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著者	Hashimoto K., Zhang B.-P., Im B.-M., Lee H.-J., Akiyama E., Habazaki H., Kawashima A., Asami K.
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## The Role of Phosphorus in Enhancing Corrosion Resistance of Amorphous Alloys\*

K. Hashimoto, B.-P. Zhang, B.-M. Im, H.-J. Lee, E. Akiyama, H. Habazaki, A. Kawashima, K. Asami

*Institute for Materials Research, Tohoku University, Sendai, 980-77 Japan*

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Phosphorus contained in amorphous metal-metalloid alloys is often beneficial in enhancing the corrosion resistance particularly in strong acids. On the basis of investigations conducted so far, the beneficial role of phosphorus is comprehensively summarized. Immersion of amorphous metal-phosphorus alloys containing passivating elements leads to the formation of elemental phosphorus layer on the topmost surface of the alloy as a result of initial alloy dissolution. The elemental phosphorus layer has high cathodic activity for oxygen and proton reduction and acts as the diffusion barrier against alloy dissolution. These beneficial effects ennoble the open circuit potential, and when the open circuit potential attains the passive region of the alloy spontaneous passivation occurs. An increase in the protectiveness of the passive film by ageing further ennoble the open circuit potential. At the high open circuit potential elemental phosphorus is no longer stable and dissolves into the solution. The passive film thus formed generally consists of passive oxyhydroxide and the phosphorus content in the film is rather low.

KEYWORDS: corrosion resistance, phosphorus, metal-metalloid alloy, passivation

### 1. High Corrosion Resistance of Amorphous Metal-Metalloid Alloys

The first study of the corrosion behavior of amorphous alloys was published in 1974. In this publication it has been reported that amorphous Fe-Cr-13P-7C alloys containing 8 at% or more chromium show several orders of magnitude lower corrosion rates than stainless steels in chloride-containing acid and neutral solutions<sup>1)</sup>.

The high corrosion resistance of chromium-bearing amorphous and crystalline alloys is based on spontaneous passivation due to formation of the passive film in which chromium oxyhydroxide is concentrated<sup>2)</sup>. The extremely high corrosion resistance of amorphous metal-metalloid alloys containing a sufficient amount of chromium has been interpreted in terms of rapid formation of the passive film with a high concentration of chromium<sup>3)</sup>. Rapid passivation is attributed to the metastable nature of amorphous alloys, that is, the high reactivity of alloys which provides rapid dissolution of unnecessary elements for passivation with a consequent rapid accumulation of chromium in the film. The homogeneous single phase nature without crystalline defects and second phases is responsible for the formation of the uniform passive film.

Among amorphous Fe-Cr-metalloid alloys the alloys with phosphorus as a metalloid show the highest corrosion resistance. Boron and silicon contained in the alloys form films containing high concentration of borate and silicate, while amorphous Fe-Cr-P-C alloys are able to form passive hydrated chromium oxyhydroxide films in which the

phosphorus content is significantly low<sup>4)</sup>. Accordingly, it was clarified that phosphorus is not detrimental in forming the passive hydrated chromium oxyhydroxide film, but the beneficial effect of phosphorus had not yet been clarified.

### 2. Corrosion Resistance of Phosphorus-Bearing Alloys

The corrosion rate of amorphous Fe-P alloys is known to be significantly higher than that of crystalline iron metal. Figure 1 shows corrosion rates of various amorphous Fe-Cr-metalloid alloys in 9 M H<sub>2</sub>SO<sub>4</sub> as a function of chromium content of alloys. An increase in chromium content of amorphous Fe-Cr-13Si-7B and Fe-Cr-20B alloys is not effective in enhancing the corrosion resistance, whereas the corrosion rate of Fe-Cr-13P-7C and Fe-Cr-13P-7B alloys decreases with chromium content. Furthermore, the corrosion resistance of Fe-Cr-13P-7C alloys is generally higher than that of Fe-Cr-13P-7B alloys. In this manner, if amorphous iron-metalloid alloys contain a passivating element, such as chromium, phosphorus is the most effective metalloid element in decreasing the corrosion rate in strong acids.

