

Effects of Alloying Elements on the Corrosion Behavior of Amorphous Cobalt-Base Alloys

著者	NAKA Masaaki, HASHIMOTO Koji, MASUMOTO									
	Tsuyoshi									
journal or	Science reports of the Research Institutes,									
publication title	ohoku University. Ser. A, Physics, chemistry									
	and metallurgy									
volume	27									
page range	246-258									
year	1979									
URL	http://hdl.handle.net/10097/28082									

Effects of Alloying Elements on the Corrosion Behavior of Amorphous Cobalt-Base Alloys*

Masaaki Naka, Koji Hashimoto and Tsuyoshi Masumoto

The Research Institute for Iron, Steel and Other Metals

(Received January 31, 1979)

Synopsis

Corrosion characteristics of amorphous cobalt-base alloys in 1N HCl have been investigated by immersion and electrochemical techniques. The corrosion resistance of amorphous Co-P-B alloy is intermediate between those of amorphous Fe-P-B and Ni-P-B alloys. The alloying with chromium, molybdenum, tungsten, nickel and copper is effective in improving the corrosion resistance. In particular, the addition of chromium and the combind addition of chromium with molybdenum lead to spontaneous passivation. The corrosion resistance of chromium-bearing alloy is improved by alloying with various metalloids but is lowered by an increase in boron and silicon. All alloys which passivate do not suffer pitting corrosion even by anodic polarization in 1N HCl.

I. Introduction

Extremely high corrosion resistance which is difficult to obtain in crystalline alloys is the most important characteristics of some amorphous alloys. Those alloys do not suffer pitting corrosion even by anodic polarization in 1 N HCl and often passivate spontaneously⁽¹⁻³⁾. Their susceptibility to crevice corrosion is also very low⁽⁴⁾. The corrosion resistance is greatly affected by alloying with various metallic and metalloidal elements⁽⁵⁻⁷⁾.

Such studies have so far mainly been focused on amorphous iron- and nickel-base alloys. The work reproted herein has been undertaken to clarify the corrosion behavior of amorphous cobalt-base alloys. Particular attention has been given to the effects of addition of a number of metallic and metalloidal elements.

^{*} The 1695th report of the Research Institute for Iron, Steel and Other Metals.

⁽¹⁾ M. Naka, K. Hashimoto and T. Masumoto, J. Japan Inst. Metals, 38 (1974), 835. Corrosion, 32 (1976), 146.

⁽²⁾ K. Hashimoto, M. Kasaya, K. Asami and T. Masumoto, Corros. Engng. (Boshoku Gijutsu), 26 (1977), 445.

⁽³⁾ M. Naka, K. Hashimoto and T. Masumoto, J. Non-Cryst. Solids, 29 (1978), 61.

⁽⁴⁾ R.B. Diegle, Corrosion, 43 (1979).

⁽⁵⁾ M. Naka, K. Hashimoto and T. Masumoto, J. Non-Cryst. Solids, 28 (1978), 403.

⁽⁶⁾ K. Hashimoto, M. Naka, K. Asami and T. Masumoto, Corros. Engng. (Boshoku Gijutsu), 27 (1978), 279.

⁽⁷⁾ M. Naka, K. Hashimoto and T. Masumoto, J. Non-Cryst. Solids, 31 (1979).

II. Experimental procedures

Rotating wheel method was applied to the preparation of amorphous cobalt-base alloys by rapid quenching from the liquid state. The amorphous alloy ribbons prepared were about 2 mm wide and 30 μ m thich and are summarized in Tables 1 and 2. The number attached to respective element of alloy formula denotes the nominal content in atomic percent. Formation of amorphous structure was confirmed by X-ray diffraction.

Corrosion tests and electrochemical measurements were carried out in 1 N HCl which was prepared by using reagent-grade chemicals and de-ionized water.

Table 1. Nominal composition of amorphous Co-13P-7B alloys (at. %).

