

Effect of Chromium Addition on Corrosion Resistance of Amorphous Fe-B-C and Fe-B-Si Alloys*

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Synopsis

Change in the corrosion resistance of amorphous Fe-B-C and Fe-B-Si alloys without phosphorus due to the addition of chromium has been investigated. In contrast to the amorphous Fe-Cr-P-C alloys, the addition of chromium scarcely improves the corrosion resistance of amorphous Fe-B-C and Fe-B-Si alloys in 0.1 N H₂SO₄, while their corrosion resistance in 3% NaCl increases by the addition of chromium. The amorphous Fe-Cr-B₁₃-C₇ and Fe-Cr-B₁₃-Si₇ alloys containing 8 and 10 at% chromium do not exhibit the critical potential for pitting on the anodic polarization curves in 3% NaCl. It is concluded from comparison among the three sets of metalloid elements that the addition of phosphorus is most effective for improving the corrosion resistance of the amorphous iron alloys containing chromium.

I. Introduction

The present authors⁽¹⁻⁷⁾ have reported the corrosion characteristics of rapidly quenched amorphous iron base alloys containing phosphorus and carbon as metalloid elements. The amorphous Fe-P-C alloy without chromium is fairly unstable in corrosive environments. However, it has been observed that the addition of chromium remarkably improves the corrosion resistance. In particular, the amorphous Fe-Cr-P-C alloys containing chromium of 8 at% or more show no weight change during immersion tests in acidic and neutral solutions containing chloride, and do not practically suffer pitting and crevice corrosion.

This superior corrosion resistance of the amorphous Fe-Cr-P-C alloys has been interpreted in terms of rapid formation of uniform, highly corrosion-resistant passive films consisting mainly of hydrated chromium oxyhydroxide at corrosion potentials because of spontaneous passivation. The high uniformity of the passive films without weak points against corrosion has been secured by the homogeneous single

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- (1) M. Naka, K. Hashimoto and T. Masumoto, *J. Japan Inst. Metals*, **38** (1974), 835.
- (2) M. Naka, K. Hashimoto and T. Masumoto, *Corrosion*, **32** (1976), 146.
- (3) K. Hashimoto and T. Masumoto, *Mater. Sci. Eng.*, **23** (1976), 285.
- (4) K. Hashimoto, T. Masumoto and S. Shimodaira, "Passivity and Its Breakdown on Iron and Iron Base Alloys", *Proc. the U.S.A.-Japan Seminar*, ed. by R.W. Staehle and H. Okada, National Association of Corrosion Engineers, Houston, 1976, p. 34.
- (5) K. Hashimoto, K. Osada, T. Masumoto and S. Shimodaira, *Corr. Sci.*, **16** (1976), 71.
- (6) K. Asami, K. Hashimoto, T. Masumoto and S. Shimodaira, *Corr. Sci.*, **16** (1976) 909.
- (7) K. Hashimoto, M. Naka and T. Masumoto, *Sci. Rep. RITU A26* (1976), 48.

phase of the amorphous alloys which do not contain crystal defects acting as nucleation sites for corrosion, such as grain boundaries, dislocations, etc. High chemical reactivity of amorphous alloys mainly due to the existence of a large amount of phosphorus results in the rapid enrichment of chromium in the passive films.

Amorphous iron base alloys can also be prepared by rapid quenching from liquids containing boron, silicon and/or carbon instead of phosphorus as metalloid elements necessary to obtain the amorphous structure. According to the recent studies^(8,9) amorphous Fe-B-C and Fe-Si-B alloys possess good mechanical properties and high thermal stability. However, the amorphous iron base alloys without chromium are, in general, unstable in corrosive environments, and the question has been raised whether phosphorus is the essential alloying element to ensure high corrosion resistance to the amorphous iron base alloys with chromium.

This paper aims to clarify whether any sufficient improvement in the corrosion resistance can be attained by the addition of chromium in the amorphous iron base alloys without phosphorus.

II. Experimental procedures

Alloy ingots have been prepared by melting commercial metals under argon atmosphere. Rapid quenching to obtain the amorphous structure has been performed by impinging a jet of liquid on the outer surface of a rotating cylinder. By this method, some amorphous alloys can be prepared in the shape of sheets of 50 mm wide and 50 μm thick⁽¹⁰⁾. We call this method "rotating cylinder method." Two kinds of amorphous alloys containing carbon or silicon besides boron as metalloid elements have been prepared and are summarized in Table 1.

