

Amorphous or / and nanocrystalline structures are usually believed to be free from crystal defects such as grain boundaries and precipitates acting as nucleation sites for corrosion, and the chemically homogeneous single-phase nature of amorphous or nanocrystalline alloys are responsible for their high corrosion resistance owing to the formation of protective passive films that are able to separate the bulk of alloys from aggressive environments. On the other hand, according to Heusler and Huerta, the extremely high corrosion resistance of the sputter-deposited alloys has been explained on the basis of homogeneity of the alloy [19].

1.5 ROLES OF TUNGSTEN, CHROMIUM AND NICKEL IN THE CORROSION RESISTANCE OF ALLOYS

Tungsten, chromium and nickel are regarded as very effective alloying elements for enhancing the corrosion resistance of the alloys in aggressive environments. Tungsten is corrosion-resistant particularly in non-oxidizing environments. With reference to potential-pH diagram of tungsten, it can be referred that tungsten is hardly corroded by most of acid solutions, except some complexing acids which attack it. However, tungsten metal may corrode in neutral and basic solutions as shown in the figure 4 [20].

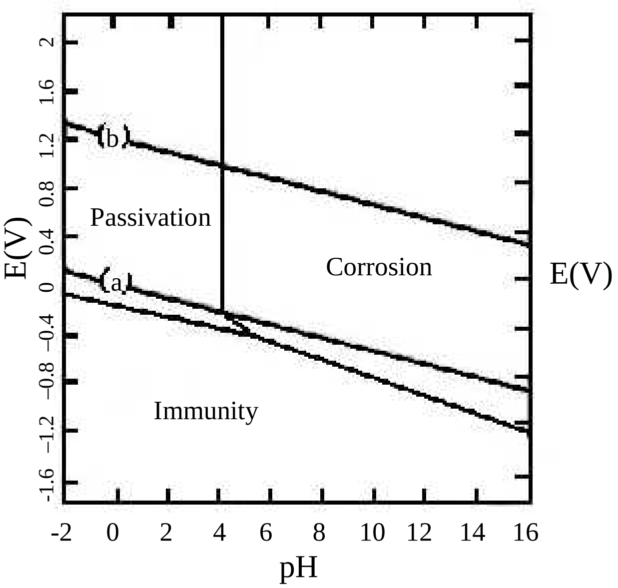

Figure 4: Theoretical domains of corrosion, immunity and passivation of tungsten at 25^{0}C [20].

Furthermore, it has been reported that the addition of small amount of tungsten to stainless steels increased the corrosion resistance [21,22]. Several surface studies have been carried out for the better understanding of the role of tungsten in the passivity of stainless steels in aggressive chloride media [21, 23-26]. It has been also reported that the addition of a small amount of tungsten to amorphous Fe-P-C alloys with or without chromium

[27-30] to Ni-Fe alloys [31] and to the amorphous Ni-P alloys [32] is effective in improving the corrosion resistance of these alloys in aggressive hydrochloric acids. Similarly, the addition of only a small amount of tungsten, that is, less than 10 at %, is enough to cause spontaneous passivation of the sputter-deposited W-91Cr alloy even in 12 M HCl and the alloy showed about five orders of magnitude lower corrosion rate than the corrosion rate of chromium metal [13, 33].

On the other hand, nickel is widely used as alloying element for preparing the corrosion-resistant amorphous or nanocrystalline alloys. Amorphous nickel-base alloys exhibited very high corrosion resistance in boiling hydrochloric acids [34-36]. Lee et al. [37,38] reported a beneficial effect of tantalum to improve the corrosion resistance of nickel-base alloys in 12 M HCl. Furthermore, the corrosion resistance of nickel depends on the pH and oxidizing agents. According to the potential-pH diagram, nickel is very corrodible in acidic or very alkaline solutions containing oxidizing agents [39]. However, it does not generally corrode in neutral or slightly alkaline oxidizing solutions, mostly due to the formation of nickel hydroxide or oxides as shown in figure 5 [39].

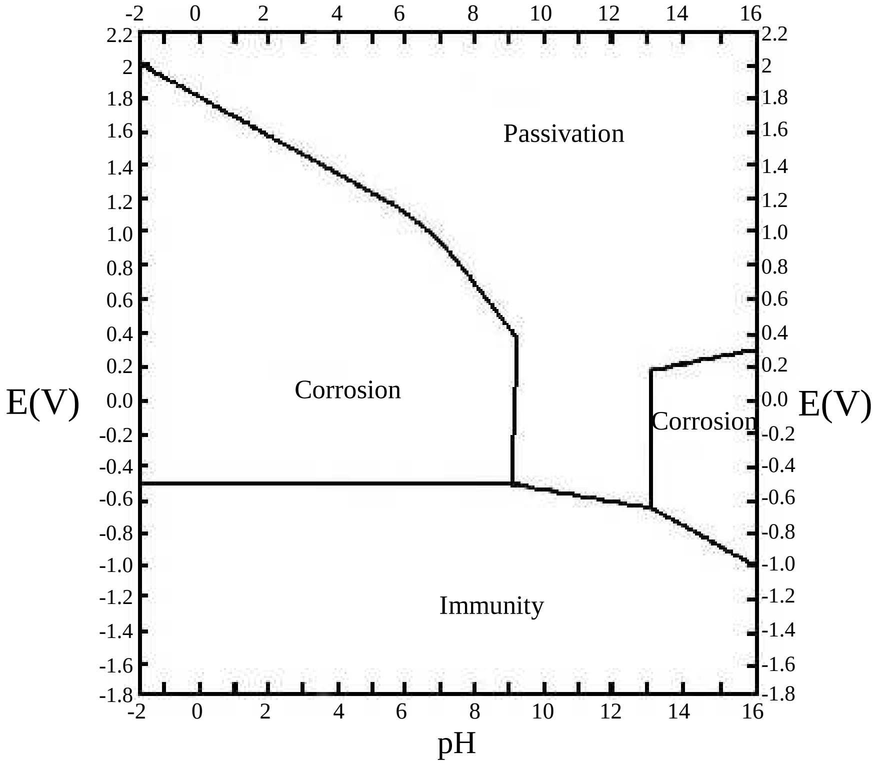

Figure 5: Theoretical domains of corrosion, immunity and passivation of nickel at 25^{0}C [39].

It has been reported that the corrosion resistance of the sputter-deposited amorphous or / and nanocrystalline W-Ni alloys in 12 M HCl solution having the pH value less than one in which regions tungsten is passive and nickel is active, are passivated spontaneously and observed significantly high corrosion resistance [14,15]. Similarly, nickel metal acts synergistically with tungsten in enhancing the corrosion resistance of the W-Ni alloys in neutral 0.5 M NaCl and alkaline NaOH solutions [40-43].

Chromium is one of the most effective alloying elements to provide a high passivating ability for conventional steels and nickel-base alloys. Only a small amount of chromium (8 at %) addition was enough to cause spontaneous passivation of Fe-Cr alloys in 1 M HCl and these alloys showed significantly higher pitting corrosion resistance than stainless steels [44]. It has been reported that a thin oxide film containing a high concentration of chromium enhances the passivity for ferritic stainless steels in aggressive environments [45]. A series of the sputter-deposited binary chromium-valve metal (Al, Ni, Ti, Mo, Nb, Ta and W) alloys exhibited superior corrosion resistance compared to chromium metal in aggressive environments [13,46-52]. It has also been reported that the addition of chromium is synergistically effective in enhancing the corrosion resistance of Al-Cr-Mo alloys in 1 M HCl hydrochloric acid [53]. It has been recently reported that the corrosion of chromium proceeds by electrochemical and chemical reactions in sulfuric acid [54].

Furthermore, regarding the potential-pH diagram of chromium metal, chromium is very corrodible in acidic or very alkaline solutions as shown in figure 6 [55]. However, chromium does not generally corrode in neutral or slightly alkaline solutions, mostly due to the formation of chromium hydroxide or oxides. Therefore, in present work, the effect of chromium on the passivation behavior of the sputter-deposited W-Cr-(4-15)Ni alloys containing 42 to 75 at % chromium is studied in 0.5 M NaCl and different concentrations of NaOH solutions.

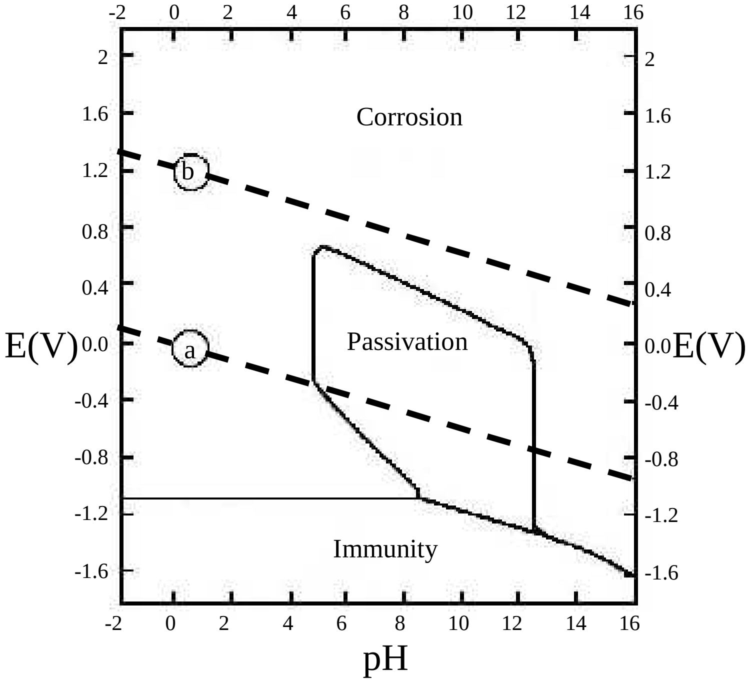

Figure 6: Theoretical domains of corrosion, immunity and passivation of chromium at 25^0C [55].