Table 1. Nonlinial composition of amorphous co-131-7D alloys (at. 70).									
Alloy	Со	Cr	Мо	W	Fe	Ni	Cu	P	В
Co-13P-7B	80	-					_	13	7
Co-Cr-13P17B	78	2	_	_	_			13	7
	}			-	_			13	7
	65	15		<u> </u>	_			13	7
	7 8		2		_			13	7
Co-Mo-13P-7B	}	-			_		_	13	7
	60		20		_			13	7
	75	-	_	_	5		-	13	7
Co-Fe-13P -7 B	}	_		<u> </u>	}			13	7
	0			-	80	_	_	13	7
Co-Ni-13P- 7 B	75					5	- '	13	7
	₹	_		_	_	}	_	13	7
	0	_	<u> </u>	_	<u> </u>	80		13	7
Co 4Cr Mo 13D 7B	73	4	3			_	_	13	7
Co-4Cr-Mo-13P-7B	71	4	5	_		_	-	13	7
	71	4		-	5	_		13	7
Co-4Cr-Fe-13P-7B	66	4		<u> </u>	10		-	13	7
	61	4			15			13	7
	71	4	_	_	_	5	_	13	7
Co-4Cr-Ni-13P-7B	66	4		_		10		13	7
	61	4		<u> </u>		15	_	13	7
Co-4Cr-Cu-13P-7B	75.5	4	<u> </u>	-		_	0.5	13	7
C0-4C1-Cu-13P-7B	74	4	-	_			2	13	7
Co-10Mo-Fe-13P-7B	70		10	_	0			13	7
	}		10		}			13	7
	0		10	_	70			13	7
	70		_	10	0	_		13	7
Co-10W-Fe-13P-7B	}		_	10	?	_	-	13	7
	0			10	70	-		13	7

Table 2. Nominal composition of amorphous Co-Cr-20B alloys (at. %).

Alloy	Со	Cr	В	Al	С	Si	Ge	Sn	P	As	Sb	S
Co-20B	80	_	20	-	-	_	_	_			-	_
Co-Cr-20B	72	8	20	_		_			_			
	`	}	20		_		-				-	
	30	50	20		_	_	_			_	_	
	69	10	21	_	_		-	_		_		
Co-10Cr-B	67	10	23			_	-			-		
	65	10	25	-	_		-				-	
Co-10Cr-20B-Al	69	10	20	1	_	_	-			-	-	_
	67	10	20	3		_			_			
	69	10	20	-	1	-		-	_	_	-	_
Co-10Cr-20B-C	67	10	20		3				_		-	-
	65	10	20		5	-	_			-		_
	69	10	20	_	_	1	-	_	_	_		_
Co-10Cr-20B-Si	67	10	20			3	-	-		-	_	_
	65	10	20		-	5	<u> </u>	<u>-</u>	_			_
	69	10	20	-	-		1	-		-	_	_
Co-10Cr-20B-Ge	67	10	22	-	_	-	3	_				-
	65	10	20	_			5					_
Co-10Cr-20B-Sn	69	10	20	-	_		_	1	_		_	-
	67	10	20	-	-	-		3	_		-	_
Co-10Cr-20B-P	69	10	20	-			_	_	1		T -	_
	67	10	20		-	-		-	3	_	-	_
	65	10	20		-	-	-	-	5	-	-	-
Co-10Cr-20B-As	69	10	20	-	_	_	_	-	_	1	-	-
	67	10	20	-			-	_	-	3	-	-
	65	10	20			<u> </u>			_	5	_	_
Co-10Cr-20B-Sb	69	10	20	_	-		-	-	_	-	1	-
	67	10	20	_	_	_	-	_	_	-	3	-
Co-10Cr-20B-S	69	10	20		-	-	-	-	-	_	-	1

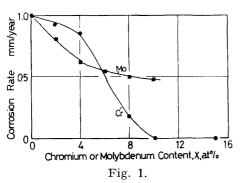
The corrosion rate of alloy was estimated from the weight loss during immersion in the solution at 303 ± 1 K, which was open to the air. The measurement of anodic polarization curves was made by a potentiadynamic method with a potential sweep rate of 2.37×10^{-3} V·s⁻¹, starting from the corrosion potential at room temperature.

