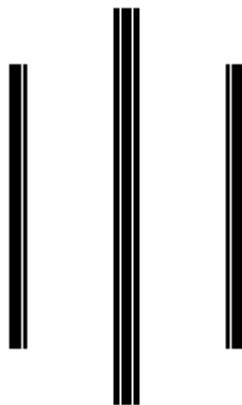


CORROSION BEHAVIOR OF SPUTTER-DEPOSITED W-Mo ALLOYS IN NaOH SOLUTIONS

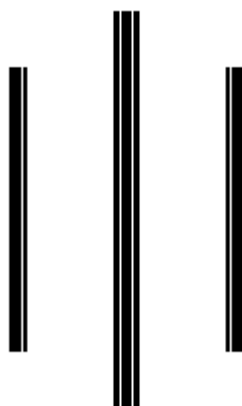


a Dissertation

Submitted to the Central Department of Chemistry
in Partial Fulfillment of the Requirement for
M. Sc. Degree in Chemistry

by

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2010

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LETTER OF ACCEPTANCE

M. Sc. dissertation entitled "**CORROSION BEHAVIOR OF SPUTTER-DEPOSITED NANOCRYSTALLINE W-Mo ALLOYS IN NaOH SOLUTIONS**" submitted by *Mr. Arun Khadka* has been accepted as a partial fulfillment of the requirement for M. Sc. Degree in Chemistry.

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FOREWORD

Mr. Arun Khadka has carried out the entire research works presented in this thesis under my supervision in the academic year 2009-2010. During the research period, he has performed the work sincerely and satisfactorily. No part of this thesis has been submitted for any other degree.

.....

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ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my respected supervisor Dr. Jagadeesh Bhattarai, Central Department of Chemistry, Tribhuvan University, for his kind help, valuable guidance and encouragement throughout this research work. Dr. Bhattarai also provided all the sputter-deposited nanocrystalline W-Mo alloys used in this research work.

I owe a much to Dr. Kedar Nath Ghimire, Head of Central Department of Chemistry, Tribhuvan University, for providing me the available research facilities. My sincere thanks goes to my respected teachers Prof; Dr. Krishna Manandhar, Prof. Dr. Rajaram Pradhananga, Dr. Deba Bahadur Khadka, Dr. Amar Prasad Yadav and all faculty members as well as administrative staffs of Central Department of Chemistry, Tribhuvan University, Kirtipur.

I am thankful to my friends Ms. Minu Basnet, Mr. Prakash Shrestha, Mr. Raju Ram Kumal and Mr. Basu Ram Aryal for their co-operation. Thanks are due to my brother Mr. Gyan Bahadur Khadka and my sister Ms. Geeta Khadka for their continuous inspiration and duly assistance in my endeavor of drafting this dissertation.

Arun Khadka

13th April, 2010

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ABSTRACT

The corrosion behavior of the sputter-deposited nanocrystalline W-Mo alloys is studied after immersion for 24-29 h in different concentrations of NaOH solutions at 25°C, open to air by using corrosion tests and open circuit potential measurements. Molybdenum metal acts synergistically with tungsten in enhancing the corrosion resistance of the sputter-deposited W-Mo alloys so as to show the lower corrosion rates than those of alloy-constituting elements (that is, tungsten and molybdenum) after immersion for 24-29 h in NaOH solutions. In general, the open circuit potentials of all the examined W-Mo alloys are shifted to the more positive (noble) direction with increasing the molybdenum content in the alloys. The stability of the spontaneous passive films of the binary W-Mo alloys is decreased with increasing the concentrations of NaOH solutions. However, the corrosion rates of all the examined W-Mo alloys are almost independent of concentrations of NaOH solutions (that is, 0.01 M, 0.1 M and 1 M NaOH).

CHAPTER-I

INTRODUCTION

1.1 GENERAL INTRODUCTION

In general, corrosion is regarded as the gradual destruction of a material or an entity with its environment by means of electrochemical and/or chemical processes. International Union of Pure and Applied Chemistry (IUPAC) defines corrosion as “an irreversible interfacial reaction of materials (metallic, ceramic or polymer) with its environment which leads to the consumption of materials” [1]. This definition of corrosion considers not only metallic substances but also other materials which can be used for engineering purposes accommodating a broad area. However, nowadays the term corrosion is specifically applied to the metallic substances. Thus, corrosion is the undesirable deterioration of metallic substances due to electrochemical reaction between electronically conducting materials and ionically conducting environment [2]. Many materials scientists and corrosionists consider that the term metallic corrosion embraces all interactions of a metal or alloy (solid or liquid) with its environment, irrespective of whether this is deliberate and beneficial or adventitious and deleterious [1]. Thus, this definition of corrosion is referred to as the transformation definition of corrosion, for example, the deliberate anodic dissolution of zinc in cathodic protection and electroplating as well as the spontaneous gradual wastage of zinc roofing sheet resulting from atmospheric exposure.

The development of new engineering materials is always done to obtain the desired properties like durability, tensile strength and improved

corrosion resistance properties of the materials. In earlier days engineers often did not give sufficient emphasis on importance of corrosion in initial designing state assuming that it can be avoided simply by additional surface treatments like thick polishing or painting. In many cases, industrial applications of novel materials will ultimately depend upon corrosion resistance properties over extended periods of service and corrosion problems have to be considered at an appropriate stage of the materials development. In this context, corrosion scientists can play two significant roles in the engineering world, first and the foremost is the practical role emphasizing engineers that the durability of structure depends on the nature of materials and environments, particularly the aggressive ions present in the environment. Second, the corrosion science fills up gap between atomic physics, chemistry, electrochemistry and metallurgy. Hence, the study of corrosion phenomena requires sound knowledge on other sciences like physics, engineering and metallurgy as well as chemistry or electrochemistry.

The development of new technology is, in part, dependent of corrosion science. The function of corrosion science is to make clear understanding of the corrosion mechanism of the materials and to formulate the available and novel means of the prevention, elimination or minimization of corrosion phenomena. The corrosion engineers apply the accumulated scientific knowledge to control the corrosion damage in practical and economically efficient way.

In general, the various measures of corrosion like anodic and/or cathodic protection are widely used. Corrosion protection by passivation was discovered early in eighteenth century when iron was corroded heavily in dilute aqueous solutions of nitric acid, but stayed as inert as platinum in concentrated solutions. Later, it has been subsequently found

that the passivation may be due to formation of passive films of oxides, hydroxides or oxyhydroxides or salts on the surface of materials that separate the materials from its environment. Another incentive to the study of corrosion was development of widely used stainless steels, which have very low corrosion rate, compared to that of iron metal [2]. Therefore, it is said that corrosion problems arose with the widespread use of stainless steels and steel enforced concrete for their tensile strengths. However, corrosion problems are encountered in all branches of industries, technologies, sciences or engineering.

From economic point of view, corrosion causes large economic loss of the most industrialized countries. With increasing dependence of civilization on mechanical than muscle power, machines have become integral part of life. Almost all machines are made of the metallic substances (metals and alloys) and the materials used for the fabrication of machines should be highly resistance to corrosion in working environments. Industrial civilization, thus, depends on crucial way upon stability of such metallic substances. Therefore, the corrosion loss accounts for enormous amount of money each year. It is believed that the cost of corrosion is 3-4 % of GNP (Gross National Products) of the most industrialized countries [2]. Furthermore, it is estimated that nearly 40 % of this corrosion loss can be avoided by proper corrosion engineering [2]. Actually, corrosion is one of the major scientific and industrial problems, which affect many industrial processes. New chemical process that seems to be attractive on paper spell doom as their practical application is limited due to pronounced corrosion damage of used materials. If the materials have to be replaced frequently due to the corrosion damages, then the system is less likely to be of industrial interest because of the economic reasons. So all the sectors, where the chemical or

electrochemical processes are involved, knowledge of corrosion scientists and engineers is essential to the success of the overall processes run for long periods. Corrosion experts are highly aware of the danger of different aggressive ions like chloride coming in contact with metallic structures. The lack of knowledge of corrosion science could lead to failure of what is otherwise an excellent environmental treatment system. This shows the importance of corrosion research to develop new approaches to minimize corrosion process in electrochemical, chemical and metallurgical processes.