1.6 LITERATURE SURVEY

The research activities on amorphous or / and nanocrystalline alloys produced by liquid quenching are of widespread interest in the field of materials science during the last five decades. When Brenner et al. [56]

reported the fact that the amorphous nickel- and cobalt- base alloys were formed by electro-deposition from electrolytic solution containing phosphate, they described the corrosion properties of the electro-deposited alloys. The development of novel metastable amorphous alloys with unique properties encouraged corrosion scientists to explore chemical properties of the amorphous or nanocrystalline alloys because, some amorphous or nanocrystalline alloys showed extremely high corrosion resistance in aggressive media [57-59]. Hoar et al. [60,61] reported that binary Ti-Mo and Ti-Ta alloys show high corrosion resistance due to the formation of mixed or compound type of oxides on the surface of the alloys without defective grain boundaries. The detail of the fifty years history of the rapidly-quenched and the sputter-deposited corrosion resistance amorphous or/and nanocrystalline metallic alloys has been recently discussed by Bhattarai [10].

Since it was found that the rapidly-quenched amorphous iron-base alloys [57,62-64] containing less than 10 at % chromium showed extremely high corrosion resistance as compared to crystalline alloys in aggressive chloride containing acidic and neutral environments, varieties of corrosion-resistant amorphous cobalt-[65], nickel-[34-38] and copper- [66-69] base alloys were reported. The extremely high corrosion resistance of these rapidly-quenched alloys has been explained on the basis of the homogeneity of the amorphous alloys [57-59, 70-72]. Extensive studies were carried out to clarify the effect of metallic elements (M = Ti, Zr, Nb, Cr, Mo, W, Mn, Co, Ni, Cu, V, Ru, Rh, Pd or Pt) in the corrosion behavior of amorphous Fe-M-13P-7C alloys [43,73,74].

It has already been pointed out that the sputtering is one of the potential methods for the preparation of varieties of corrosion-resistant amorphous or nanocrystalline metastable alloys. Anderson et al. [18] studied the corrosion behavior of the sputter-deposited amorphous Ni-Nb coatings on commercial 316L stainless steel in different aggressive media and they found that the amorphous or nanocrystalline Ni-Nb coatings have good corrosion resistance. Furthermore, successful attempts were reported to prepare the corrosion-resistant single-phase amorphous aluminum-refractory metal (Mo, W, Nb and Ta) [75-77] and magnesium-transition metal (Ti, Zr, Nb and Ta) [78] alloys by using advantages of sputtering. Shimamura et al. [79,80] reported that the sputter-deposited amorphous Ni-Ta, Cu-Ta and Cu-Nb alloys were spontaneously passivated in 12 M HCl solution, showing a very high corrosion resistance. Yashioka et al. [81,82] reported extremely high corrosion resistance of the sputter-deposited Al-Nb and Al-Ta alloys, and these alloys were immune to corrosion in 1 M HCl at 30°C. Furthermore, a series of sputter-deposited binary chromium-metalloid alloys showed superior corrosion resistance compared to pure chromium in aggressive media [83-86].

Further studies of the sputter-deposited aluminum-transition metal (Zr, Nb, Ta, Mo and W) alloys were carried out in early 1990's by Yashioka et al. [87-92]. All these aluminum-base alloys were spontaneously passivated in 1 M HCl. It is noteworthy to mention here that all these alloys discussed above showed high corrosion resistance in aggressive media even though these alloys did not show higher corrosion resistance than those of alloy-constituting elements of alloys before the early 1990's.

In general, designing of corrosion-resistant alloys is carried out to bring the corrosion resistance of the alloys close to that of the corrosion-resistant alloy-constituting elements. However, the most interesting fact is observed since the beginning of 1990's that the corrosion rates of some sputter-deposited amorphous or nanocrystalline alloys are lower than those of alloy-constituting elements in aggressive media [93].

Various amorphous or nanocrystalline chromium-transition metal (aluminum, titanium, zirconium, niobium and tantalum) alloys were prepared by sputter deposition technique, and their corrosion rates were reported lower than those of the alloy-constituting elements in hydrochloric acid solutions [47,48-51]. Furthermore, the sputter-deposited amorphous or nanocrystalline molybdenum-transition metal (titanium, zirconium, niobium and tantalum) alloys showed higher corrosion resistance than those of the alloy-constituting elements in 12 M HCl solution at 30°C similar to the sputter-deposited amorphous chromium-transition metal alloys [52, 94-96]. Such interesting findings of the lower corrosion rates of chromium- and molybdenum-transition metal alloys than those of alloy-constituting elements have recently encouraged scientists to tailor new series of highly corrosion resistance binary tungsten-transition metal (titanium, zirconium, niobium, tantalum, molybdenum, chromium and nickel) alloys by sputtering [13-16,33,93,97-114]. The sputter-deposited amorphous and /or nanocrystalline tungsten-transition metal alloys showed higher corrosion resistance than those of the alloy-constituting elements similar to the sputter-deposited chromium- and molybdenum-transition metal alloys in hydrochloric acid solutions. Furthermore, the sputter-deposited W-Nb [115-118], W-Mo [118,119], W-Ni [40-43,118], and W-Ti [118,120-121] alloys which are composed of either an amorphous or a nanocrystalline single-phase showed high corrosion resistance in NaCl and NaOH solutions.

In particular, only small amount of tungsten addition (that is, less than 10 at %) was enough to cause spontaneous passivation of the sputter-deposited nanocrystalline W-Cr alloys even in 12 M HCl and these alloys showed about five orders of magnitude lower corrosion rate than the corrosion rate of chromium metal, and about one order of magnitude lower corrosion rate than that of tungsten [13,33]. Similarly, it has been reported that the corrosion resistance of the sputter-deposited amorphous or nanocrystalline W-Ni alloys were passivated spontaneously and observed significantly high corrosion resistance in aggressive environments [15,40-43]. The corrosion rates of the sputter-deposited W-Ni alloys cannot exceed that of tungsten although the addition of tungsten greatly enhances the corrosion resistance of nickel in 12 M HCl and 0.5 M NaCl solutions. However, nickel acts synergistically with tungsten in enhancing the corrosion resistance of the sputter-deposited W-Ni alloys so as to show higher corrosion resistance than those of alloys-constituting elements (that is, tungsten and nickel) in 1 M NaOH at 25^0C [42]. It has been also reported that the additions of nickel and chromium in the binary tungsten-base alloys enhances the corrosion resistance of the sputter-deposited W-Cr-Ni alloys in 12 M HCl at 30^0C [16].

In these contexts, one more step is pursued in this research work to study the effects of chromium and nickel on the passivation behavior of the sputter-deposited ternary W-Cr-(4-15)Ni alloys in 0.5 M NaCl and NaOH solutions at 25^0C.

1.7 OBJECTIVES OF THE STUDY

A novel corrosion resistance properties of the rapidly-quenched alloys even in aggressive environments generated tremendous interest for corrosion scientists. Since the extremely high corrosion resistance amorphous iron-base alloys were reported, a varieties of corrosion-resistant alloys were developed during the last four decades. By the end of 1990's, it has been reported that the sputter-deposited tungsten-transition metal (titanium, zirconium, chromium, niobium, tantalum, molybdenum and nickel) alloys showed higher corrosion resistance than those of alloy-constituting elements in concentrated hydrochloric acid solutions at 30°C. Furthermore, in recent years, tungsten-, nickel- and chromium-based alloys are used in diverse fields of science and technology like electronic, electrodes and catalysts. Therefore, it is very interesting to study the effects of chromium and nickel on the passivation behavior of the sputter-deposited W-Cr-(4-15)Ni alloys containing 42-75 at % chromium in 0.5 M NaCl and NaOH solutions at 25°C, open to air. The main objectives of this study are as follows:

(a) to estimate the corrosion rates of the sputter-deposited amorphous or nanocrystalline W-Cr-(4-15)Ni alloys in 0.5 M NaCl and in 1 M NaOH solutions at 25°C, open to air.

(b) to study the electrochemical behavior of the sputter-deposited W-Cr-(4-15)Ni alloys in 0.5 M NaCl and in different concentrations of NaOH solutions at 25°C, and

(c) to study the effects of chromium and nickel in the passivation behavior of the sputter-deposited W-Cr-(4-15)Ni alloys.