III. Results

III-1. Effects of metallic additives

Figures 1-3 reveal the change in corrosion rate of amorphous Co-M-13P-7B alloys in 1 N HCl as a function of content of metallic element, M. The addition of certain amounts of chromium is most effective for increasing the corrosion resistance of alloys. When the addition is made in a small amount, molybdenum is more effective than chromium, but the lowering of corrosion rate by the alloying with a large amount of molybdenum is smaller in comparison with the addition of chromium. The addition of iron and nickel up to 20 at.% does not result in an appreciable change in the corrosion rate. When large amounts of these elements are added, the alloying with nickel which is more noble than the base metal of alloy, that is, cobalt leads to the lowering of the corrosion rate toward that of nickel-base alloy, while the alloying with iron which is more active than cobalt results in the rise in the corrosion rate toward that of iron-base alloy. corrosion rates of Ni-13P-7B (80 at.% Ni in Fig. 2) and Fe-13P-7B (80 at.% Fe in Fig. 3) alloys are about one-fifth and twelve times as high as that of Co-13P-7B alloy in 1 N HCl.

These changes by alloying can clearly be seen from anodic polarization curves measured in 1 N HCl. As shown in Figs. 4 and 5, the addition of chromium,



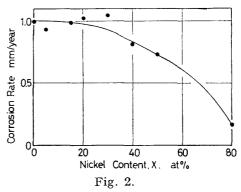


Fig. 1. Average corrosion rates estimated from the weight loss of amorphous Co-Cr-13P-7B and Co-Mo-13P-7B aloys in 1 N HCl.

Fig. 2. Average corrosion rate of amorphous Co-Ni-13P-7B alloys in 1N HCl.

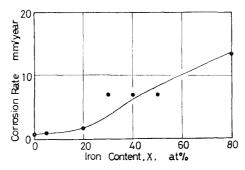


Fig. 3. Average corrosion rate of amorphous Co-Fe-13P-7B alloys in 1 N HCl.

molybdenum and nickel decreases the anodic current density and raises the corrosion potential, whereas the alloying with iron increases the anodic current density and lowers the corrosion potential. The alloys containing certain amounts of chromium tend to passivate by anodic polarization. The addition of 10 at.% or more chromium leads to spontaneous passivation even in 1 N HCl and an abrupt rise in current density due to pitting is not observed up to the transpassive region of chromium.

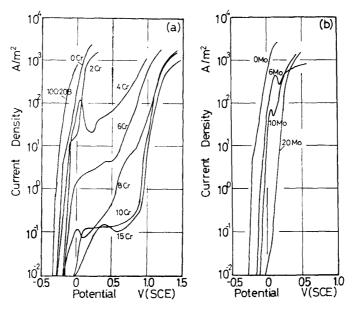


Fig. 4. Potentiodynamic polarization curves of amorphous Co-Cr-13P-7B (a) and Co-Mo-13P-7B (b) alloys measured in 1 N HCl.

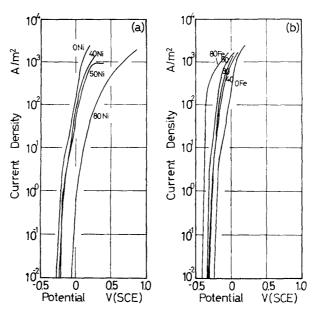


Fig. 5. Potentiodynamic polarization curves of amorphous Co-Ni-13P-7B (a) and Co-Fe-13P-7B (b) alloys measured in 1 N HCl.

Combined effect of metallic additives on corrosion behavior of amorphous Co-13P-7B alloys was examined by the addition of several metallic elements. Figs. 6—8 reveal the effect of combined addition of a small amount of chromium and other metallic elements on the corrosion behavior in 1 N HCl. The addition of a small amount of copper is most effective among four metallic elements for decreasing the corrosion rate and for increasing the corrosion potential in 1 N HCl. One of disadvantages is, however, the fact that it becomes difficult to prepare amorphous

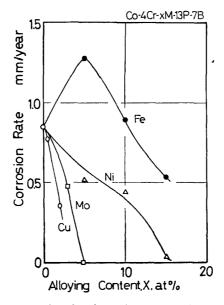


Fig. 6. Effect of metallic alloying elements, M, on the corrosion rate of amorphous Co-4Cr-M-13P-7B alloys in 1 N HCl.