Contrary to amorphous iron-metalloid alloys, Ni-P alloys without passivating elements show better corrosion

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resistance than crystalline nickel metal as an example is shown in Fig. 2. As shown in Fig. 3, the addition of phosphorus generally increases cathodic activity for oxygen and proton reduction and decreases the anodic current density with a consequent ennoblement of the open circuit potential. The beneficial effect of a small amount of phosphorus addition has been found in amorphous Ni-Ta-P alloys. As can be seen in Fig. 4 the addition of only 2 or 5 at% phosphorus to amorphous Ni-30Ta alloy leads to more than four orders of magnitude decrease in the corrosion rate in boiling 6 M HCl and to spontaneous passivation of actively dissolving amorphous Ni-30Ta alloy<sup>5</sup>. Figure 5 shows a comparison of corrosion rates of crystalline Ni-Cr and amorphous Ni-Cr-P alloys in 47% HF<sup>6</sup>. Because chromium is more active than nickel, the addition of chromium to nickel increases the corrosion rate in this aggressive solution. By contrast, because of spontaneous passivation, amorphous Ni-Cr-P alloys show significantly low corrosion rates.

**3. Presence of Elemental Phosphorus on the Alloy Surface**

Confusion was brought into the interpretation of the role of phosphorus when X-ray photoelectron spectroscopy was used for analysis of the surface of alloys. A large amount of phosphate was found on the amorphous Ni-Cr-P-B alloy after immersion in 1 M HCl<sup>7</sup>. By contrast, Diegle *et al.*<sup>8</sup>) found hypophosphite in addition to elemental phosphorus and phosphate when they made XPS analysis for the specimen transferred to the X-ray photoelectron spectrometer under an argon atmosphere after polarization at 0 V(SCE) in deaerated 0.2 M HCl and 0.1 M H<sub>2</sub>SO<sub>4</sub>. They proposed chemical passivity by adsorption of hypophosphite ions on the alloy

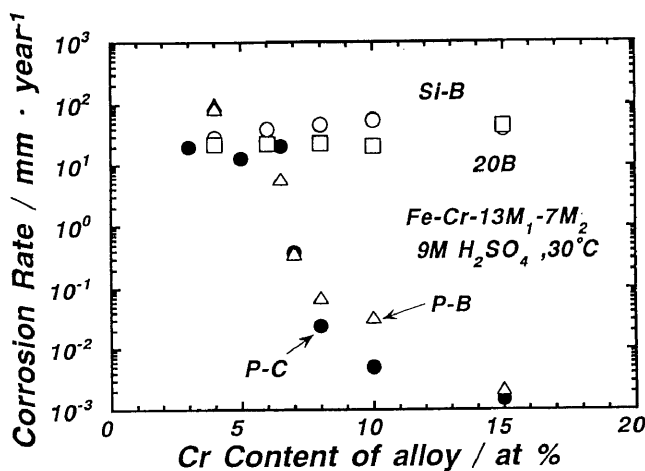


Fig. 1 Average corrosion rates of melt-spun amorphous Fe-Cr-13M<sub>1</sub>-7M<sub>2</sub> alloys in 9 M H<sub>2</sub>SO<sub>4</sub> at 30°C as a function of chromium content. M<sub>1</sub> and M<sub>2</sub> are metalloids.

surface.