CHAPTER - II

EXPERIMENTAL METHOD

2.1 SPUTTER-DEPOSITED W-Cr-(4-15)Ni ALLOYS

All the sputter-deposited W-Cr-(4-15)Ni alloys used to carry out this research work were provided by Dr. Jagadeesh Bhattarai of Central Department of Chemistry, Tribhuvan University, Nepal. The apparatus used and conditions subjected for sputter deposition of the alloys were same as those described elsewhere [14,93]. The provided sputter-deposited W-Cr-(4-15)Ni alloys containing 42-75 at % chromium have been characterized as single-phase solid solutions of amorphous or nanocrystalline structures having apparent grain size ranges from 1.5 to 10.2 nm as summarized in Table 1[16]. The compositions of the sputter-deposited W-Cr-(4-15)Ni alloys hereafter are all denoted in atomic percentage (at %).

2.2 CORROSION TEST

Corrosion tests of the sputter-deposited amorphous or nanocrystalline W-Cr-(4-15)Ni alloys were carried out in 0.5 M NaCl and 1 M NaOH solutions at 25 ± 1^0C, open to air. Prior to corrosion tests, the surface of each specimen of the alloys, which was cut into pieces having the area of 25 to 50 cm^2, was mechanically polished with silicon carbide paper grit number 1500, rinsed with acetone and dried with air blower. The weight loss method was used to estimate the corrosion rate of the alloys. The specimens of alloys were immersed in 0.5 M NaCl and 1 M NaOH solutions for 168 hours. The loss of weight of specimens of various alloys was calculated from the difference of weights of the specimens before and after immersion in the electrolytic solutions. The measurement of corrosion rate by weight loss method was done two times or more so as to get precise results. The average corrosion rate of individual alloy was estimated by using the following equation [115].

$$\text{Corrosion Rate (mm y}^{-1}\text{)} = \frac{\Delta w \times 8760 \times 10}{d \times A \times t} \tag{7}$$

where,

Δw = weight loss of the specimen of the alloy in gram,

d = density of the specimen of the alloy in gm/cm^3,

A = area of the specimen of the alloy in cm^2, and

t = time of immersion in hour

2.3 ELECTROCHEMICAL MEASUREMENTS

2.3.1 Preparation of alloy specimens

The sputter-deposited W-Cr-(4-15)Ni alloys were cut into small pieces of 20 to 30 mm in length and 10 mm in width. Each specimen was mechanically polished with silicon carbide paper as described in previous section 2.2. The alloy specimen was clipped by the sample holder that was made by welding the crocodile pin with a stainless steel rod. The specimen was immersed in an electrolyte in such a way that about 100 mm^2 area of the alloy specimen was used for electrochemical measurements. All the electrochemical measurements were performed two times or more so as to obtain precise result.

2.3.2 Electrolytic solutions

The electrolytes used in the electrochemical measurements were 0.5 M NaCl and different concentrations of NaOH solutions at 25 ± 1^0C, open to air.

2.3.3 Electrodes

A saturated calomel electrode (SCE) and a platinum mesh were used as the reference and counter electrodes, respectively. An alloy specimen was used as a working electrode.

2.3.4 Measurement of open circuit corrosion potential

The open circuit potential (OCP) of the W-Cr-(4-15)Ni alloys specimens in different electrolytic solutions at 25 ± 1^0C, open to air, were measured using a potentiometer. The readings were taken immediately after immersion of the alloy specimen in the electrolytic solutions of NaCl and NaOH for two hours. The electrochemical measurements were repeated two times or more to get precise results.

Table: 1 Chemical composition, structure and apparent grain size of the sputter-deposited W-Cr-(4-15)Ni alloys [16]

Name of alloy	Structure	Apparent grain size (nm)
W-42Cr-5Ni	Amorphous + Nanocrystalline	3.5
W-63Cr-15Ni	Amorphous	1.6
W-67Cr-9Ni	Amorphous	1.5
W-75Cr-4Ni	Amorphous + Nanocrystalline	10.2
Tungsten	Nanocrystalline	20
Nickel	Nanocrystalline	19
Chromium	Nanocrystalline	40

CHAPTER – III

RESULTS AND DISCUSSION

3.1 CORROSION RATES OF SPUTTER-DEPOSITED W-Cr-(4-15)Ni ALLOYS

The corrosion rates of the sputter-deposited amorphous or nanocrystalline W-Cr-(4-15)Ni alloys were estimated from the weight loss after immersion for 168 hours in 0.5 M NaCl and 1 M NaOH solutions at 25°C, open to air. The weight loss for each alloy was estimated two times or more and the average corrosion rate was calculated. The time dependence of the corrosion rate of the alloys was also estimated at various time intervals.

3.1.1 Corrosion rate in 0.5 M NaCl solution

Figure 7 shows the change in corrosion rates of the sputter-deposited W-Cr-(4-15)Ni alloys after immersion for 168 hours in 0.5 M NaCl solution at 25°C. Corrosion rates of the sputter-deposited W-(7-15)Ni alloys, tungsten, chromium and nickel metal are also shown for comparison. Corrosion rates of tungsten, chromium and nickel are about 2.5×10^{-2} mm.y^{-1}, 7.4×10^{-3} mm.y^{-1} and 3.0×10^{-1} mm.y^{-1}, respectively, in 0.5 M NaCl solution. Corrosion rates of the W-Cr-(4-15)Ni alloys containing 42-75 at%

chromium are about one order of magnitude lower than those of the sputter-deposited W-(7-15)Ni alloys and tungsten, and even lower than that of the sputter-deposited chromium. These results clearly revealed that the addition of chromium to the W-(7-15)Ni alloys is effective in enhancing the corrosion resistance of the sputter-deposited W-Cr-(4-15)Ni alloys in 0.5 M NaCl solution.

The nature of passive films formed on the W-Cr-(4-15)Ni alloys play a vital role for high corrosion resistance of the alloys. The passivation of the alloys generally occurs through the active dissolution of alloys at the initial periods of immersion in a solution. The high chemical reactivity of the alloys leads to the rapid accumulation of a beneficial species in the passive films formed on the alloys. This accounts for the high corrosion resistance of the alloys. Therefore, it is important to identify the role of immersion time for rational understanding of the corrosion behavior of the alloys.

In order to clarify the time dependence of corrosion rate of the sputter-deposited W-Cr-(4-15)Ni alloys, the corrosion rates of the W-42Cr-5Ni, W-63Cr-15Ni and W-75Cr-4Ni alloys, and the sputter-deposited chromium metal were measured after immersion in 0.5 M NaCl solution at various time intervals. Figure 8 shows the changes in the corrosion rates of the W-Cr-(4-15)Ni alloys including chromium metal in 0.5 M NaCl solution at 25°C, as a

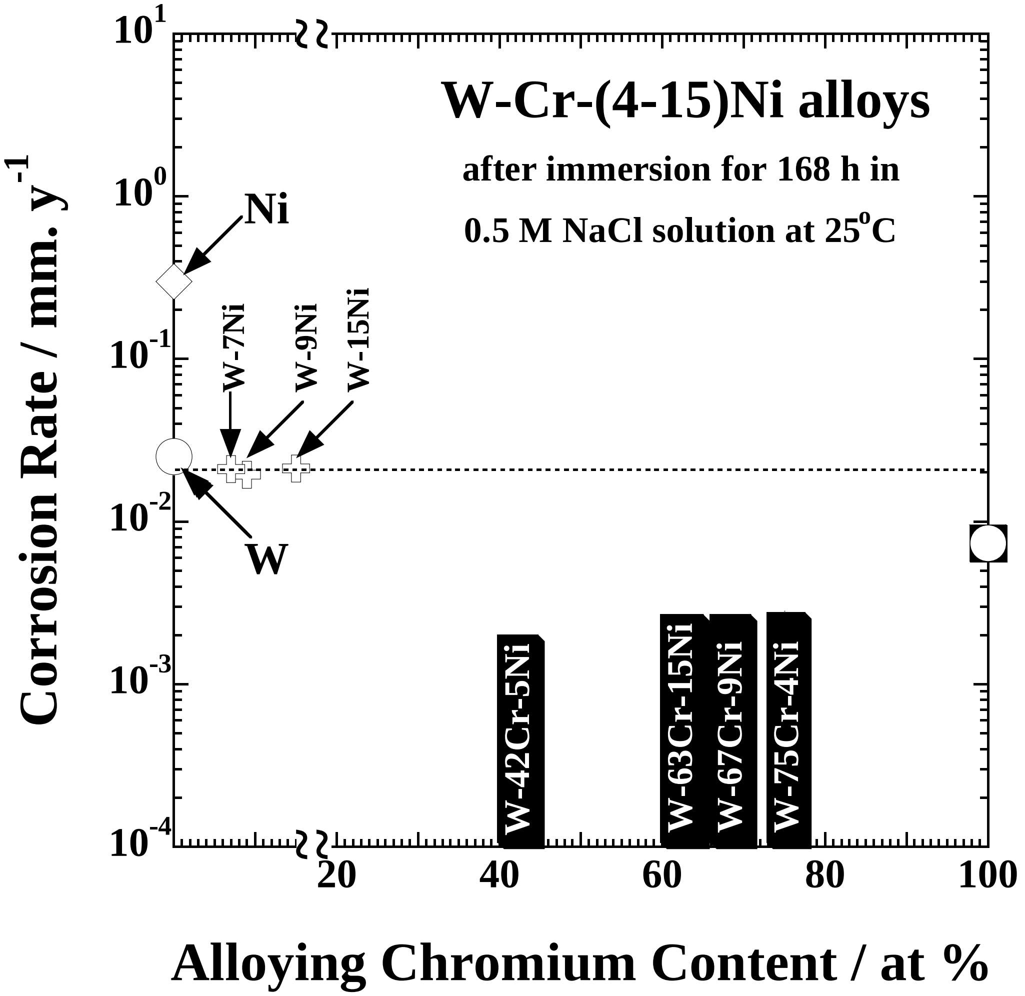

Figure 7: Changes in corrosion rates of the sputter-deposited W-Cr-(4-15)Ni alloys including W-(7-15)Ni alloys[43], tungsten, nickel and chromium metal in 0.5 M NaCl solution at 25°C, as a function of chromium content.