Table 1. Nominal composition of amorphous iron base alloys (atomic percent).

	Fe	Cr	B	C	Si	P
Fe-Cr-B-C	78	2	13	7	0	0
	75	5	13	7	0	0
	72	8	13	7	0	0
	70	10	13	7	0	0
Fe-Cr-B-Si	78	2	13	0	7	0
	75	5	13	0	7	0
	72	8	13	0	7	0
	70	10	13	0	7	0
Fe-Cr-P-C	75	5	0	7	0	13

(8) T. Masumoto, A. Inoue and H.I. Kimura, to be published in J. Japan Inst. Metals.

(9) M. Naka, T. Murata and T. Masumoto, presented at Autumn Symposium of the Japan Institute of Metals, 1976.

(10) Y. Kobayashi and T. Masumoto, to be published.

The corrosion characteristics have been examined by total immersion tests and potentiodynamic polarization measurements with a potential sweep rate of 0.142 V/min from the cathodic potential region. Electrolytes employed are 3% NaCl and 0.1 N H_2SO_4 at 30°C which have been prepared by using reagent grade chemicals and deionized water. The average corrosion rates have been estimated from the weight loss of specimens during immersion tests.

III. Results and discussion

The amorphous Fe-Cr-B-C and Fe-Cr-B-Si alloys immersed in 0.1 N H_2SO_4 , and 3% NaCl suffer general corrosion, except for those with high chromium concentration which show no pitting and general corrosion in 3% NaCl. The corrosion rates of the amorphous Fe-Cr-B-C and Fe-Cr-B-Si alloys in 0.1 N H_2SO_4 and 3% NaCl are shown as a function of the chromium content in Fig. 1. The corrosion rates of these alloys are very high in general, but the measured values are poorly reproducible. In contrast to the case of amorphous Fe-Cr-P-C alloys^(1,2), the corrosion resistance of these alloys immersed in 0.1 N H_2SO_4 is scarcely improved by an increase in the chromium content, although the corrosion rates in 3% NaCl tend to decrease with the increase in the chromium content.

Figures 2 and 3 show the potentiodynamic polarization curves of the amorphous Fe-Cr-B-C and Fe-Cr-B-Si alloys measured in 0.1 N H_2SO_4 . Because of high dissolution rates the anodic polarization curves of alloys with low chromium contents cannot be obtained. With the increase in the chromium content the passivation is observed on the anodic polarization curves. The passivation current densities of these alloys in 0.1 N H_2SO_4 are fairly higher than

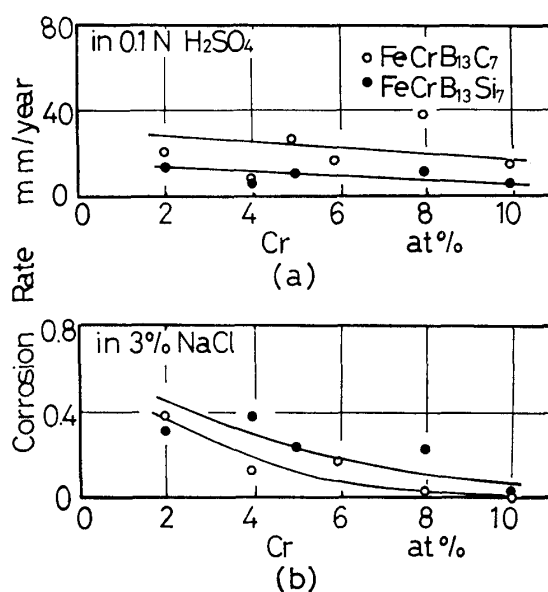


Fig. 1. Change in corrosion rates with the chromium content of the amorphous Fe-Cr-B₁₃-C₇ and Fe-Cr-B₁₃-Si₇ alloys in 0.1 N H_2SO_4 and 3% NaCl.
 (a) 0.1 N H_2SO_4 . (b) 3% NaCl.