The detailed examination of potentiostatic polarization curves of amorphous Ni-19P alloy in 1 M HCl showed that no clear active-passive transition occurs and that the current density in the active region under potentiostatic condition decays asymptotically with time of polarization<sup>9</sup>. Accordingly, the anodic current decay observed in the potential region around open circuit condition is not based on passivation. According to the XPS analyses<sup>7,8</sup>) mentioned above, when specimens were exposed to air after immersion or polarization a large amount of phosphate is found in the surface film, and when intentional air exposure is avoided after

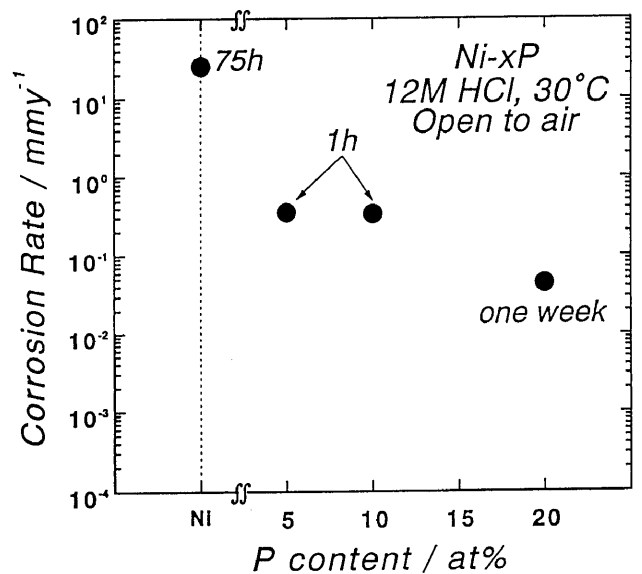


Fig. 2 Corrosion rates of nickel and melt-spun Ni-P alloys in 12 M HCl at 30°C as a function of phosphorus content.

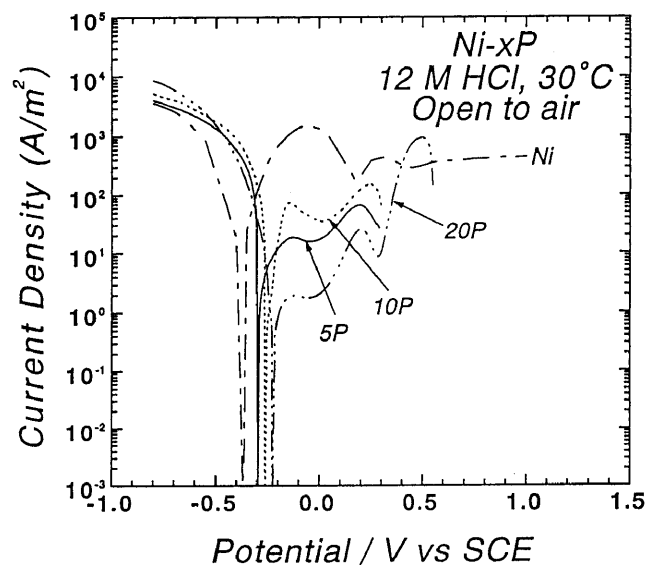


Fig. 3 Potentiodynamic anodic and cathodic polarization curves of nickel and rapidly quenched Ni-P alloys in 12 M HCl at 30°C.