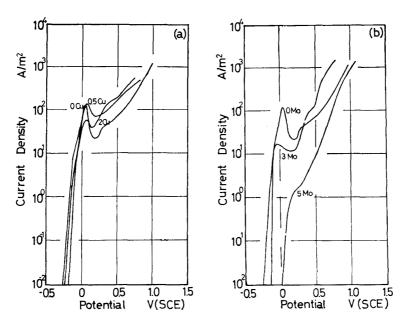


Fig. 7. Potentiodynamic polarization curves of amorphous Co-4Cr-Cu-13P-7B (a) and Co-4Cr-Mo-13P-7B (b) alloys measured in 1 N HCl.

alloys with an increase in the copper content. The alloying with molybdenum significantly reduces the corrosion rate and anodic current density. In particular, Co-4Cr-5Mo-13P-7B alloy passivate spontaneously even in 1 N HCl and does not show a detectable corrosion rate. The addition of nickel to Co-4Cr-13P-7B alloy is also effective for decreasing the corrosion rate and anodic current density and for raising the corrosion potential but less effective than the addition of molybdenum. The corrosion rate and anodic current density of Co-3Cr-Fe-13P-7B alloys increase at 5 at. % iron but decrease with further increase in iron content.

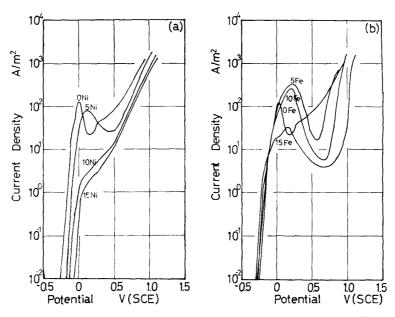


Fig. 8. Potentiodynamic polarization curves of amorphous Co-4Cr-Ni-13P-7B (a) and Co-4Cr-Fe-13P-7B (b) alloys measured in 1 N HCl.

As shown in Figs. 9 and 10, the corrosion rate and anodic current density of Co-13P-7B alloys containing 10 at.% molybdenum or tungsten decrease by the addition of iron up to 20 or 30 at.% but increase by further addition of iron.

III-2. Effects of metalloid additives

Figure 11 illustrates the change in average corrosion rate of amorphous Co-Cr-20B and Co-Cr-13P-7B alloys in 1 N HCl as a function of chromium content of alloys. When phosphorus is contained as a major metalloid, the corrosion rate of the alloy decreases by the addition of chromium and the alloy becomes immune to corrosion at 10 at.% chromium. On the other hand, when only boron is contained as a metalloid, Co-Cr-20B alloys containing chromium up to 20 at.% show high corrosion rates similarly to Co-20B alloy and the addition of 50 at.% chromium is required for immunity to corrosion in 1 N HCl. In contrast to anodic polarization curves of Co-Cr-13P-7B alloy shown in Fig. 4 (a), those of Co-Cr-20B alloys do not greatly change by the addition of chromium less than 20 at.% and do not

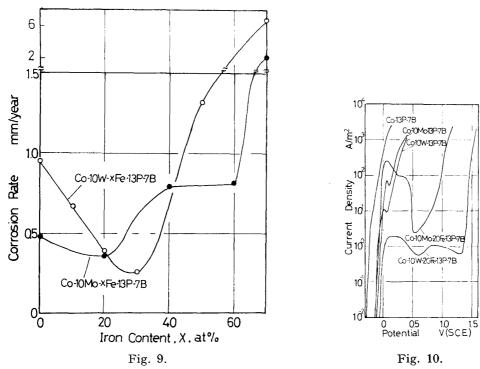


Fig. 9. Average corrosion rates of amorphous Co-10Mo-Fe-13P-7B and Co-10W-13P-7B alloys in 1 N HCl.

Fig. 10. Potentiodynamic polarization curves of various amorphous Co-13P-7B alloys measured in 1 N HCl.

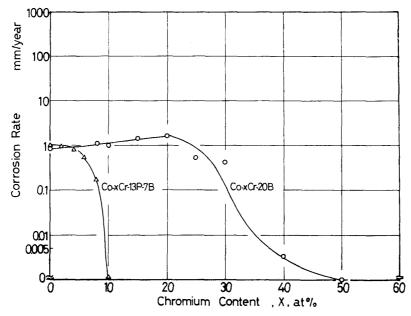


Fig. 11. Average corrosion rates of amorphous Co-Cr-13P-7B and Co-Cr-20B alloys in 1 N HCl.