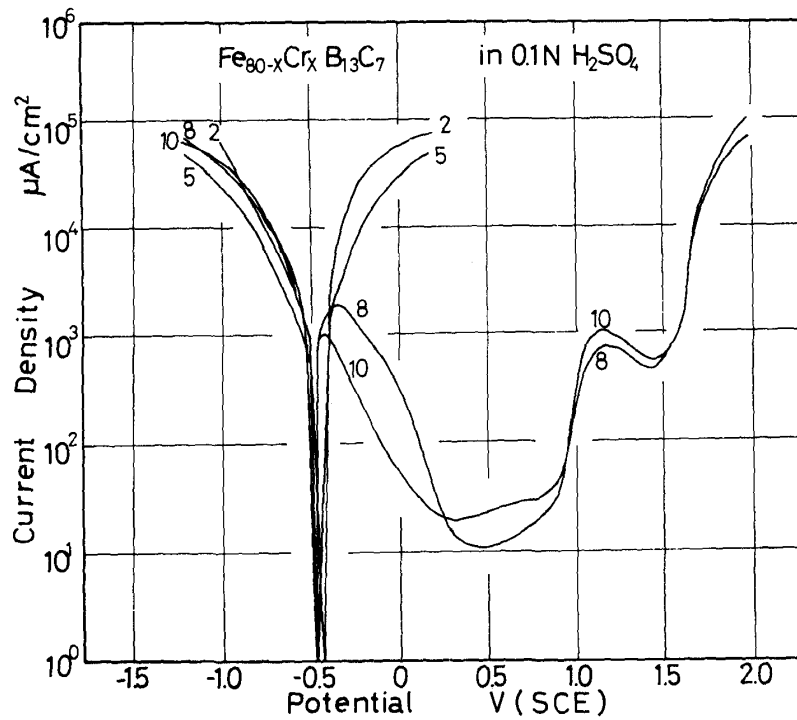


Fig. 2. Potentiodynamic polarization curves of a series of amorphous $\text{Fe}_{80-x}\text{Cr}_x\text{B}_{13}\text{C}_7$ alloys in $0.1\text{N H}_2\text{SO}_4$. The chromium content of the alloy is indicated by the number in atomic percent in the figure.

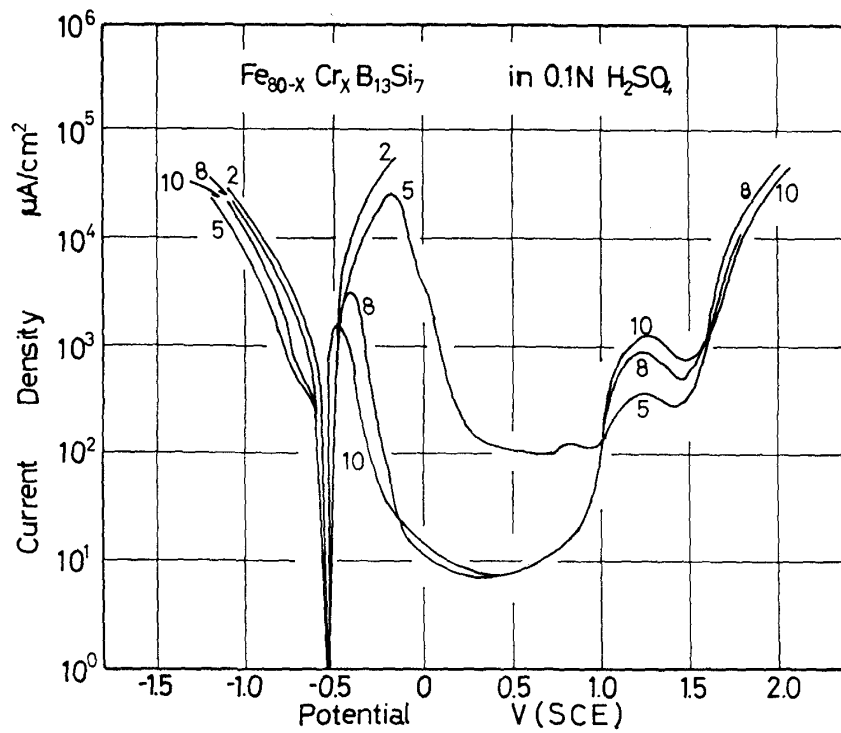


Fig. 3. Potentiodynamic polarization curves of a series of amorphous $\text{Fe}_{80-x}\text{Cr}_x\text{B}_{13}\text{Si}_7$ alloys in $0.1\text{N H}_2\text{SO}_4$. The chromium content of the alloy is indicated by the number in atomic percent in the figure.

those of the amorphous Fe-Cr-P-C alloys with the same chromium content in 1 M H_2SO_4 ^(1,2). The corrosion potentials of the amorphous Fe-Cr-B-C and Fe-Cr-B-Si alloys are in the active region and remain almost unchanged with the change in the chromium content, while the amorphous Fe-Cr-P-C alloys show spontaneous passivation with the increase in the chromium content^(1,2). Accordingly, the addition of chromium improves the corrosion resistance of the amorphous Fe-B-C and Fe-B-Si alloys, but is not practically effective for obtaining good corrosion resistance even in dilute sulfuric acid.