In the study of corrosion, the surface reactions of interest include anodic dissolution (the passage of metal atoms from the surface to the solution which is fundamental reaction of corrosion), passivation (the formation of thin layer of insoluble oxides, hydroxides, oxyhydroxides or salts of few nanometers, that protect metal or alloy from further dissolution) and passivity breakdown (localized rupture of passive film leading to the localized corrosion) and so on. These surface phenomena are extremely useful to find the remedies of corrosion problems that almost all countries are confronted with and which are extremely costly. Furthermore, the degradation of industrial materials can cause the shutdown of the entire process system with subsequent loss of productivity, system reputation and money. Nowadays, corrosion remained no more of the interest only for corrosion scientists but interest also of those industrialists whose processes are susceptible to materials degradation. Materials degradation is a problem that influences all areas of modern technology. In fact, corrosion touches everywhere on road, in sea, oil pipelines, aerospace vehicle and even cooking pots and so on. This is a burning topic of today world because of its profound and all encompassing grip.

1.2 ELECTROCHEMISTRY 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 or alloy dissolution (an electrochemical anodic oxidation) must be balanced with cathodic current on the metal or alloy. The cathodic reaction is the reduction of oxygen dissolved in the electrolytic solution or/and the reduction of proton, that is, hydrogen evolution. The magnitude of the currents 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 [3]. 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, the mixed potential theory is a versatile tool to have better understanding of metallic corrosion [4].

The mixed potential theory of corrosion 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 Evans diagram (figure 1), for the case of a metal or alloy (M) immersed in an acidic environment.

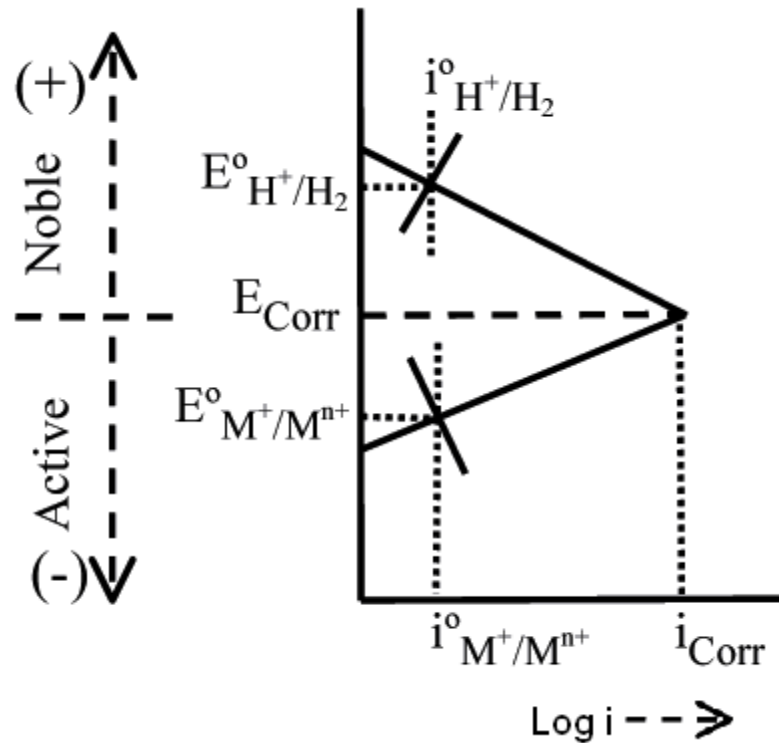


Figure 1: Schematic Evans diagram showing corrosion potential (E_{corr}) or open circuit corrosion potential (OCP) and corrosion current (i_{corr}).

On the other hand, Nario Sato of Hokkaido university of Japan had proposed that the corrosion process involved not only electrochemical oxidation-reduction reactions but was also accompanied by chemical acid-base reactions [5]. According to Sato, the anodic metal dissolution commenced with the ionization of metal atoms on the surface, and hence the metal ions 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. Therefore, both electrochemical and chemical reactions are involved in the corrosion process.

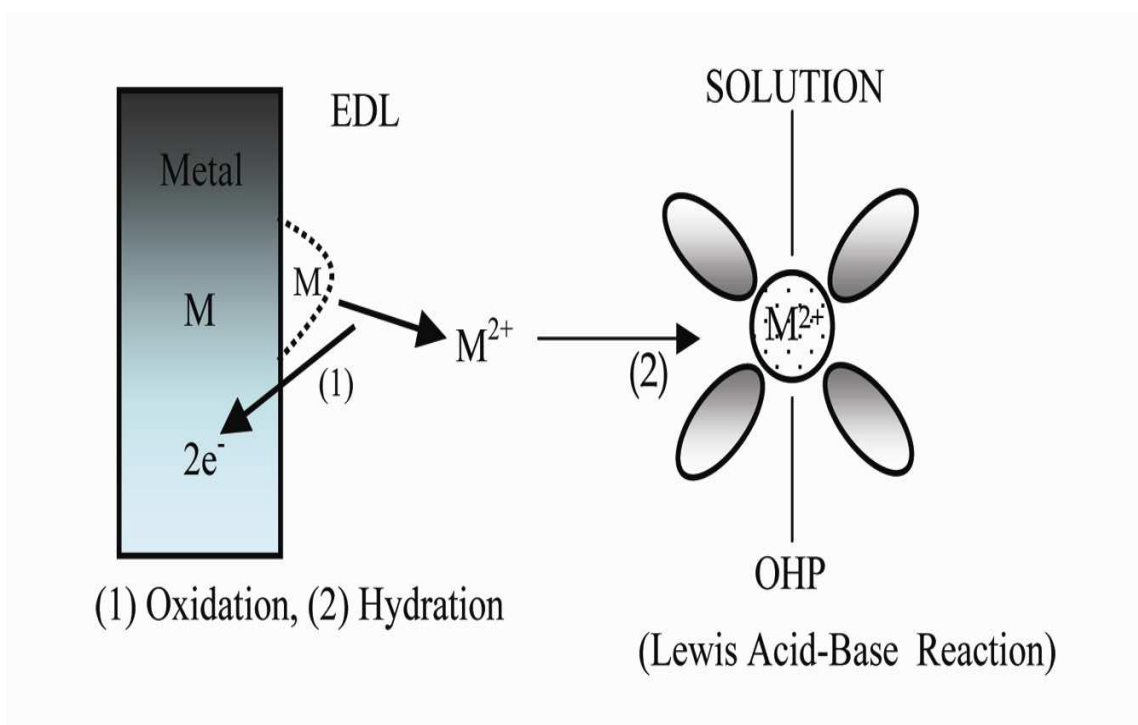


Figure 2: Anodic metal dissolution comprising of metal atom ionization (oxidation) and metal ion hydration (Lewis acid-base reaction [5]).

Corrosion of metals or alloys is an electrochemical reaction occurring on metals' or alloys' surface due to the influence of their environments. So the corrosion behavior of various metals or alloys can be compared by polarization measurements. Corrosion scientists have noticed that shifting direction of the corrosion potential of the substance may in principle be used as diagnostic test by indicating whether anodic or cathodic kinetics are most effective for corrosion behavior [2]. Some typical examples of the anodic polarization curves are shown in the figure 3. These

polarization curves are also very useful to explain the corrosion behavior and mechanism of the metastable metals or alloys.

Let us consider the dissolution reaction of a metal or an alloy (M) in a corrosive environment as given by equation (1):



If stable surface film is not formed on the surface of metal or alloy and neither of the current density is limited by the mass transport, the dissolution rate is measured by the anodic current density (i_a), which is given by the equation (2).

$$i_a = i_a^{\circ} \exp[\beta (E - E_m)] \quad (2)$$

where, i_a° is the equilibrium exchange current density at anode, β 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.

This equation reveals that anodic current density (i_a) is increased logarithmically with increasing potential. A rise in potential results in the formation of a new corrosion product that is a stable solid product of oxides, hydroxides, oxyhydroxides or salts in the corrosive environments and able to cover the metal or alloy surface spontaneously. This results a substantial decrease in the dissolution rate of the metal or alloy. This corresponds to the spontaneous passivation (figure 3.a) and the oxides, hydroxides, oxyhydroxides or salts corrosion product film covering metal surface is called as the passive film. If the solution contains more aggressive ions like halides, pitting corrosion for some materials can be easily detected by anodic polarization of materials as shown in figure 3.b.

Besides pitting corrosion, anodic polarization of the material beyond certain potential leads transpassive dissolution as a result of the formation

of soluble cations at higher potential which usually have higher valence than cations of same metal forming a passive film as shown in figure 3.c. Thus, clear understanding of the anodic passivity, pitting corrosion and transpassivity can be obtained from knowledge of electrochemistry.