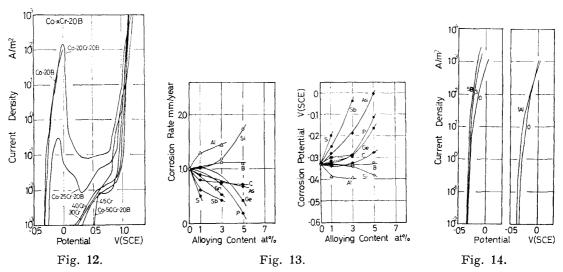


Fig. 12. Potentiodynamic polarization curves of amorphous Co-Cr-20B alloys measured in 1 N HCl.

Fig. 13. Effect of minor alloying elements on the corrosion rate (a) and corrosion potential (b) of amorphous Co-10Cr-20B alloys measured in 1 N HCl.

Fig. 14. Change in potentiodynamic polarization curves of amorphous Co-10Cr-20B alloys measured in 1 N HCl by alloying with boron or aluminum.

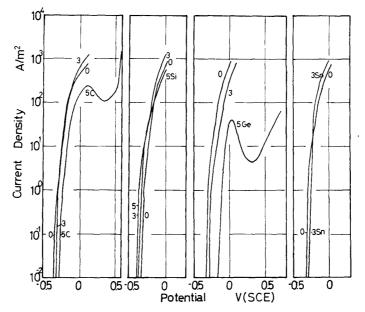


Fig. 15. Change in potentiodynamic polarization curves of amorphous Co-10Cr-20B alloys measured in 1 N HCl by alloying with carbon, silicon, germanium or tin.

exhibit passivation by anodic polarization as shown in Fig. 12. When the Co-Cr-20B alloys contain 20 at.% or more chromium, the anodic passivation takes place and the anodic current density decreases with an increase in chromium content. The spontaneous passivation occurs at 30 at.% or more chromium.

Effects of minor metalloid elements in amorphous Co-10Cr-20B alloy are given

in Figs. 13-16. The corrosion rate in 1 N HCl increases by the alloying with boron, aluminum and silicon but decreases by the addition of other metalloidal elements. Anodic polarization curves indicate the fact that the addition of beneficial elements reduces the anodic current density and raises the corrosion potential. In particular, the addition of phosphorus, germanium and carbon tends to passivate the Co-10Cr-20B alloy by anodic polarization.

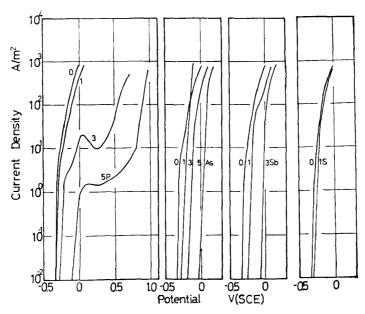


Fig. 16. Change in potentiodynamic polarization curves of amorphous Co-10Cr-20B alloys measured in 1 N HCl by alloying with phosphorus, arsenic, antimony or sulfur.

IV. Discussion

One of the most important characteristics of amorphous alloys, that is, the immunity to pitting corrosion even by anodic polarization in 1 N HCl is again confirmed for cobalt-base alloys.

The comparison of anodic polarization curves of amorphous Fe-13P-7B (80 at.% Fe in Fig. 5 (b)), Co-13P-7B (0 at.% Fe in Fig. 5 (b)) and Ni-13P-7B (80 at.% Ni in Fig. 5 (a)) alloys measured in 1 N HCl clearly reveals the fact that, when the base metal of alloy is more noble, the anodic activity is lower. Because the stability and protective quality of corrosion products of iron, cobalt and nickel are not greatly different from each other, the addition of iron or nickel to cobalt-base alloys changes the corrosion resistance according to the change in the anodic activity of alloys. The same interpretation can be made to the lowering of corrosion rate of Co-4Cr-13P-7B alloy by the addition of nickel and copper (Fig. 4). These extra metallic elements do not constitute the surface film and simply reduce the anodic activity of alloy depending upon their contents and nobleness (7). Therefore, the addition of very noble copper to the Co-4Cr-13P-7B alloy is sufficient in a small amount for the reduction of corrosion, but nickel is necessary to be added in a large

amount.