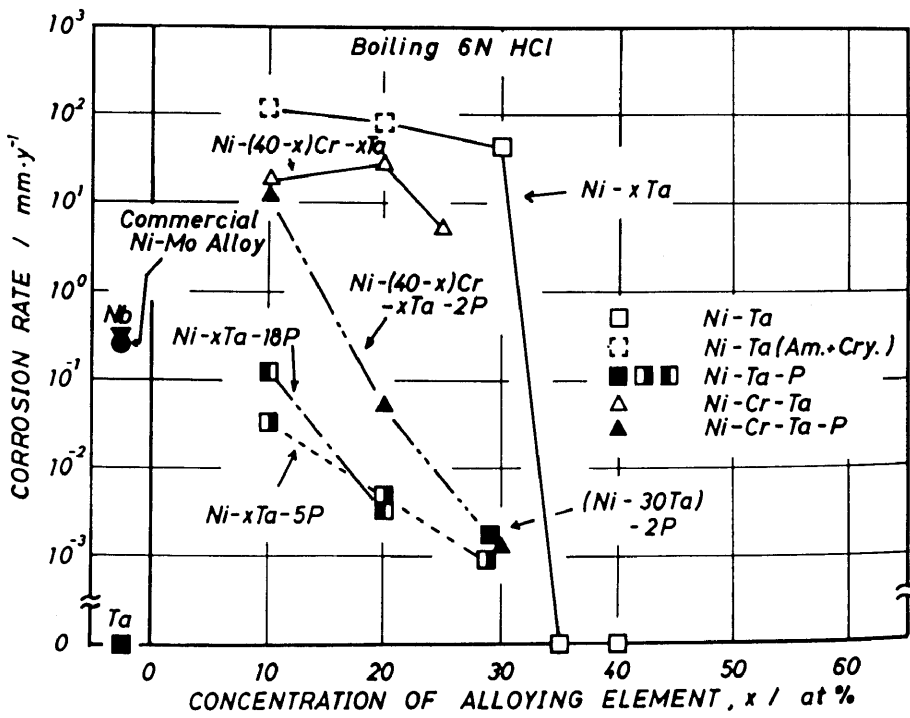


Fig. 4 Corrosion rates of amorphous Ni-Ta alloys in a boiling 6 M HCl<sup>5)</sup>.

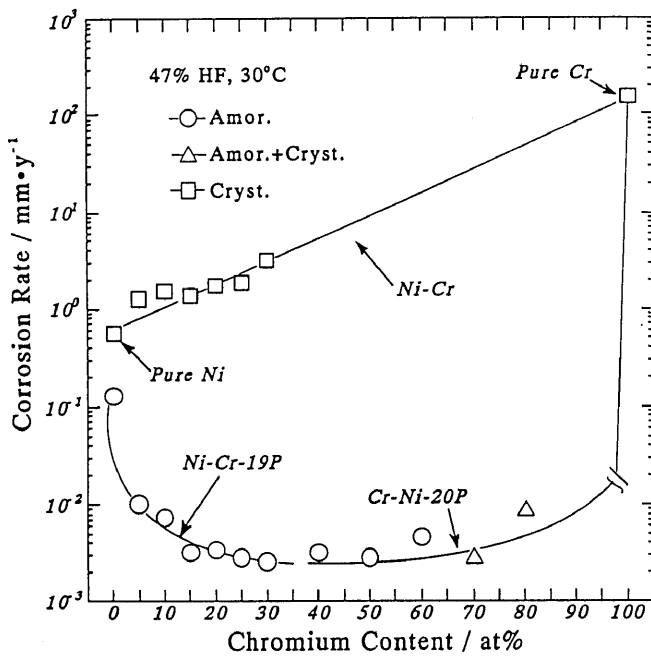


Fig. 5 Corrosion rates of amorphous Ni-Cr-P and crystalline Ni-Cr alloys in 47 % HF at 30°C<sup>6)</sup>.

immersion or polarization hypophosphite is found together with elemental phosphorus and phosphate. Preferential dissolution of some alloy components often occurs before establishment of the steady state dissolution, and if other alloy components remaining without dissolution form a layer on the alloy surface, the layer thus formed acts as a diffusion barrier. The results of the XPS analyses<sup>7,8)</sup> suggest the formation of an elemental phosphorus layer on the alloy surface

in the active region including the open circuit condition in acids. If the elemental phosphorus layer is formed and acts as a diffusion barrier against further alloy dissolution, the thickness of the elemental phosphorus layer should increase with time and the current should decrease following the Fick's second law, that is

$$1/i^2 = V^2\pi(t + t_0) / (nFa_1)^2D$$

where  $i$  is the anodic current density at a given anodic potential,  $V$  the molar volume of the alloy,  $t$  the time after the onset of polarization,  $t_0$  the hypothetical time passed for phosphorus layer formation before potentiostatic polarization,  $n$  the charge number of the electrode reaction,  $F$  the Faraday constant,  $a_1$  the bulk atomic fraction of the dissolving component and  $D$  the chemical diffusion coefficient.