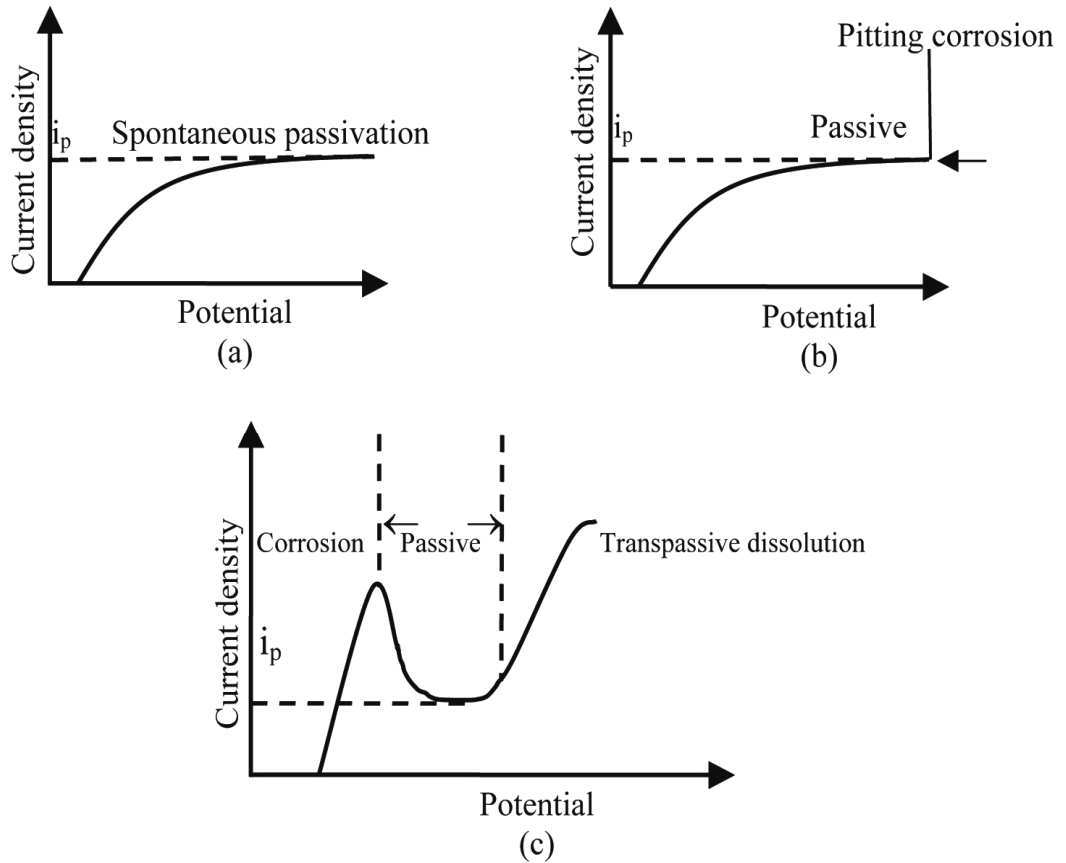


Figure 3: Anodic Polarization curves showing (a) spontaneous passivation, (b) pitting corrosion and (c) active-passive and transpassive dissolution.

On the other hand, hydrogen ion and/or dissolved oxygen in the corrosive environment undergoes cathodic reactions on the surface of the materials as given in equations (3) and (4) below.



The rates of these cathodic reactions rise logarithmically with lowering of the measured potential (E) of the cathodic reaction as given in the equation (5) as;

$$i_c = i_c^0 \exp[\beta (E - E_c)] \quad (5)$$

where, i_c is the cathodic current density, i_c^0 is the equilibrium exchange current density at cathode, β is a constant value for the cathodic reactions (3) and (4) and E_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 [3, 4], that is:

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

1.3 DEVELOPMENT OF SPUTTER-DEPOSITED METASTABLE METALLIC ALLOYS

It is generally believed that the preparation of homogeneous 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 ultra-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 [4]. 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 [6]. After the preparation of the amorphous Au-25Si alloy, Duwez and his co-workers developed series of new metastable amorphous or/and nanocrystalline single-phase solid solutions by using various techniques like vapor quenching, electrodeposition from mixture electrolyte, mechanical alloying and so on. Among these techniques, the vapor quenching method is one of the mostly used methods to prepare a homogeneous mixture of components.

Sputtering is one of the main methods of the vapor quenching techniques and used as one of the potential methods for the preparation of varieties of amorphous or nanocrystalline alloys [4, 7]. For last two decades, this technique of the sputter deposition method is known to form amorphous or/and nanocrystalline structures over the widest composition range among the various other methods. Therefore, the use of sputter deposition method is quite suitable for tailoring of the corrosion-resistant metastable amorphous or/and nanocrystalline alloys. Furthermore, even if amorphous alloys are not formed by the sputter deposition method, 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 structure regarding the corrosion-resistant properties of the 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 the sputter deposition method does not require melting of alloying components for the alloy formation. For instance, boiling points of chromium (2670°C) and nickel (2900°C) are far lower than the melting point of tungsten metal (3420°C). However, successful attempts were reported to prepare single-phase amorphous or nanocrystalline W-Cr [8, 9], W-Ni [10, 11] alloys by using

the advantages of sputtering. Similarly, it has been successfully prepared sputter-deposited amorphous or/and nanocrystalline W-Mo alloys in a wide composition ranges, even though there is a large difference between the melting points of tungsten and molybdenum [10].

For about last two decades, the sputter deposition method has emerged as one of the best techniques to prepare chemically homogeneous amorphous or nanocrystalline alloys because, the chemically homogeneous single-phase nature of amorphous or nanocrystalline alloys are generally responsible for their high corrosion resistance, owing to the formation of uniform protective passive films that are able to separate the bulk of the alloy from aggressive environments [4]. 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 [12] and Anderson et al. [13]. The importance of the sputter deposition method for the coating on stainless steels is another incentive to use of sputtering in technology.

1.4 STRUCTURES AND CORROSION BEHAVIOR OF METASTABLE ALLOYS

Nanocrystalline structures are usually believed to be free from crystal defects such as dislocation grain boundaries and precipitates acting as nucleation sites for corrosion, and the chemically homogeneous single-phase nature of nanocrystalline alloys are responsible for their high corrosion resistance. This is because of formation of uniform protective passive films, which are nonporous and insoluble and thus are able to separate the bulk alloys from aggressive Environments. On other hand

according to Heusler and Heurta, the extremely high corrosion resistance of the sputter deposited alloys has been explained on the basis of homogeneity of the alloys [14]

1.5 ROLES OF TUNGSTEN AND MOLYBDENUM METALS IN THE CORROSION RESISTANCE OF W-Mo ALLOYS

Tungsten and Molybdenum are regarded as very effective alloying elements for enhancing the corrosion resistance of the alloys in aggressive environments. In alkaline and neutral media, tungsten shows corrosion behavior with spontaneous dissolution to tungstate ion, but it is passivated in acidic media, except for complexing acids as shown in figure 4 [15].

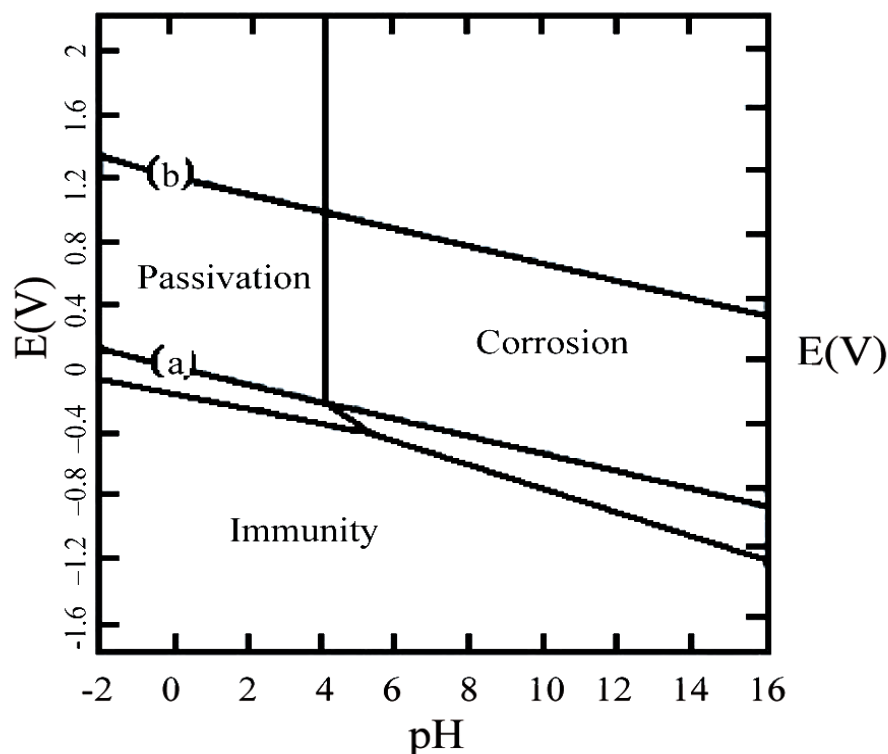


Figure 4: Theoretical domains of corrosion, immunity and passivation of tungsten metal at 25°C [15].