The corrosion behavior of amorphous Co-P-B and Fe-P-C(7) alloys is affected similarly to each other by alloying with other elements. When chromium or molybdenum is added to the cobalt-base alloys, the open circuit corrosion rate in the active region of the alloys decreases due to the improvement of protective quality of corrosion product film in which the cations of these alloying elements are concentrated (7,8). In other words, these elements are more active than cobalt but their corrosion products are more stable than that of cobalt at the corrosion potential of alloys. Accordingly, the corrosion resistance of alloys is dependent upon the stability and content of corrosion product of alloying elements in the corrosion product films formed on the alloys. When certain amounts of chromium is added, the active dissolution rate of alloys lowers significantly by marked enrichment of chromic ion in the surface film and spontaneous passivation often takes place by the formation of passive hydrated chromium oxy-hydroxide film (9).

Similarly, the alloying with molybdenum enhances the formation of corrosion product film, in which molybdenum species are highly enriched, and hence reduces the corrosion rate and anodic current density in the active region of alloys (10). In this connection, a small addition of molybdenum is more effective than that of chromium. This suggests the fact that the corrosion product of molybdenum is more stable than that of chromium in the active region of the alloys. When the alloys are polarized at higher potentials, the molybdenum species become unstable because of transpassive reaction of molybdenum⁽¹¹⁾. Therefore, Co-Mo-P-B alloys do not passivate by anodic polarization, despite the fact that the anodic current density decreases with an increase in molybdenum content (Fig. 4 (b)). On the contrary, the anodic passivation takes place on amorphous Fe-Mo-P-C⁽³⁾ and Fe-Mo-C⁽¹²⁾ alloys in 1 N HCl by the formation of hydrated iron oxyhydroxide film with the aid of molybdenum. The beneficial effect of molybdenum for passivation has been interpreted in detail elsewhere (10,12-15). The corrosion product of molybdenum assists the formation of passive hydrated chromium or iron oxy-hydroxide film between the corrosion product film and the underlying stainless steels or amorphous iron-base alloys. The corrosion product of molybdenum is formed as a result of rapid active dissolution of alloy and is not stable at high potentials in the passive region. Accordingly, when the condition for the rapid supply of molybdenum species to form the corrosion product film fails though the

⁽⁸⁾ K. Hashimoto, K. Asami, M. Naka and T. Masumoto, Corros. Sci., in press.

⁽⁹⁾ K. Hashimoto, K. Asami, M. Naka and T. Masumoto, Corros. Engng. (Boshoku Gijutsu), 28 (1979), 271.

⁽¹⁰⁾ K. Hashimoto, M. Naka, K. Asami and T. Masumoto, Corros. Sci., 19 (1979).

⁽¹¹⁾ K. Sugimoto and Y. Sawada, Corros. Sci., 17 (1977), 425.

⁽¹²⁾ M. Naka, K. Hashimoto and T. Masumoto, J. Non-Cryst. Solids, 31 (1979).

⁽¹³⁾ K. Hashimoto, K. Asami and K. Teramoto, Corros. Sci., 19 (1979), 3.

⁽¹⁴⁾ K. Hashimoto and K. Asami, Corros. Sci., 19 (1979).

⁽¹⁵⁾ K. Hashimoto, K. Asami, M. Naka and T. Masumoto, Sci. Rep. RITU, A27 (1979), 237.

lowering of dissolution rate of alloy, the corrosion product dissolves out into solution. In this manner, the beneficial effect of molybdenum for passivation of amorphous alloys appears when the active dissolution rate of alloys is sufficiently high to form rapidly the molybdenum enriched corrosion product film which is able to act an effective diffusion barrier to dissolution of alloys in the passive region. As mentioned previously, the anodic activity of iron-base alloy is greatly higher than that of cobalt-base alloy. This fact seems mainly responsible for the difference in the passivation tendency between amorphous cobalt-molybdenum and iron-molybdenum alloys. In other words, the anodic activity of cobalt-base alloys containing molybdenum is high enough to form the corrosion procut film which can definitely reduce the corrosion rate in the active region but is not sufficiently high to form the corrosion product film which can assist the passivation of alloys by the formation of passive film consisting mainly of cobalt as cations.