function of immersion time. In general, the corrosion rates of the W-Cr-(4-15)Ni alloys are significantly high at initial period of immersion (for example, for about 2-6 h). The corrosion rate is decreased with immersion time till 24 h for the W-42Cr-5Ni alloy, and decreased till 48 h for the W-63Cr-15Ni, W-75Cr-4Ni alloys and the chromium metal in 0.5 M NaCl solution. Accordingly, initially fast dissolution of the W-42Cr-5Ni alloy results in fast passivation by forming more protective passive films in comparison with the W-63Cr-15Ni and W-75Cr-4Ni alloys and the chromium metal in 0.5 M NaCl solution at 25°C. As a result, the average corrosion rate of the W-42Cr-5Ni alloy is slightly lower than those of the W-63Cr-15Ni, W-75Cr-4Ni alloys after immersion for 168 h as shown in figure 7 also.

3.1.2 Corrosion rate in 1 M NaOH solution

Figure 9 shows the change in the corrosion rates of the sputter-deposited W-Cr-(4-15)Ni alloys after immersion for 168 h in 1 M NaOH solution at 25°C. The corrosion rates of the sputter-deposited W-(7-15)Ni alloys, tungsten, chromium and nickel metals are also shown for comparison. The corrosion rates of tungsten, chromium and nickel are about 3.5×10^{-1} mm.y^{-1}, 2.2×10^{-2} mm.y^{-1} and 4.9×10^{-3} mm.y^{-1}, respectively. It is noteworthy to mention here that corrosion rates of the sputter-deposited W-

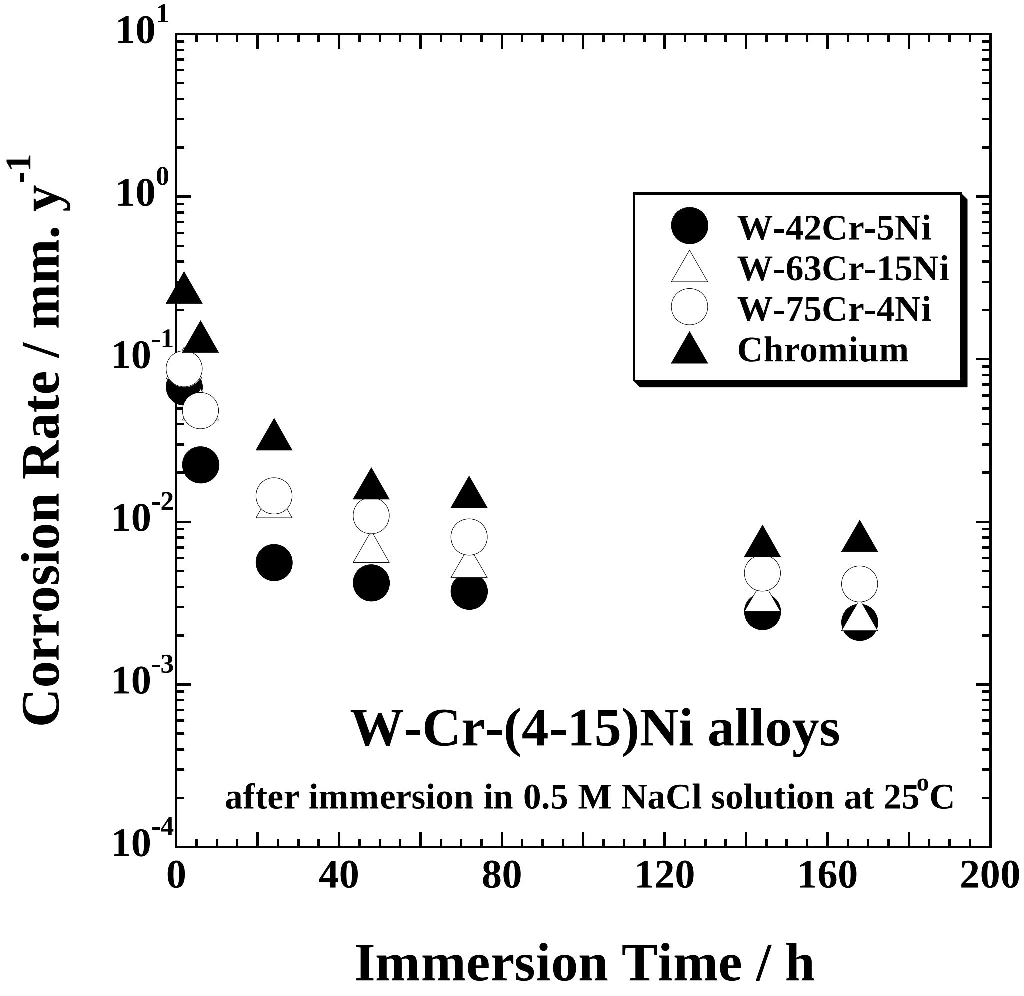

Figure 8: Changes in corrosion rates of the sputter-deposited W-Cr-(4-15)Ni alloys and chromium metal in 0.5 M NaCl at 25 °C, as a function of immersion time.

7Ni, W-9Ni and W-15Ni alloys were 3.0×10^{-1}, 2.2×10^{-1} and 2.1×10^{-2} mm/y, respectively, in 1 M NaOH solution at 25°C [42], and shown here the corrosion rates for comparison with W-Cr-(4-15)Ni alloys. Corrosion rates of the W-Cr-(4-15)Ni alloys containing 42-75 at% chromium are about two orders of magnitude lower than those of the sputter-deposited W-(7-9)Ni alloys and tungsten, and about one order of magnitude lower than that of the sputter-deposited deposited W-15Ni alloy and chromium metal in 1 M NaOH solution. These results clearly revealed that all the examined sputter-deposited W-Cr-(4-15)Ni alloys, which are composed of either amorphous or /and nanocrystalline single phase solid solution, show higher corrosion resistance than those of alloy-constituting elements (that is, tungsten, chromium and nickel) even for prolonged immersion in an aggressive 1 M NaOH solution at 25°C. Consequently, the addition of chromium to the sputter-deposited W-Ni alloys is very effective in enhancing the corrosion resistance in alkaline NaOH solutions.

Furthermore, to clarify the time dependence of corrosion rate of the sputter-deposited W-Cr-(4-15)Ni alloys in alkaline NaOH, the corrosion rates of the W-42Cr-5Ni, W-63Cr-15Ni and W-75Cr-4Ni alloys were calculated after immersion for various time intervals. Figure 10 shows the changes of corrosion rates of the W-Cr-(4-15)Ni alloys including chromium