It has been reported that addition of small amount of tungsten increased corrosion resistance of steels and stainless steels [16]. Several surface studies have been carried out for better understanding of the role of the tungsten in the passivity of stainless steels in aggressive chloride media [17-19]. It has been also reported that the addition of a small amount of tungsten to amorphous Fe-P-C alloys with or without chromium [20-23], to Ni-Fe alloys [23] and to the amorphous Ni-P alloys [24, 25] was effective in improving the corrosion resistance of these alloys in aggressive hydrochloric acids. Similarly, the addition of only small amounts of tungsten, (that is, 9 at %), was enough to cause spontaneous passivation of the sputter-deposited W-91Cr alloy in 12 M HCl solution and the alloy showed about five orders of magnitude lower corrosion rate than the corrosion rate of chromium metal [8].

Molybdenum as an alloying element for the steels and stainless steels has been found to reinforce their corrosion resistance. Molybdenum is thought to play its role either by promoting the enrichment of chromium on the surface films of stainless steels [26-31] or by blocking and eliminating the active surface site [32]. Wanklyn [33] emphasized inhibitive effects of insoluble tetravalent molybdenum oxide (MoO_2) while others elucidated the beneficial effects of molybdenum by considering the elimination of active surface sites by MoO_4^{-2} or the cation selectivity of the surface films enhanced by MoO_4^{-2} [29-31].

On the other hand, it is well known that the addition of molybdenum to crystalline Fe-Cr alloys [32, 34, 35] and amorphous Fe-C metalloid alloys [36, 37] improved their corrosion resistance to pitting corrosion in aggressive chloride solutions. Hashimoto et al. [32] reported that the beneficial effect of molybdenum appears for ferritic stainless steels in 1

M HCl at 30°C. They found that the surface film formed on the stainless steels in active region contain a large amount of molybdenum cations. The beneficial effects of molybdenum is interpreted based on the fact that molybdenum eliminates the active sites, on which the stable passive film is hardly formed, by the formation of tetravalent molybdenum oxide or oxyhydroxide and assists the formation of chromium enriched passive film [32, 38]. Furthermore, it has been reported that the addition of molybdenum enhanced the stability of the inner layer at the oxide- metal interface creating a barrier layer [36].

In the middle of 1990's Park et al. [39-44] have been reported the synergistic effect of molybdenum addition on the sputter-deposited binary amorphous and/or nanocrystalline molybdenum-transition metal (chromium, titanium, zirconium, niobium, tantalum and nickel) alloys for significantly high corrosion resistance properties in aggressive environments. Furthermore, it has been considered that the addition of molybdenum improved the passivating ability of the sputter-deposited ternary Al-Cr-Mo alloys not by formation of molybdenum enriched passive film, but by the formation of chromium enriched passive film [45, 46]. High corrosion resistance properties for molybdenum based alloys were observed in the case of the sputter-deposited binary nanocrystalline W-Mo alloys in 12 M HCl [9, 47]. It has been reported that the sputter-deposited nanocrystalline W-Mo alloys showed high corrosion resistance than those of tungsten and molybdenum metals in 12 M HCl [47] and 0.5 M NaCl solutions [48]. It is meaningful for mentioning here that the tungsten is passive in the acidic environments having $\text{pH} < 4$, whereas it corrodes in alkaline and neutral solutions [15]. On the other hand, molybdenum is passive in only a very narrow potential range at $\text{pH} 4\text{-}8$ of the environments as shown in figure 5 [49]. The molybdenum corrodes in

both acidic and alkaline environments. In this context, present work is focused to study the effect of molybdenum on the corrosion behavior of the binary nanocrystalline W-Mo alloys in NaOH solutions.

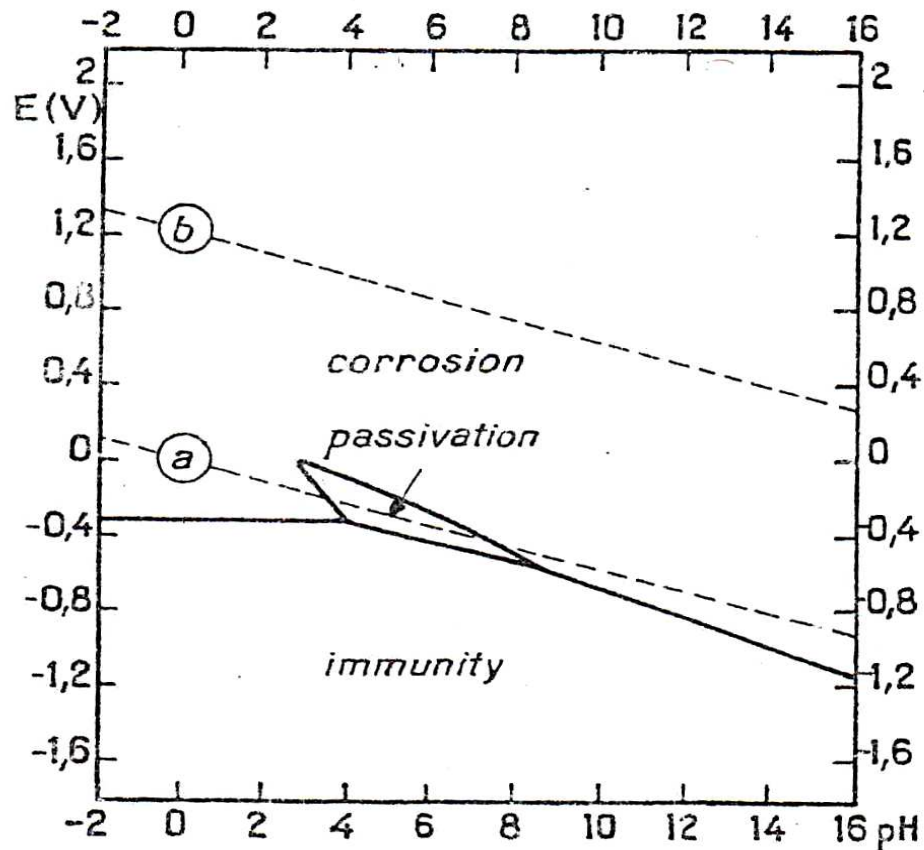


Figure 5: Theoretical conditions of corrosion, immunity and passivation of molybdenum at 25°C [49].

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. [50] 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 [51-53]. Hoar et al. [54, 55] reported that the binary Ti-Mo and Ti-Ta alloys showed 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 in detail by Bhattarai [56].

Since it was found that the rapidly-quenched amorphous iron-base alloys [57-59] 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-[60], nickel-[61-64] and copper-[65-68] 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 [69, 70]. 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 [71-73].

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. [13] 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 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) [74-76] alloys by using advantages of sputtering. Shimamura et al. [77] reported that the sputter-deposited nanocrystalline Cu-Nb alloys were spontaneously passivated in 12 M HCl solution, showing a very high corrosion resistance. Yashioka et al. [78, 79] 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 [80-83]. Further studies of the sputter-deposited aluminum-transition metal alloys were carried out in early 1990's by Yashioka et al. [84, 85]. 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 chromium-, molybdenum-, and tungsten- base amorphous or nanocrystalline alloys are lower than those of alloy-constituting elements in hydrochloric acid solutions at 30°C.

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 [86-89]. Furthermore, the sputter-deposited amorphous or nanocrystalline molybdenum-transition metal (titanium, zirconium, niobium and tantalum) alloys [39-44, 90, 91] 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.