The combined addition of a small amount of chromium and other extra metallic elements is particularly interesting. The addition of elements more active than base metal of alloy either raises the corrosion rate by an increase in the anodic activity or reduces the corrosion rate (8). The improvement of corrosion resistance of chromium-bearing alloy by the addition of the active elements is made due to the rapid enrichment of chromic ion in the surface film through the accelerated dissolution of alloy and/or due to the decrease in the dissolution rate of alloy by the rapid formation of the corrosion product film in which the extra alloying elements are concentrated. The addition of molybdenum to Co-4Cr-13P-7B alloy satisfies both the requirements for the improvement of corrosion resistance and hence leads to the spontaneous passivation of alloy at 5 at.% molybdenum by forming a passive hydrated chromium oxy-hydroxide film. On the other hand, the addition of 5 at.% iron to Co-4Cr-13P-7B alloy is not sufficient to accelerate the active dissolution for the enrichment of chromic ion and accordingly increases the corrosion rate and anodic current density. However, the alloying with a large amount of iron such as 15 at.% enhances the enrichment of chromic ion and reduces the corrosion rate and anodic current density. Similarly, the anodic polarization facilitates the enrichment of chromic ion by the accelerated active dissolution and leads to passivation even at 5 at.% iron.

The addition of iron to Co-13P-7B alloys containing molybdenum or tungsten increases the anodic activity of alloys and raises the protective quality of corrosion product film in which molybdenum or tungsten species are concentrated. However, when the ratio of iron to cobalt in the alloy exceeds about unity, the change in base metal of alloy from cobalt to iron results in the excess increase in the anodic activity in preference to the rise in the protective quality of corrosion product film and hence lowers the corrosion resistance. Nevertheless, the addition of a large amount of iron facilitates the anodic passivation of alloy because the high anodic activity induces the beneficial effect of molybdenum for the passivation.

The present anthors, in reporting X-ray photoelectron spectroscopic and electrochemical studies (6,9), have stated that the effects of metalloids on the corrosion behavior of amorphous alloys have been determined by the acceleration of active dissolution of alloys and by the incorporation of metalloids as polyanions in the surface film formed. In general, the anodic activity of amorphous alloys is higher than those of corresponding crystalline metals and binary metal-metal systems because of high content of metalloids (1,7). The high anodic activity provides the high corrosion resistance if the alloy contains the element such as chromium which can form a protective film. In particular, phosphorus is the most effective metalloid for increasing the corrosion resistance through the rapid and significant enrichment of chromic ion in the surface film and leads often to the spontaneous passivation by the formation of passive hydrated chromium oxy-hydroxide film in which phosphate content is very low (6,9,16).

On the other hand, an increase in the content of boron or silicon lowers the corrosion resistance (Fig. 13). This fact has also been found on amorphous iron-chromium alloys (5,6). The following interpretation has been made (6,9): even if the surface film consists exclusively of chromic ion as a cation, the sponteneous passivation does not always occur, when the concentration of hydrated chromium oxy-hydroxide in the film is not sufficiently high on account of the incorporation of polyanions such as borate and silicate in the film.

V. Conclusion

The corrosion behavior of amrophous cobalt-base alloys containing various metallic and metalloidal elements in 1 N HCl has been studied by immersion test and electrochemical techniques. The following conclusion can be drawn:

- 1. The addition of chromium is most effective for improving the corrosion resistance by forming chromium enriched surface film.
- 2. The alloying with molybdenum is also effective in the active region of alloys on account of the formation of protective surface film, but is not effective for the passivation of alloys unless other beneficial elements such as chromium and iron are contained.
- 3. The addition of iron is detrimental since the alloying increases the anodic activity of alloy. However, when chromium, molybdenum or tungsten is contained in the alloy, the addition of iron sometimes increases the corrosion resistance and leads to passivation by anodic polarization.
- 4. The addition of copper and nickel increases the corrosion resistance by decreasing the anodic activity of alloy.
- 5. The corrosion resistance of chromium-bearing alloy is improved by alloying with various metalloids but is decreased by an increase in boron and silicon.

⁽¹⁶⁾ K. Asami, K. Hashimoto, T. Masumoto and S. Shimodaria, Corros. Sci., 16 (1976), 909.