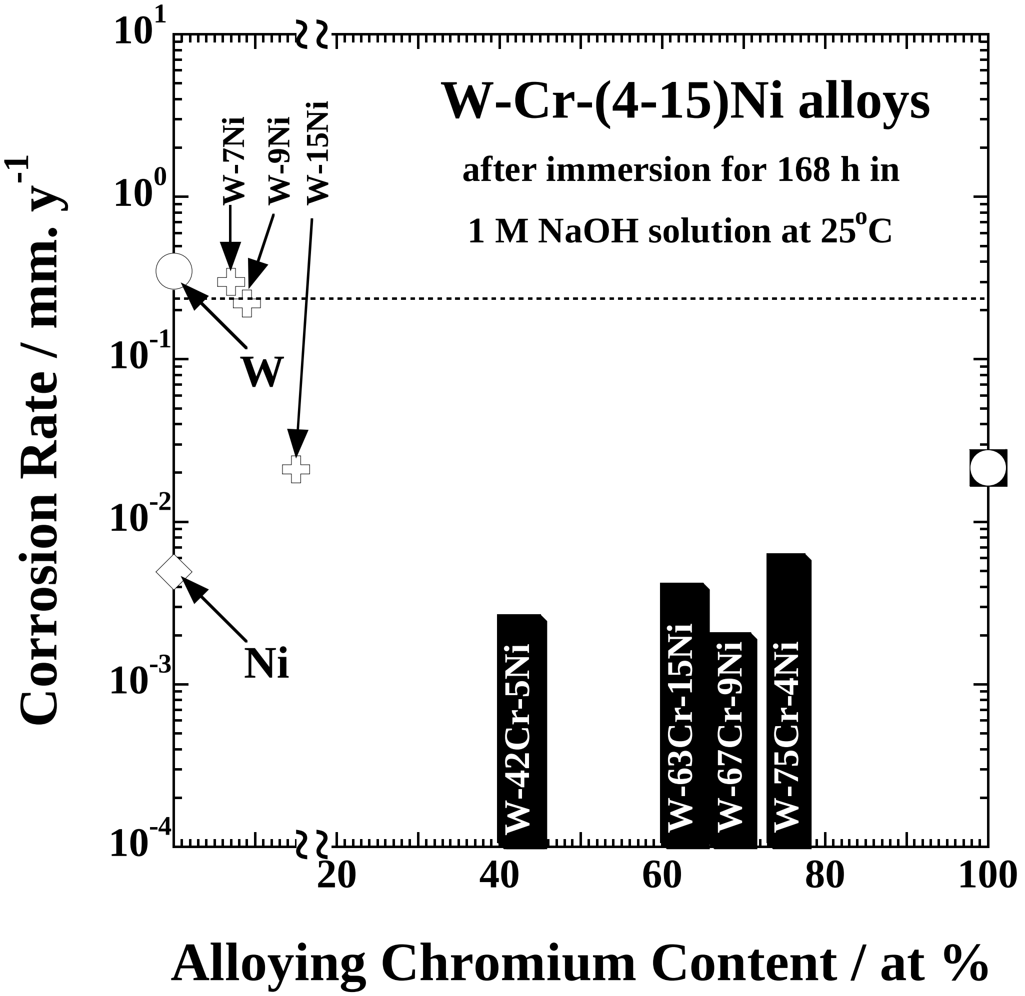

Figure 9: Changes in corrosion rates of the sputter-deposited W-Cr-(4-15)Ni alloys including W-(7-15)Ni alloys[42], tungsten ,nickel and chromium metal in 1 M NaOH solution at 25°C, as a function of chromium content.

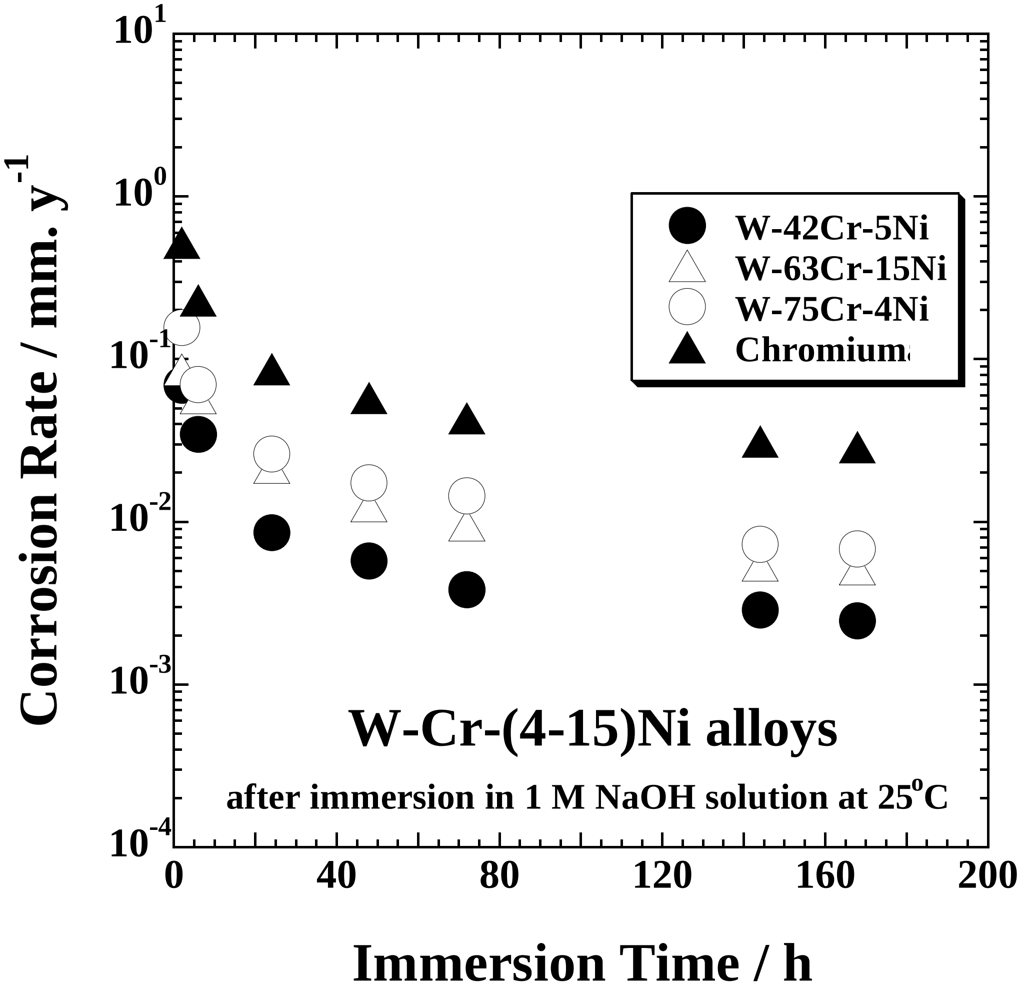

Figure 10: Changes in corrosion rates of the sputter-deposited W-Cr-(4-15)Ni alloys and chromium metal in 1 M NaOH solution at 25 °C, as a function of immersion time.

metal in 1 M NaOH solution at 25°C, as a function of immersion time. The corrosion rates of all the examined W-Cr-(4-15)Ni alloys and chromium metal are generally high at initial periods of immersion (for example, for about 2-24 h). The corrosion rate is decreased with immersion time till 48 h and after that the corrosion rates of the W-Cr-(4-15)Ni alloys including chromium metal become nearly steady in 1 M NaOH solution at 25°C.

3.2 ELECTROCHEMICAL MEASUREMENTS OF SPUTTER-DEPOSITED W-Cr-(4-15)Ni ALLOYS

Electrochemical measurements were carried out for a better understanding of the passivation behavior and high corrosion resistance properties of the sputter-deposited amorphous or nanocrystalline W-Cr-(4-15)Ni alloys in 0.5 M NaCl and different concentration of NaOH solutions at 25°C, open to air.

3.2.1 Open circuit potential in 0.5 M NaCl solution

Figure 11 shows the changes in open circuit potentials for the sputter-deposited W-Cr-(4-15)Ni alloys as well as the tungsten, chromium and nickel metals in 0.5 M NaCl solution at 25°C, as a function of immersion time. The open circuit potentials of the chromium and nickel are about –570 and –440 mV (SCE), respectively, after immersion for 2 seconds and gradually increases with immersion time up to about –70 and – 60 mV (SCE) after immersion for 2 h. The open circuit potential of the tungsten metal reaches a stationary value of about – 635 mV (SCE) within 20 minutes. The open circuit potentials of all the examined sputter-deposited W-Cr-(4-15)Ni alloys are shifted towards more noble (or positive) direction with immersion time. The ennoblement of the open circuit potentials of the W-63Cr-15Ni, W-67Cr-9Ni and W-75Cr-4Ni alloys are clearly observed as compared to those of the W-42Cr-5Ni alloy, chromium, nickel and tungsten metals. The open circuit potential of the W-42Cr-5Ni alloy is located between those of chromium, nickel and tungsten metals. In contrast, the open circuit potentials of the W-63Cr-15Ni, W-67Cr-9Ni and W-75Cr-4Ni alloys are shifted to more positive direction than those of chromium and nickel metals in 0.5 M NaCl solution. These facts coincide with the change in the corrosion rates of the W-Cr-(4-15)Ni alloys as shown in figures 7 and 8. These results revealed that the sputter-deposited W-Cr-(4-15)Ni alloys containing an adequate amount of tungsten show the more stable passivity and show higher corrosion resistance than those of alloy-constituting elements (that is, tungsten, chromium and nickel) in neutral 0.5 M NaCl solution.