Such interesting findings of the lower corrosion rates of chromium- and molybdenum-transition metal alloys than those of alloy-constituting elements have recently encouraged corrosionists to tailor new series of highly corrosion resistance binary tungsten-transition metal (titanium, zirconium, niobium, tantalum, molybdenum, chromium and nickel) alloys by sputtering [8, 11, 47, 90-103]. In addition, the sputter-deposited ternary W-Cr-Ni [104-106] and Cr-Zr-W [107, 108] alloys are recently been prepared and all these 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 [109-112], W-Ni [112-116], W-Ti [112, 117-121], W-Cr-Ni [122, 123], W-Zr [124, 125], W-Cr [126, 127], and Zr-Cr-W [128, 129] alloys which are composed of either amorphous or nanocrystalline single phase solid solution showed high corrosion resistance in neutral NaCl and alkaline NaOH solutions at 25°C.

In these contexts, one more step is pursued in this research work to study the effects of molybdenum and tungsten on the corrosion behavior

of the sputter-deposited nanocrystalline W-Mo alloys in alkaline NaOH solutions at 25°C, open to air.

1.7 OBJECTIVES OF THE STUDY

The novel corrosion resistance properties of the rapidly quenched materials has stimulated the interest of corrosion scientists since in 1960's because, some single-phase amorphous and/or nanocrystalline alloys showed remarkably high corrosion resistance in the corrosive environment having aggressive ions.

Since the extremely high corrosion resistance of the rapidly quenched iron base alloys was reported in 1970's, varieties of corrosion resistant ultra-rapidly quenched alloys were developed during last four decades. Toward the end of 1990's, it had reported that the sputter-deposited amorphous and/or nanocrystalline tungsten-base alloys alloying with titanium, zirconium, chromium, niobium, tantalum, molybdenum and nickel showed high corrosion resistance than alloy-constituting elements in concentrated hydrochloric acids open to air at 30°C. In particular, the sputter-deposited nanocrystalline W-Mo alloys of wide range of composition showed high corrosion resistance properties in 12 M HCl and neutral 0.5 M NaCl solutions. Thus, it becomes a matter of interest to study the corrosion behavior of the sputter-deposited nanocrystalline W-Mo alloys in NaOH solutions in this time. The main objectives of this research work are:

1. to estimate the corrosion rates of the W-Mo alloys in 0.01 M, 0.1 M, 1 M NaOH solutions open to air at 25°C, and

2. to study the electrochemical behavior of the W-Mo alloys in NaOH solutions open to air at 25°C.

CHAPTER- II

EXPERIMENTAL METHOD

2.1 SPUTTER-DEPOSITED W-Mo ALLOYS

All the sputter-deposited W-Mo 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 W-Mo alloys were same as those described elsewhere [10]. The provided sputter-deposited W-Mo alloys containing 24-83 at % molybdenum were characterized as single-phase solid solutions of nanocrystalline structure having apparent grain size less than 20 nm as summarized in Table 1 [10]. The compositions of the sputter-deposited W-Mo alloys hereafter are all denoted in atomic percentage (at %).

2.2 CORROSION TEST

Corrosion tests of the sputter-deposited nanocrystalline W-Mo alloys were carried out in alkaline 0.01 M, 0.1 M and 1 M NaOH solutions at $25\pm 1^\circ\text{C}$, open to air. Prior to corrosion tests, the surface of each alloy specimen, which was cut into pieces having the area of 15 to 30 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 0.01, 0.1 and 1 M NaOH solutions for about 24-29 hours. The weight loss of alloy specimens 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 equation (7).

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

where,

Δw = weight loss of the alloy specimen in gram,

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

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

t = time of immersion in hour

Table 1: Chemical composition, apparent grain size and structure of the sputter-deposited W–Mo alloys, including sputter-deposited tungsten and molybdenum metal [10, 47].

Name of Alloy	Mo Content (at %)	Apparent Grain Size (nm)	Structure
Tungsten	0.0	20.0	Nanocrystalline
W-24Mo	24.2	19.8	Nanocrystalline
W-34Mo	34.2	16.0	Nanocrystalline
W-52Mo	51.8	15.0	Nanocrystalline
W-83Mo	82.8	16.5	Nanocrystalline
Molybdenum	100.0	20.0	Nanocrystalline

2.3 ELECTROCHEMICAL MEASUREMENT

2.3.1 Preparation of alloy specimen

The sputter-deposited nanocrystalline W-Mo alloys were cut into small pieces of 2 to 3 cm in length and 1 cm 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 or titanium rod. The specimen was immersed in an electrolyte in such a way that about 1 cm² area of the alloy specimens 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 solution

The electrolytes used in the electrochemical measurements were 0.01, 0.1 and 1 M NaOH solutions at $25 \pm 1^\circ\text{C}$, open to air.

2.3.3 Electrode

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 nanocrystalline W-Mo alloy specimens in different concentrations of sodium hydroxide solutions at $25 \pm 1^\circ\text{C}$, open to air, were measured using a potentiometer. The readings were taken immediately after immersion of the alloy specimen

in the electrolytic NaOH solutions for two hours. The electrochemical measurements were repeated two times or more to get precise results.

CHAPTER-III
RESULTS AND DISCUSSION

3.1 CORROSION RATE OF NANOCRYSTALLINE W-Mo ALLOYS

The corrosion rates of the sputter-deposited nanocrystalline W-Mo alloys were estimated from the weight loss after immersion for 24 hours in alkaline NaOH solutions at 25°C, open to air. The weight loss for each alloy specimen was estimated two times or more and the average corrosion rate was calculated. The time dependence of the corrosion rates of the alloy specimens were also estimated at various time intervals in 0.01, 0.1 and 1 M NaOH solutions.

3.1.1 Average corrosion rate in 1 M NaOH solution

Figure 6 shows changes of the average corrosion rates of the sputter-deposited nanocrystalline W-Mo alloys including tungsten and molybdenum metals after immersion for 24 hours in alkaline 1 M NaOH solution at 25°C, open to air as a function of alloy molybdenum content. The corrosion rates of the sputter-deposited tungsten and molybdenum are about 5.25×10^{-1} mm.y⁻¹ and 1.04×10^{-1} mm.y⁻¹, respectively. Corrosion rates of the sputter-deposited binary W-Mo alloys containing 24-83 at % molybdenum show about one order of magnitude lower corrosion rates than that of tungsten and even lower corrosion rates than that of the sputter-deposited molybdenum metal in 1 M NaOH solution at 25°C. In particular, the sputter-deposited W-Mo alloys containing 24-52 at % molybdenum show lowest corrosion rates (that is, about 4.5×10^{-2} mm.y⁻¹) among all the examined W-Mo alloys than those of alloy-

constituting elements (that is, tungsten and molybdenum) after immersion for 24 h in an aggressive 1 M NaOH solution at 25°C. These results revealed that the synergistic effects of the simultaneous additions of tungsten and molybdenum metals to the sputter-deposited nanocrystalline W-Mo alloys is clearly observed in alkaline 1 M NaOH solution.

3.1.2 Time dependence corrosion rate in NaOH solutions

It is generally said that the nature and compositions of passive films formed on alloys play a vital role for high corrosion resistance of the alloys. In general, alloys show high corrosion resistance through the active dissolution of the alloys at the initial periods of immersion in the corrosive environments. Furthermore, the high chemical reactivity of the alloys leads to the rapid accumulation of a beneficial species in the passive films. This accounts for the high corrosion resistance of the alloys. Therefore, it is important to identify the role of immersion time for better understanding of the corrosion nature of the alloys.

In order to clarify the time dependence of corrosion rates of the sputter-deposited nanocrystalline W-xMo alloys, corrosion rates of W-24Mo, W-34Mo, W-52Mo and W-83Mo alloys were estimated after immersion in different concentrations of alkaline NaOH solutions at various time intervals. Figure 7 shows the changes in the corrosion rates of W-24Mo, W-34Mo, W-52Mo and W-83Mo alloys in 0.01, 0.1 and 1 M NaOH solutions open to air at 25°C, as a function of immersion time.

In general, the corrosion rates of all the examined W-Mo alloys are significantly high at initial period of immersion (that is, for 2 h). The corrosion rate is decreased with immersion time till about 8 h for W-Mo alloys containing 24-83 at % molybdenum and the corrosion rates of all the examined sputter-deposited nanocrystalline W-Mo alloys become

almost steady after immersion for about 24 h. In particular, the corrosion rate of the alloys is significantly higher in 1 M NaOH solution than those in 0.1 and 0.01 M NaOH solutions after immersion for 2 hours. However, the corrosion rates of all the examined W-Mo alloys are almost same in all three different concentrations of the NaOH solutions after immersion for 8-29 h. Accordingly, initially fast dissolution of the W-Mo alloys results in fast passivation by forming more protective passive films formed on the alloys in alkaline NaOH solutions open to air at 25°C. Consequently, the average corrosion resistance of the sputter-deposited W-Mo alloys containing 24-83 at % molybdenum is higher than those of tungsten as well as molybdenum metals after immersion for about 24 to 29 h as shown in figure 6.