Figures 4 and 5 show the potentiodynamic polarization curves of the amorphous Fe-Cr-B-C and Fe-Cr-B-Si alloys in 3% NaCl. The anodic polarization curves of the amorphous alloys containing chromium of 5 at% or less have not been measured over a wide range of potential because of rapid dissolution. The alloys with chromium of 8 and 10 at% are passivated and an abrupt rise in dissolution current by pitting corrosion does not appear. The corrosion potentials of these alloys tend to increase with the increase in the chromium content, but the spontaneous passivation does not take place at the chromium content up to 10 at%.

Figure 6 shows the change in the polarization curves in 0.1 N H_2SO_4 of the amorphous alloys with the constant chromium content of 5 at% caused by the addition of three sets of metalloids. The anodic polarization curves of amorphous $\text{Fe}_{75}\text{Cr}_5\text{B}_{13}\text{C}_7$ alloy have not been measured over a wide range of

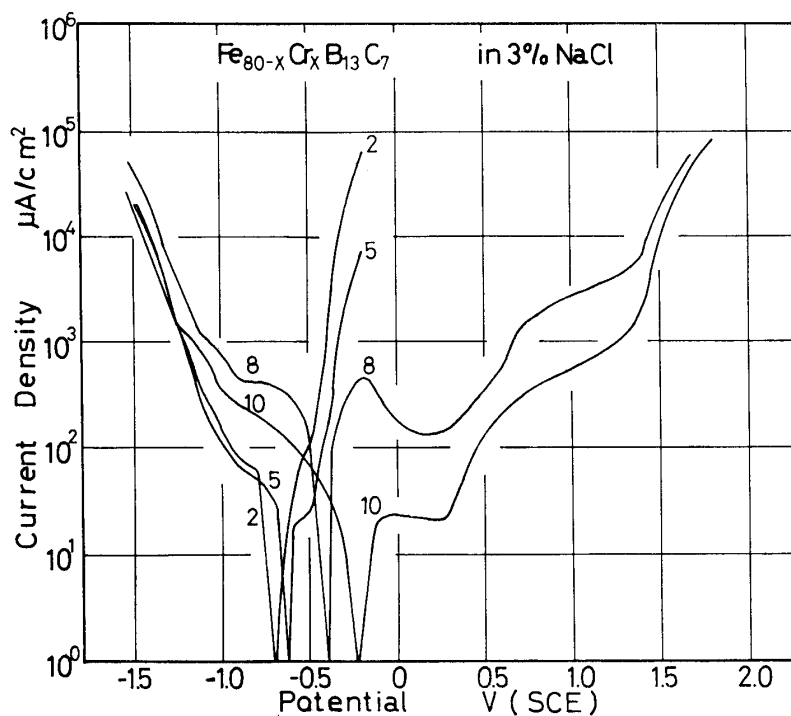


Fig. 4. Potentiodynamic polarization curves of a series of amorphous $\text{Fe-Cr-B}_{13}\text{-C}_7$ alloys in 3% NaCl. The chromium content of the alloy is indicated by the number in atomic percent in the figure.