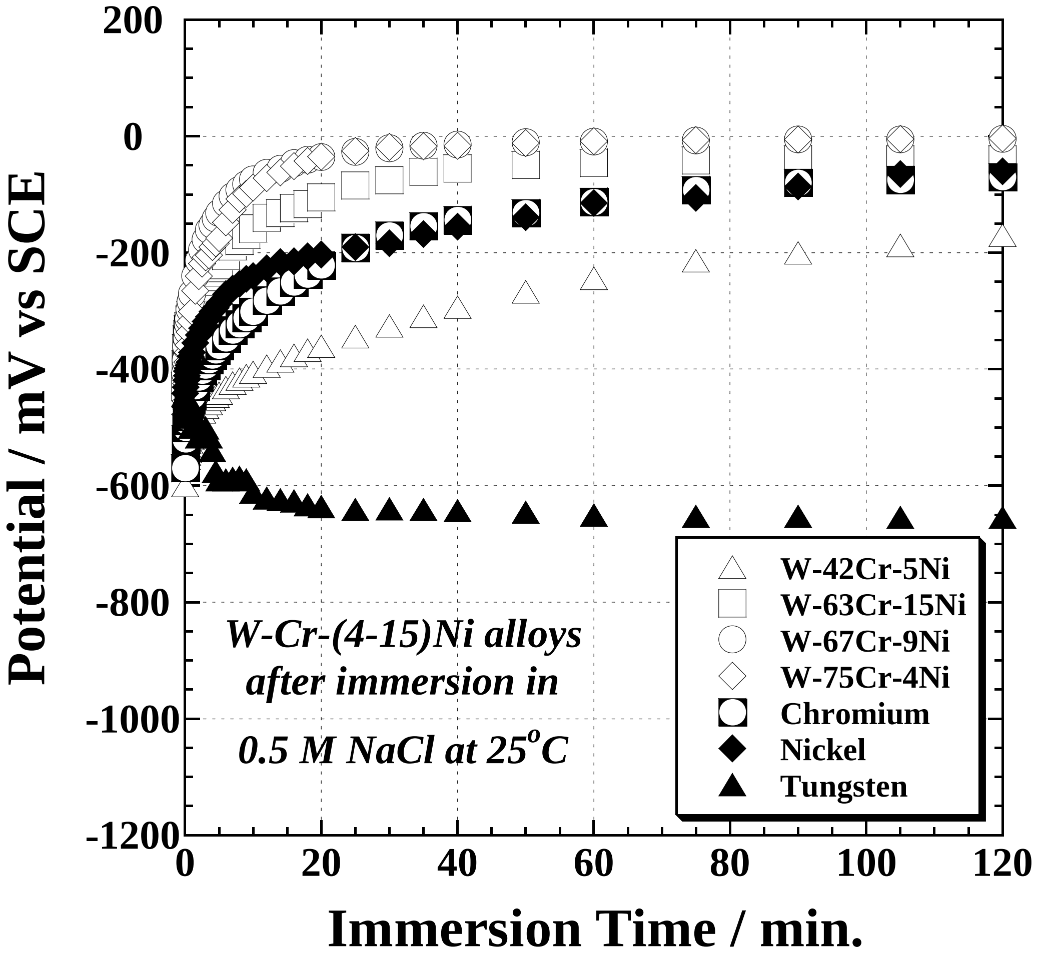

Figure 11: Changes in open circuit potentials for W-Cr-(4-15)Ni alloys including tungsten, chromium and nickel metals in 0.5 M NaCl solution at 25°C, as a function of immersion time.

3.2.2 Open circuit potential in NaOH solutions

Figure 12 shows the changes in open circuit potentials for the sputter-deposited W-Cr-(4-15)Ni alloys including tungsten, chromium and nickel metals in 1 M NaOH solution at 25°C, as a function of immersion time. The open circuit potential of the sputter-deposited chromium is about -760 mV (SCE) after immersion for 2 seconds and shifted very fast towards the more noble direction with immersion time and reached a potential of about -150 mV (SCE) after immersion for 2 hours. The similar behavior of the change of open circuit potential is shown for the nickel metal also. However, the open circuit potential of the sputter-deposited tungsten shifted very slightly towards more negative direction with immersion time and a steady state open circuit potential of about -900 mV (SCE) is attained after immersion for about 5 minutes. On the other hand, the open circuit potentials of all the examined W-Cr-(4-15)Ni alloys are found to shift towards more positive direction with immersion time. The open circuit potentials of W-63Cr-15Ni, W-67Cr-9Ni and W-75Cr-4Ni alloys are located very close to those of nickel and chromium metals. However, the open circuit potential of the W-42Cr-5Ni alloy is in more negative direction than those of other W-Cr-(4-15)Ni alloys and located between those of the tungsten and chromium in 1 M NaOH solution. These facts coincide with the change in the corrosion rates of the sputter-deposited amorphous or nanocrystalline W-Cr-(4-15)Ni alloys in 1 M NaOH solution as shown in figures 9 and 10.

Furthermore, figures 13-17 show the changes in the open circuit potentials for the W-42Cr-5Ni, W-63Cr-15Ni, W-67Cr-9Ni, W-75Cr-4Ni alloys and chromium metal, respectively, in different concentrations of NaOH solutions with immersion time. In general, the open circuit potentials of all the examined W-Cr-(4-15)Ni alloys and chromium metal are shifted towards noble direction with decreasing the concentration of NaOH solutions. The similar behavior of the ennoblement of the open circuit potentials of the sputter-deposited tungsten and nickel were reported with different concentration of NaOH solutions at 25^{o}C [41]. These facts indicate that the stability of the passive films formed on the sputter-deposited W-Cr-(4-15)Ni alloys increased with decreasing the concentrations of NaOH solutions.

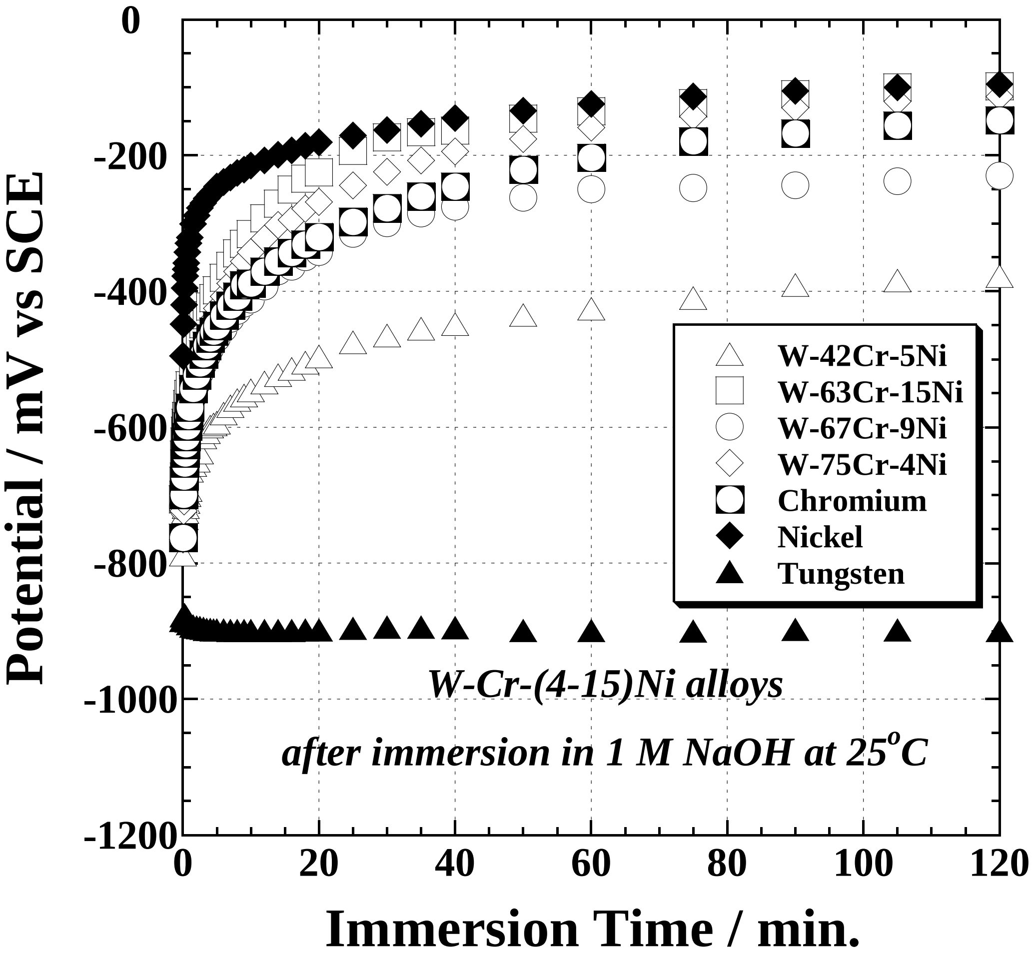

Figure 12: Changes in open circuit potentials for W-Cr-(4-15)Ni alloys including tungsten, chromium and nickel metals in 1 M NaOH solution at 25°C, as a function of immersion time.