The reciprocal of the square of the current density for amorphous Ni-19P alloys in 1 M HCl is plotted in Fig. 6<sup>9)</sup>. The linear relationship is observed for the curves measured at three different temperatures. It has, therefore, been concluded that the immersion of amorphous Ni-P alloys in acids results in the formation of the elemental phosphorus layer acting as the diffusion barrier against alloy dissolution.

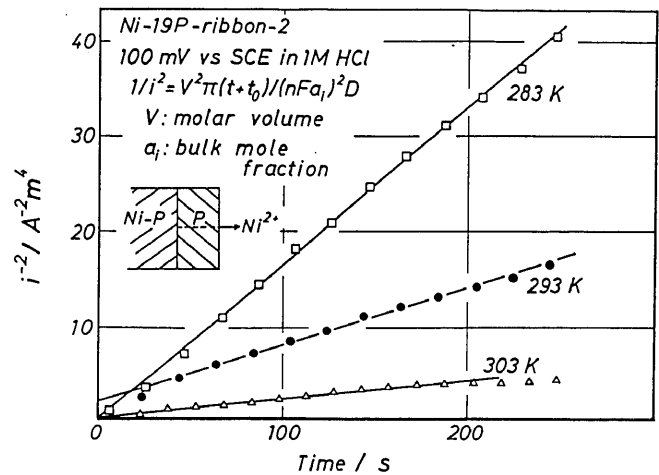


Fig. 6 Reciprocal of the square of the current density  $i$  for dissolution of nickel from a melt-spun amorphous Ni-19P alloy specimen polarized at 100 mV(SCE) in 1 M HCl at 10, 20 and 30°C as a function of time  $t$ <sup>9)</sup>.

Even if chromium is added if the open circuit potential is located in the active region of alloys a similar behavior has been found. As shown in Fig. 7, the current decay of amorphous Ni-5Cr-19P alloy in 47% HF at 30°C seems to follow the Fick's second law, although a further faster decrease in the current density is found for amorphous Ni-Cr-19P alloys with 10-20 at% chromium due to spontaneous passivation<sup>10</sup>.

#### 4. Confirmation of the Presence of Elemental Phosphorus on the Alloy Surface

Because elemental phosphorus is readily oxidized to the pentavalent state by air exposure, it is difficult to confirm the formation of the elemental phosphorus layer by X-ray photoelectron spectroscopy after immersion or potentiostatic polarization. An attempt to prove the formation of elemental phosphorus has been performed for amorphous Fe-8Cr-13P-7C alloy passivated spontaneously in stirred 9 M H<sub>2</sub>SO<sub>4</sub> open to air at 30°C<sup>11</sup>. As can be seen in Fig. 8, air exposure after immersion definitely results in an increase in the thickness of the film on the alloy. This clearly shows film thickening due to air oxidation occurs by air exposure after immersion. Nevertheless, Fig. 9 shows no effect of air exposure on the cationic composition of the film. This suggests that no further oxidation of underlying alloy surface occurs by air exposure. Fig. 10 shows the change in the P 2p spectrum by air exposure. The P 2p spectra are composed of two peaks. The lower binding energy peak at about 129.7 eV corresponds to the elemental state, and the higher binding energy peak at about