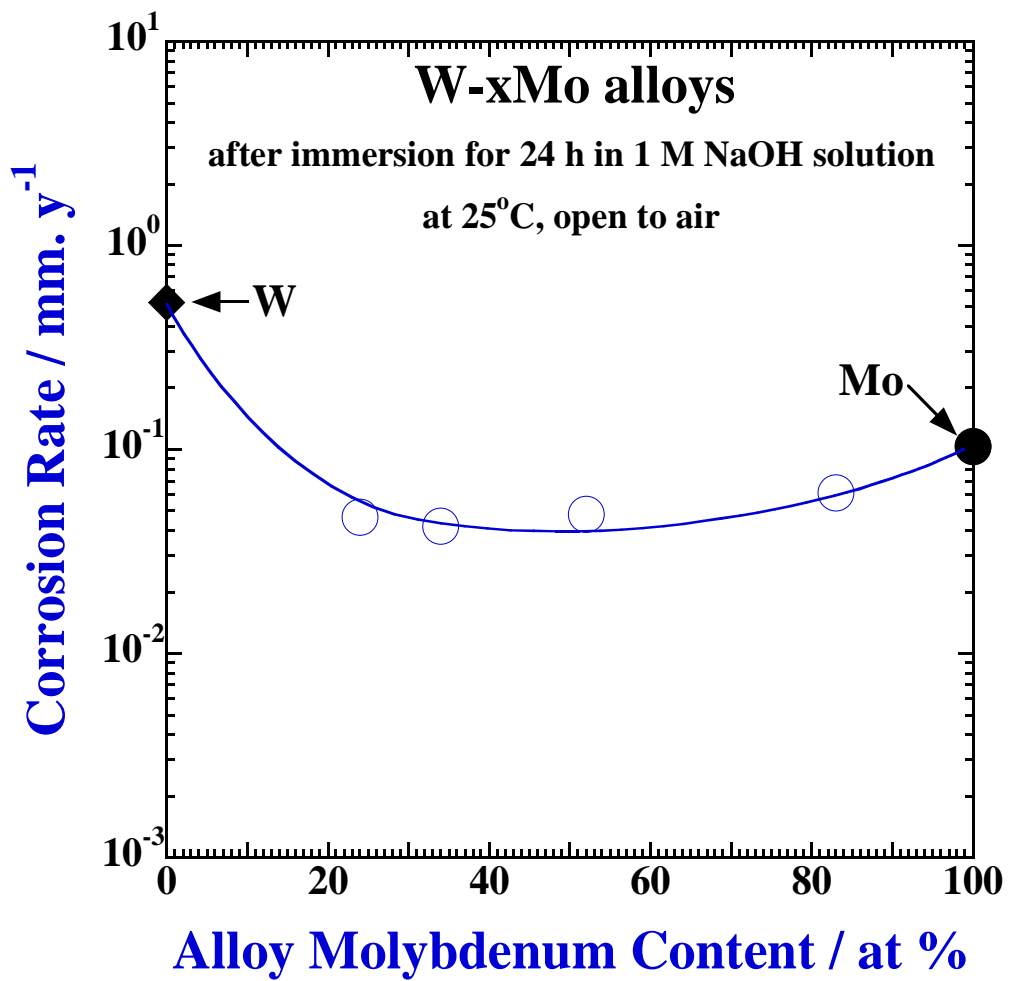


Figure 6: Changes in corrosion rates of the sputter-deposited nano-crystalline W-Mo alloys including tungsten and molybdenum metals in 1 M NaOH solution at 25°C, as a function of alloy molybdenum content.

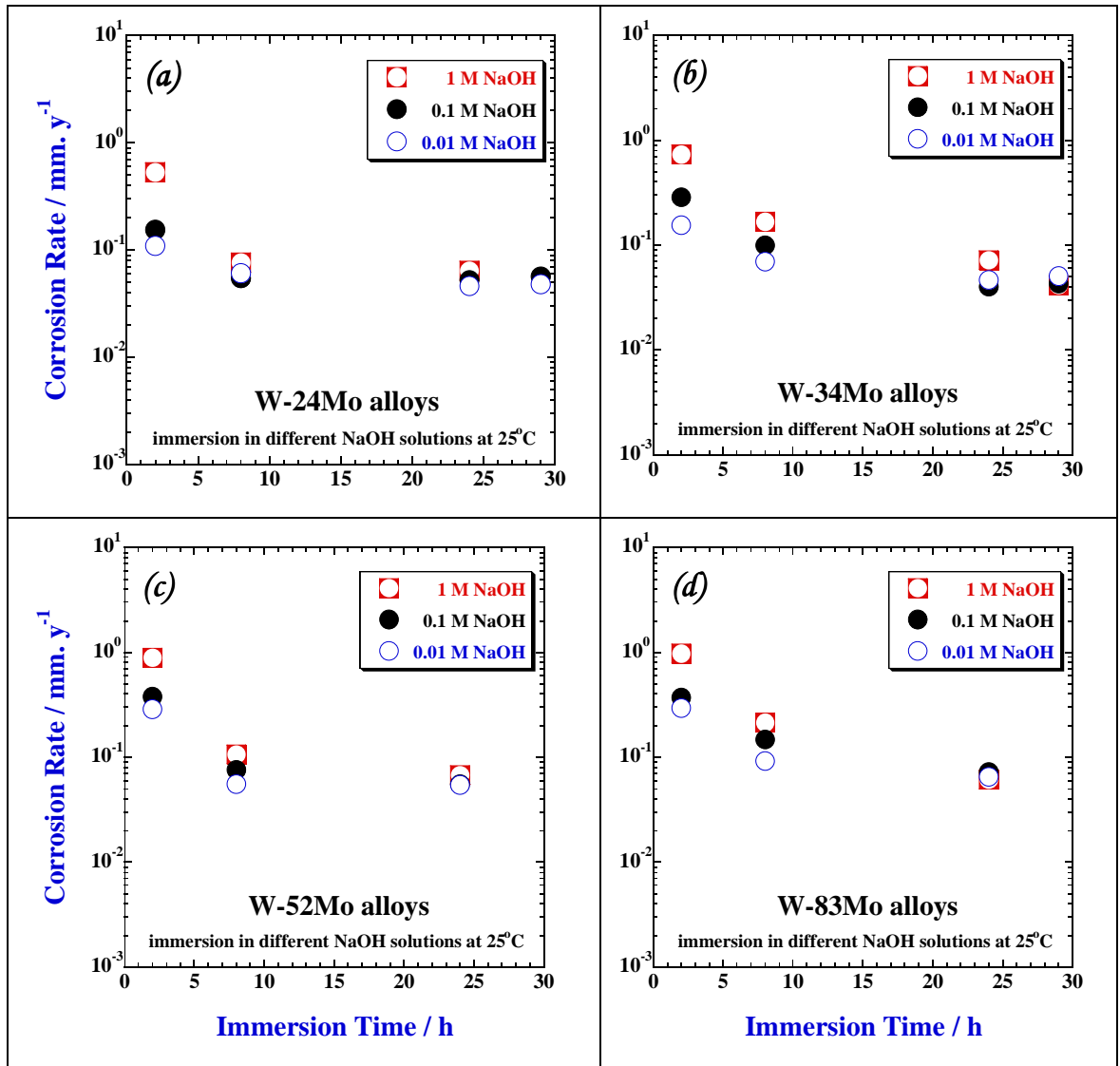


Figure 7: The change in corrosion rate of the sputter-deposited nanocrystalline W-Mo alloys in 0.01 M, 0.1 M and 1 M NaOH solutions open to air at 25°C, as a function of immersion time.

3.2 ELECTROCHEMICAL MEASUREMENTS OF THE SPUTTER-DEPOSITED NANOCRYSTALLINE W-Mo ALLOYS

Electrochemical measurements were carried out for a better understanding of the corrosion behavior of the sputter-deposited nanocrystalline W-Mo alloys for about 2 hours in alkaline 0.01 M, 0.1 M and 1 M NaOH solutions open to air at 25°C.