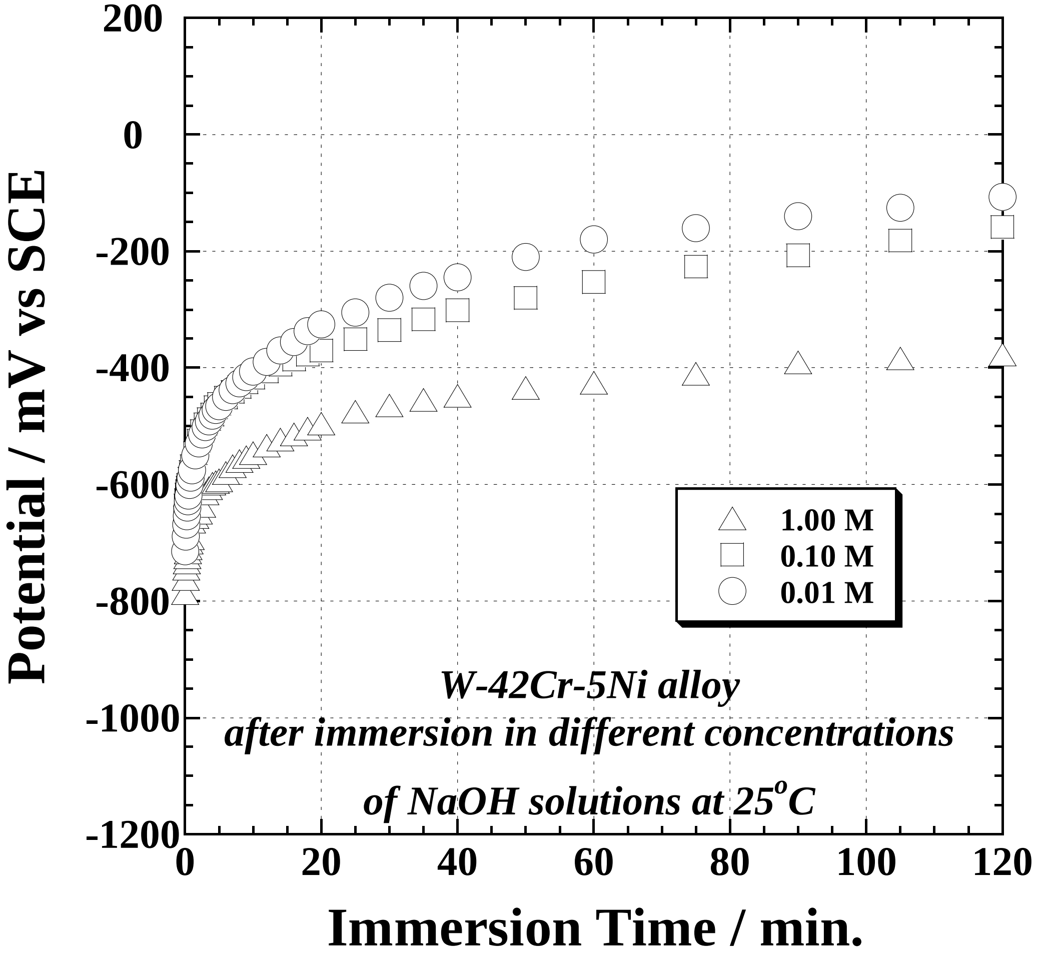

Figure 13: Changes in open circuit potentials for the W-42Cr-5Ni alloy in different concentrations of NaOH solutions at 25°C, as a function of immersion time.

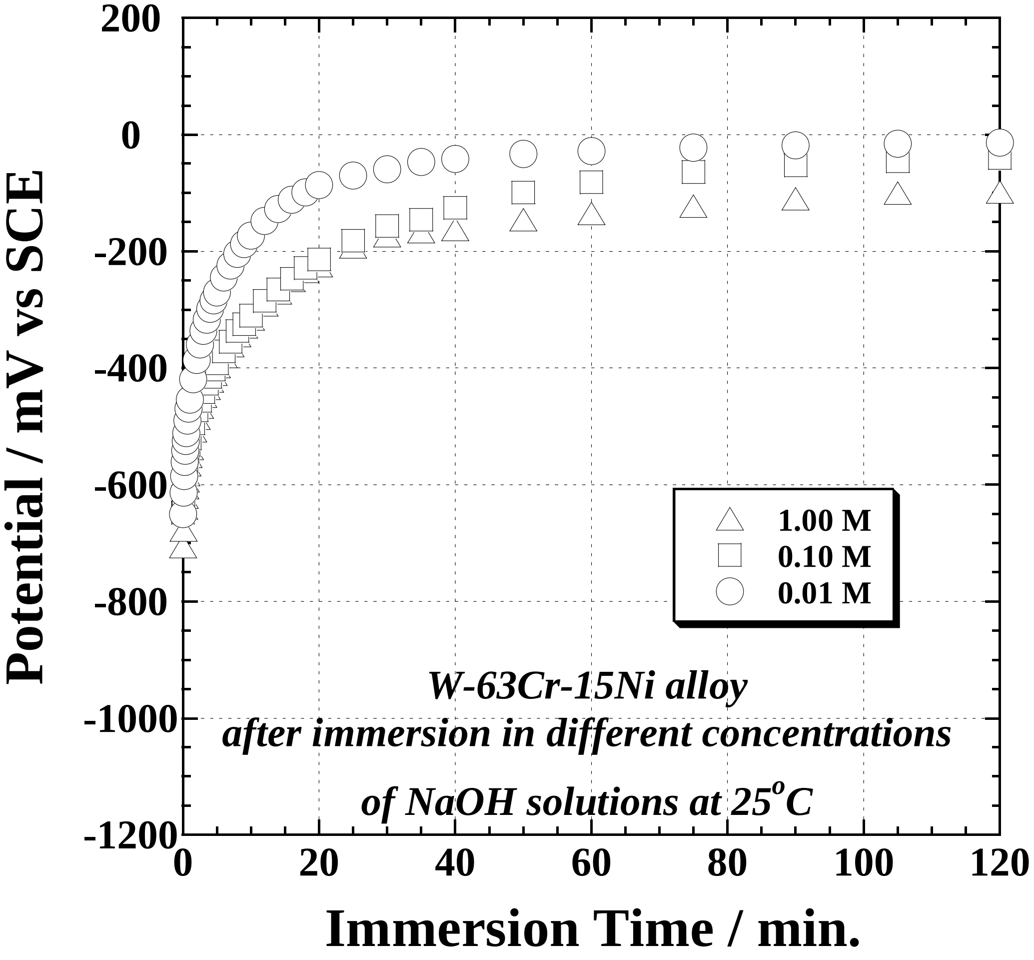

Figure 14: Changes in open circuit potentials for the W-63Cr-15Ni alloy in different concentrations of NaOH solutions at 25°C, as a function of immersion time.

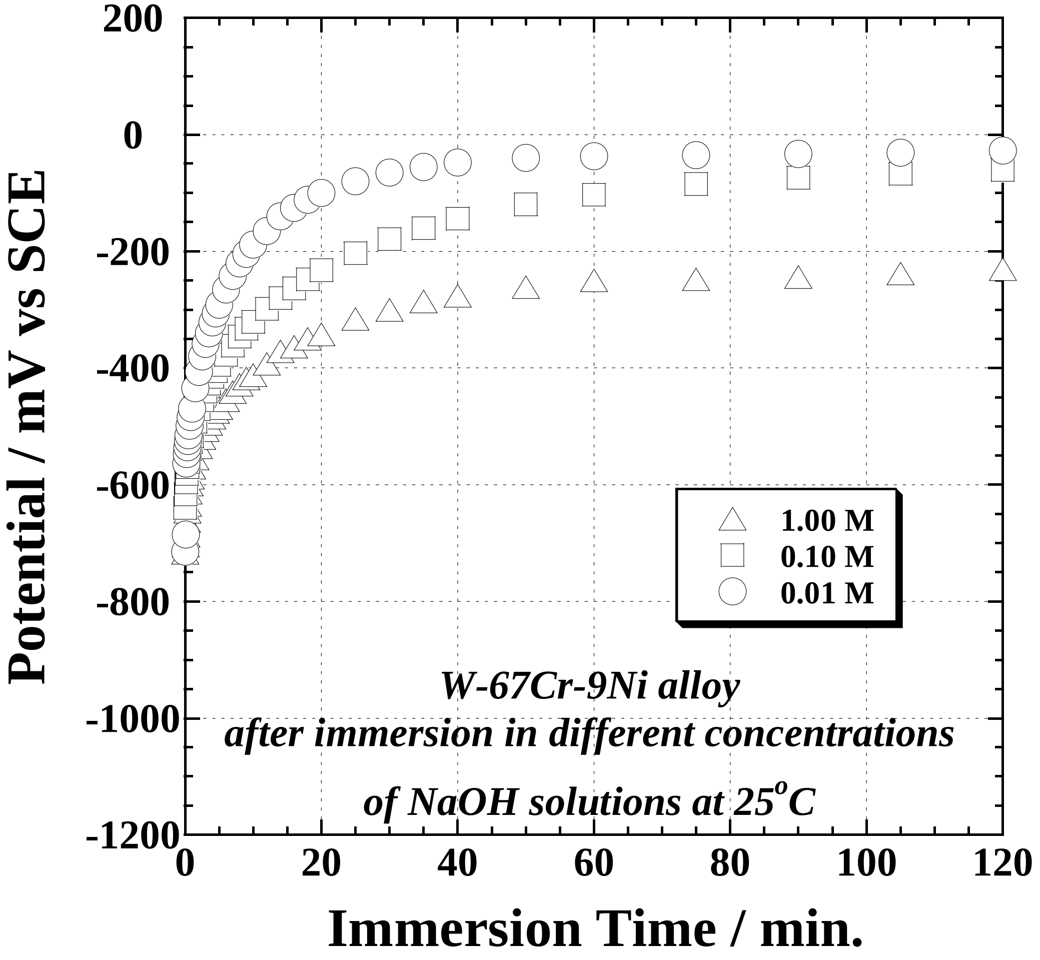

Figure 15: Changes in open circuit potentials for the W-67Cr-9Ni alloy in different concentrations of NaOH solutions at 25°C, as a function of immersion time.