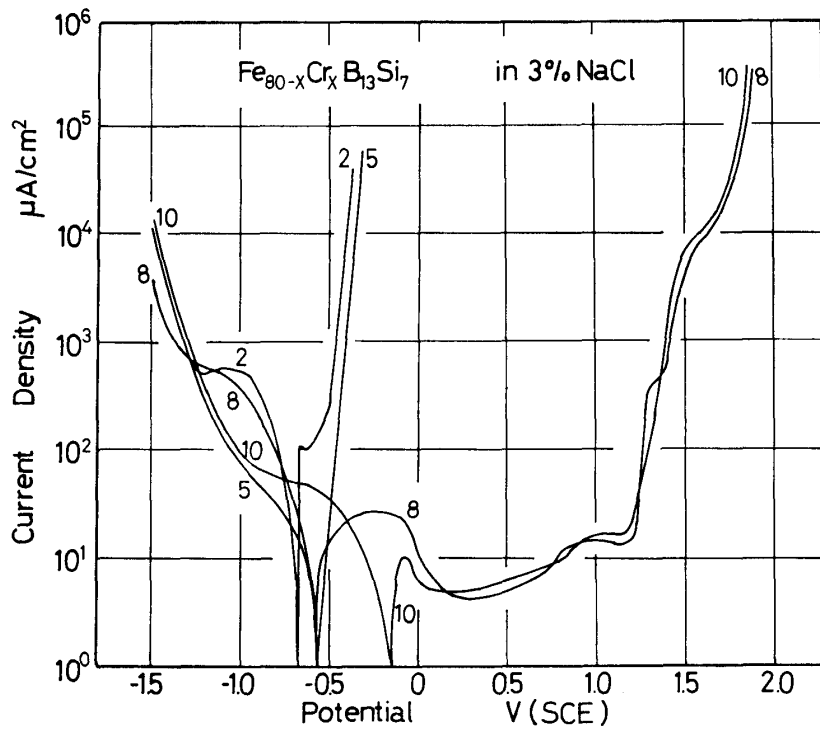


Fig. 5. Potentiodynamic polarization curves of a series of amorphous Fe-Cr-B₁₃-Si₇ alloys in 3% NaCl. The chromium content of the alloy is indicated by the number in atomic percent in the figure.

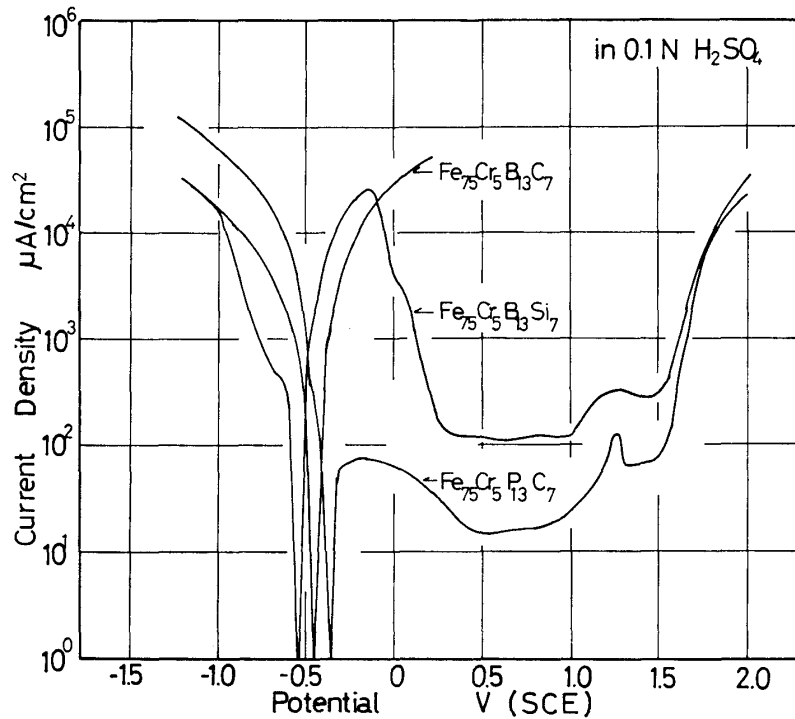


Fig. 6. Effect of metalloid element on the polarization curve of amorphous iron base alloys containing 5 at% chromium in 0.1 N H₂SO₄.

potential because of rapid dissolution. Both amorphous $\text{Fe}_{75}\text{Cr}_5\text{B}_{13}\text{Si}_7$ and $\text{Fe}_{75}\text{Cr}_5\text{P}_{13}\text{C}_7$ alloys are passivated. The passivation current density of the latter is more than two orders of magnitude lower than that of the former and is lower than that of amorphous $\text{Fe}_{70}\text{Cr}_{10}\text{B}_{13}\text{Si}_7$ alloy as shown in Fig. 3. The current density in the passive state of amorphous $\text{Fe}_{75}\text{Cr}_5\text{P}_{13}\text{C}_7$ alloy is also almost one order of magnitude lower than that of $\text{Fe}_{75}\text{Cr}_5\text{B}_{13}\text{Si}_7$ alloy. The corrosion potential of the former is the highest among three amorphous alloys with different sets of metalloid elements.

Consequently, phosphorus is the most effective metalloid element among phosphorus, carbon, silicon and boron for improvement of the corrosion resistance of the amorphous iron base alloys containing chromium, and a sufficient increase in the corrosion resistance of the amorphous iron base alloys by the addition of chromium cannot be attained unless phosphorus is contained as a metalloid element.