3.2.1 Open circuit potential in NaOH solutions

Figures 8, 9 and 10 show the changes in open circuit potentials for the sputter-deposited nanocrystalline W-Mo alloys as well as the tungsten metal in 1 M, 0.1 M and 0.01 M NaOH solutions, respectively, as a function of immersion time. The open circuit potentials of the sputter-deposited nanocrystalline W-Mo alloys are in more noble (positive) direction with increasing the molybdenum content particularly in 1 M NaOH solution (Figure 8). Furthermore, the open circuit potentials of all the examined W-Mo alloys are increased with immersion time and attained a steady state after immersion for about 10 minutes in different concentrations of NaOH solutions. In particular, the open circuit potentials of all the W-Mo alloys containing 24-83 at % molybdenum are almost same in 0.01 M NaOH solution. These facts coincide with the changes in the corrosion rates of the sputter-deposited nanocrystalline W-Mo alloys after immersion for 2 hours in different concentrations of NaOH solutions as shown in figure 7.

A comparative study of the changes in the open circuit potentials for the sputter-deposited nanocrystalline W-Mo alloys in three different concentrations (that is, 0.01 M, 0.1 M and 1 M) of NaOH solutions are also discussed to explain the changes in the corrosion rates of the alloys

in the alkaline environments. Figure 11 shows the changes in open circuit potentials of the sputter-deposited nanocrystalline W-24Mo, W-34Mo, W-52Mo and W-83Mo alloys in different concentrations of NaOH solutions at 25°C, as a function of immersion time. It is cleared from these figures that the open circuit potentials of the tungsten-rich W-24Mo alloy are in more noble (positive) potential value in 0.01 M NaOH solution. The ennoblement of the open circuit potentials of the tungsten-rich W-Mo alloys is clearly observed with decreasing the concentration of NaOH solutions. However, the open circuit potentials of the molybdenum-rich W-Mo alloys are almost same in all three different concentrations (that is, 0.01 M, 0.1 M and 1 M) of the NaOH solutions open to air at 25°C.

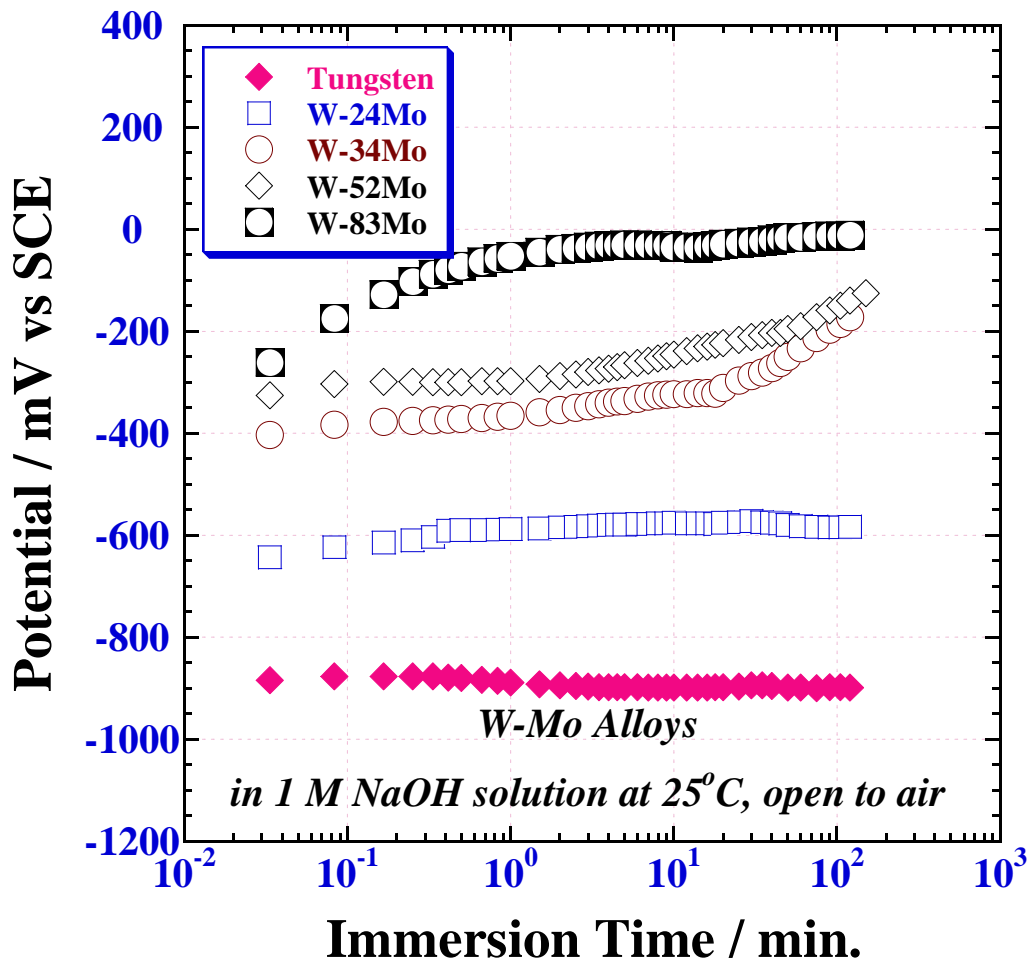


Figure 8: Changes in open circuit potentials for the sputter-deposited nanocrystalline W-Mo alloys including tungsten metals in 1 M NaOH solution at 25°C, as a function of immersion time.

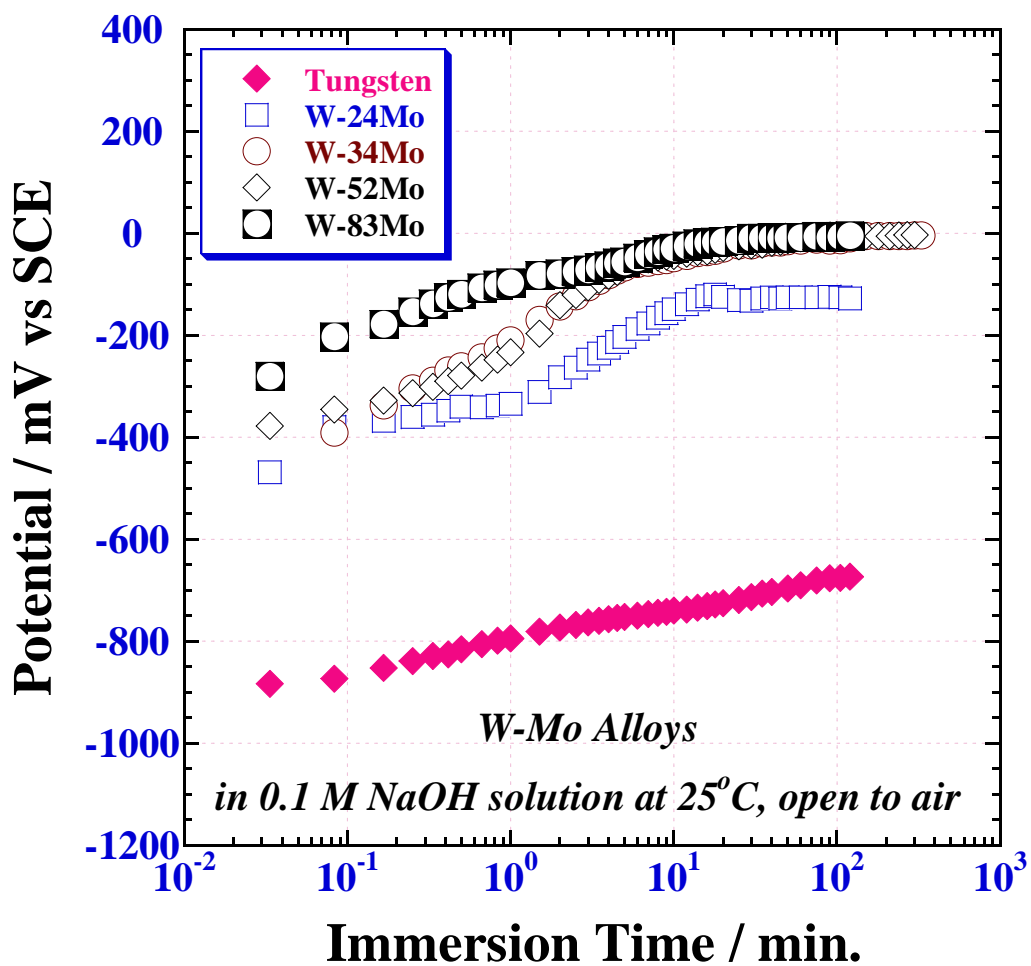


Figure 9: Changes in open circuit potentials for the sputter-deposited nanocrystalline W-Mo alloys including tungsten metals in 0.1 M NaOH solution at 25°C, as a function of immersion time.