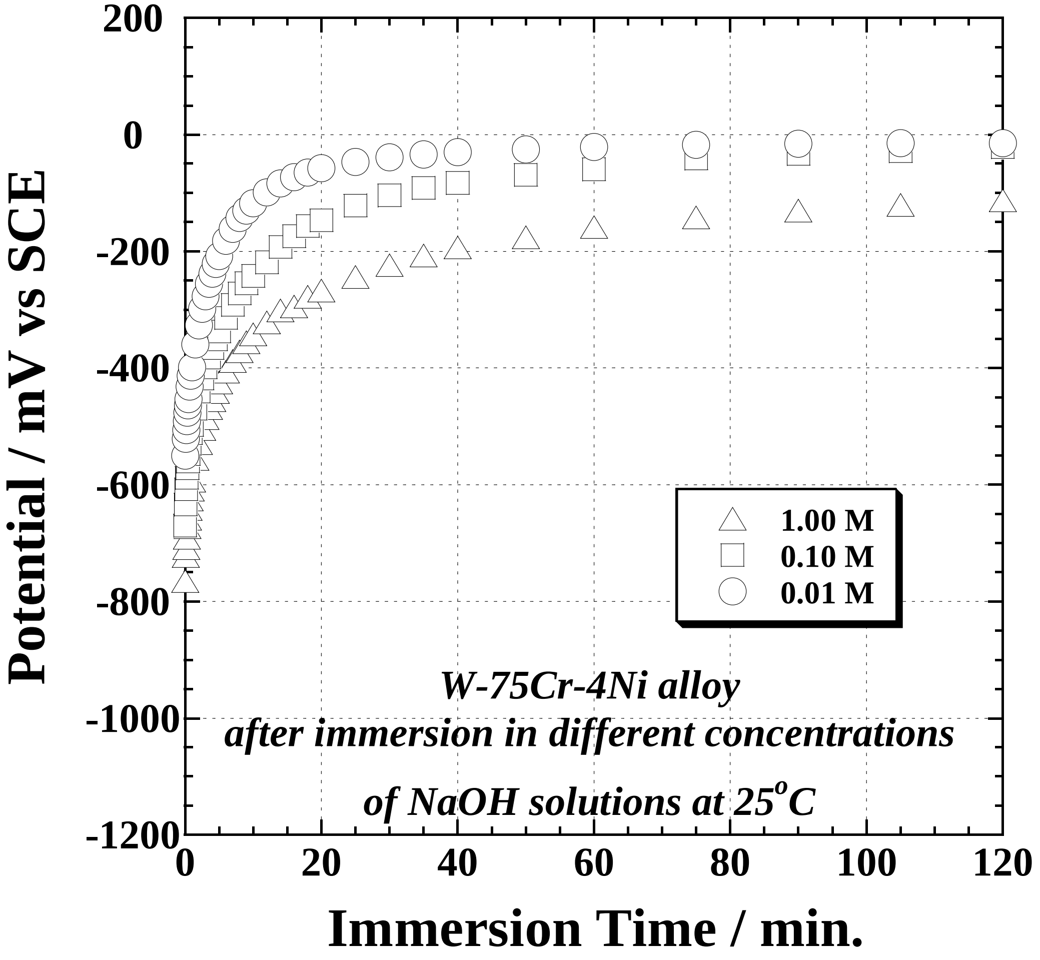

Figure 16: Changes in open circuit potentials for the W-75Cr-4Ni alloy in different concentrations of NaOH solutions at 25°C, as a function of immersion time.

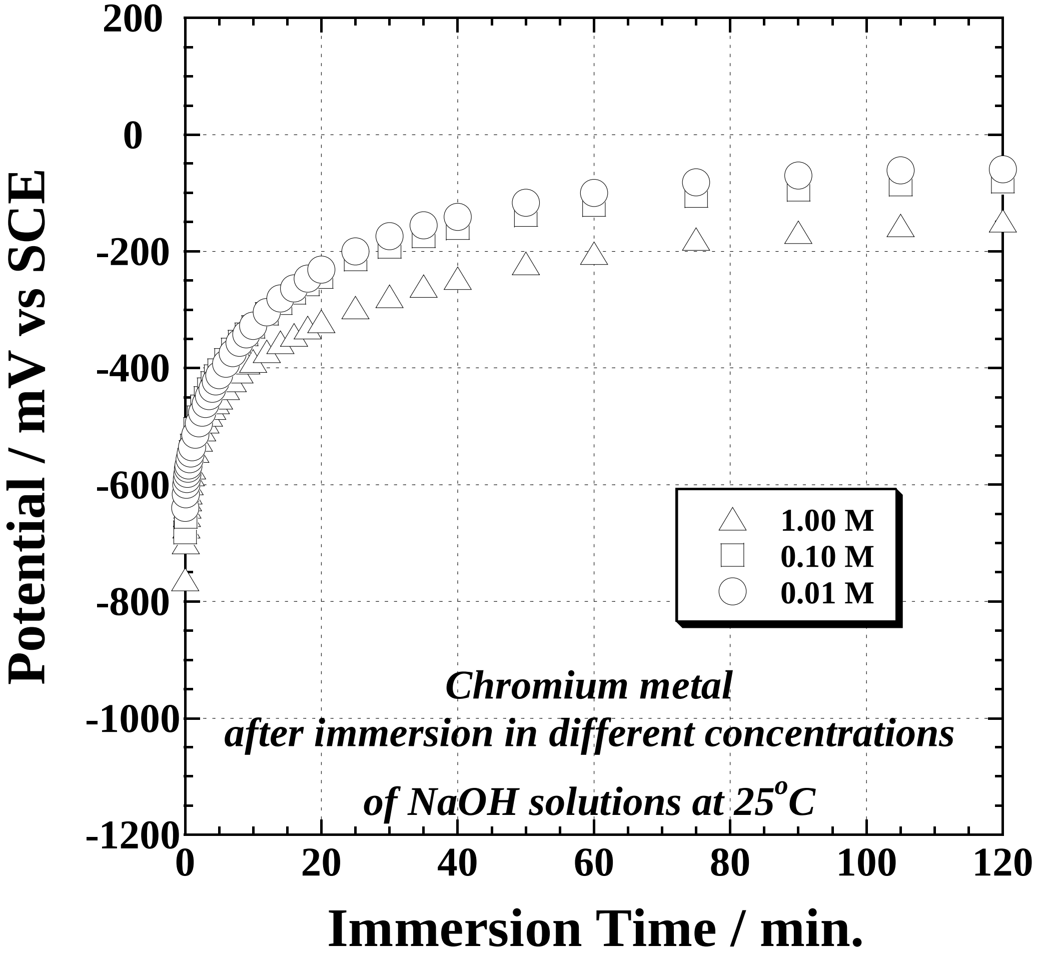

Figure 17: Changes in open circuit potentials for the sputter-deposited chromium in different concentrations of NaOH solutions at 25°C, as a function of immersion time.

3.3 CONCLUSIONS

The synergistic effect of chromium and nickel enhancing the corrosion resistance of the sputter-deposited amorphous or nanocrystalline W-Cr-(4-15)Ni alloys is studied in 0.5 M NaCl and NaOH solutions at 25°C, open to air, by immersion tests and electrochemical measurements. The following conclusions are drawn from the experimental results of the study:

1. Chromium and nickel metals act synergistically with tungsten in enhancing the corrosion resistance of the sputter-deposited W-Cr-(4-15)Ni alloys so as to show lower corrosion rates than the corrosion rates of the alloy-constituting elements (that is, tungsten, chromium and titanium) in 0.5 M NaCl solution. The corrosion rates of the W-Cr-(4-15)Ni alloys containing 42-75 at% chromium are nearly one order of magnitude lower (that is, in the range of 2-3 x 10^{-3} mm/y) than that of the sputter-deposited tungsten and even lower than that of chromium.
2. All the examined sputter-deposited W-Cr-(4-15)Ni alloys, which are composed of either amorphous or nanocrystalline single phase solid solution, show higher corrosion resistance than those of alloy-constituting elements (that is, tungsten, chromium and nickel) in an alkaline 1 M NaOH solution at 25°C. Corrosion rates of the W-Cr-(4-15)Ni alloys containing 42-67 at% chromium are about two orders of

magnitude lower (that is, in the range of 2-5 x 10^{-3} mm/y) than those of the sputter-deposited tungsten and nearly one order of magnitude lower than that of chromium metal in 1 M NaOH solution at 25°C.

3. The open circuit potentials of the W-63Cr-15Ni, W-67Cr-9Ni and W-75Cr-4Ni alloys are shifted to more positive direction than those of all alloy-constituting elements in 0.5 M NaCl solution. However, the open circuit potential of the W-42Cr-5Ni alloy is located between those of chromium, nickel and tungsten, but very close to those of chromium and nickel in 0.5 M NaCl solution.
4. The open circuit potentials of W-Cr-(4-15)Ni alloys containing 42-75 at% chromium are located very close to those of chromium and nickel metals in different concentrations of NaOH solutions. Furthermore, the open circuit potentials of all the examined W-Cr-(4-15)Ni alloys are shifted to more positive direction than that of tungsten in NaOH solutions.
5. The stability of the passive films formed on the sputter-deposited W-Cr-(4-15)Ni alloys is increased with dilution of NaOH solutions because, the open circuit potentials of these alloys are shifted to more positive direction with decreasing the concentration of NaOH solutions at 25°C.

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