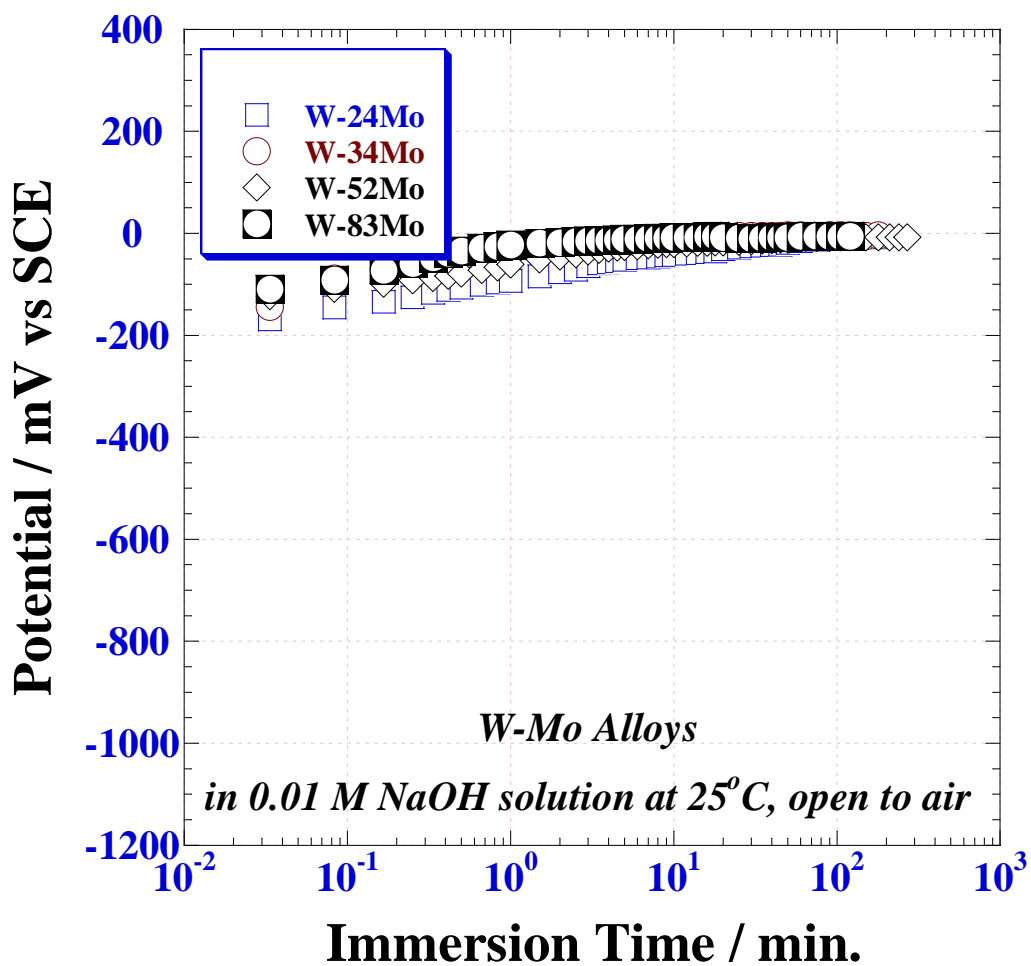


Figure 10: Changes in open circuit potentials for the sputter-deposited nanocrystalline W-Mo alloys in 0.01 M NaOH solution at 25°C, as a function of immersion time.

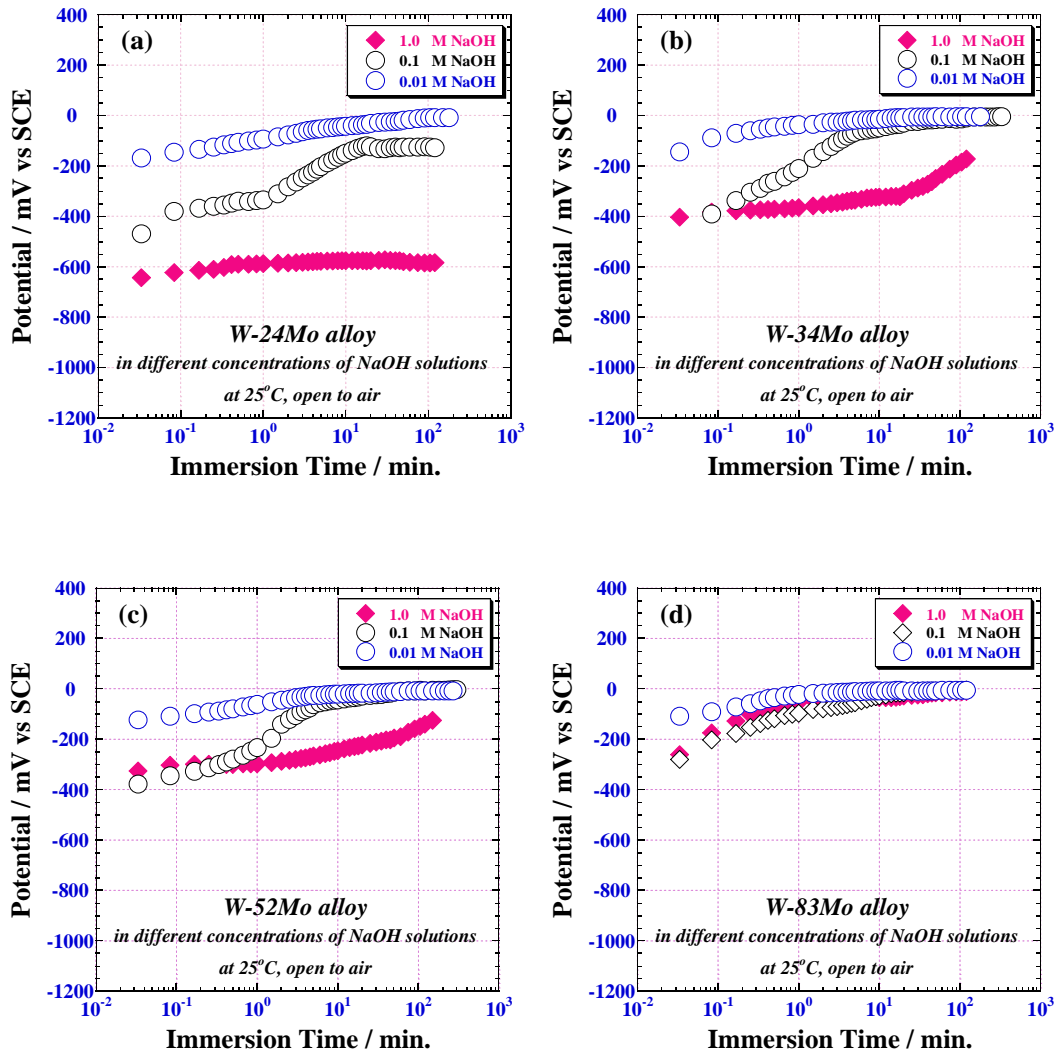


Figure 11: Changes in open circuit potentials for the sputter-deposited nanocrystalline (a) W-24Mo, (b) W-34Mo, (c) W-52Mo and (d) W-83Mo alloys in different concentrations of NaOH solutions open to air at 25°C, as a function of immersion time.

3.3 CONCLUSIONS

The corrosion behavior of the sputter-deposited nanocrystalline W-Mo alloys is studied in alkaline NaOH solutions at 25°C, open to air by using immersion tests and electrochemical measurements. The following conclusions are drawn:

1. The corrosion rates of W-Mo alloys containing 24-83 at % of molybdenum showed about one order of magnitude lower corrosion rates (i.e., $4-5 \times 10^{-2} \text{ mm.y}^{-1}$) than that of sputter-deposited tungsten and even lower corrosion rate than that of molybdenum after immersion for 24 hours in alkaline NaOH solutions.
2. The corrosion rates of all the examined W-Mo alloys are almost independent of concentrations of NaOH solutions.
3. The open circuit potentials of the sputter-deposited W-Mo alloys are shifted to the noble (more positive) direction with increasing the molybdenum content in the alloys in alkaline NaOH solutions.
4. The stability of the spontaneously formed films formed on the binary tungsten-rich W-Mo alloys is increase with decreasing the concentrations of NaOH solution, although such effect is not observed for the molybdenum-rich W-Mo alloys after immersion for two hours in alkaline NaOH solutions.

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