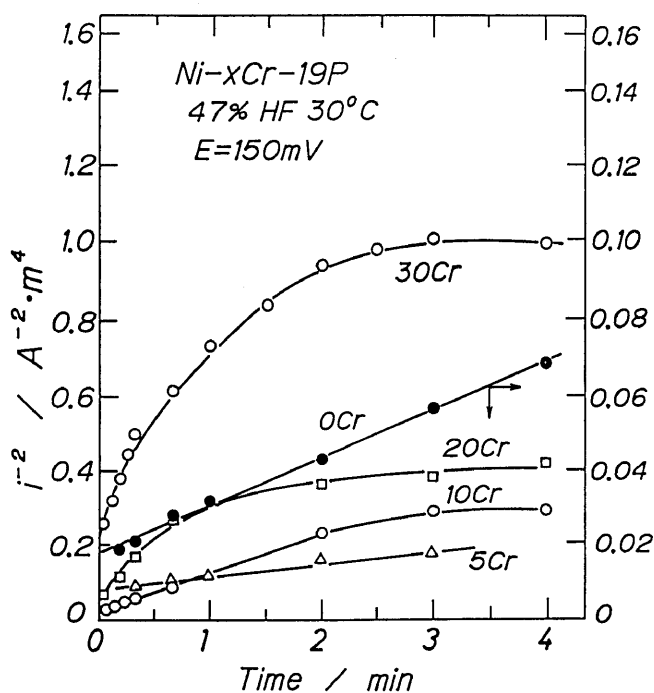


Fig. 7 Reciprocal of the square of the current density  $i$  for melt-spun amorphous Ni-Cr-19P alloy specimens polarized at 150 mV (SCE) in 47% HF at 30°C as a function of time  $t$ <sup>10</sup>.

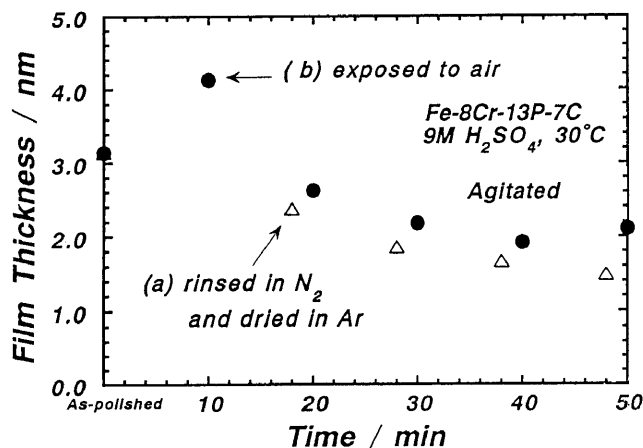


Fig. 8 Change in thickness of the film formed on amorphous Fe-8Cr-13P-7C alloy immersed in stirred 9 M H<sub>2</sub>SO<sub>4</sub> open to air at 30°C<sup>11</sup>.

- (a) XPS measurements were carried out without intentional air exposure of specimens after immersion.
- (b) XPS measurements were carried out for the specimens washed and dried in air after immersion.

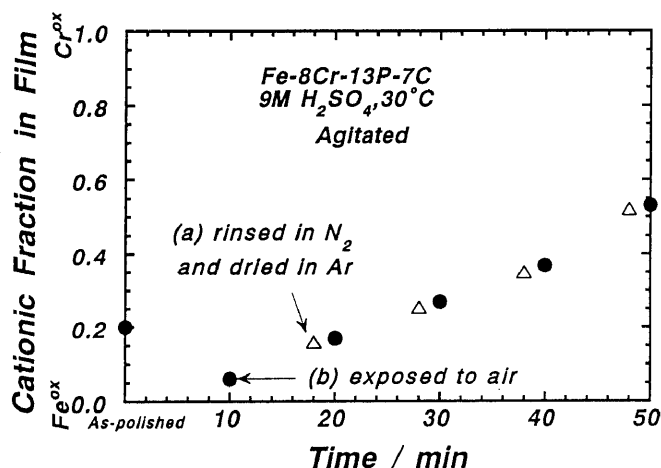


Fig. 9 Change in fraction of cations in the film formed on amorphous Fe-8Cr-13P-7C alloy immersed in stirred 9 M H<sub>2</sub>SO<sub>4</sub> open to air at 30°C<sup>11</sup>.

- (a) XPS measurements were carried out without intentional air exposure of specimens after immersion.
- (b) XPS measurements were carried out for the specimens washed and dried in air after immersion.

133.5 eV is assigned to the P<sup>5+</sup> state in phosphate. Air exposure after immersion results in significant increase in the P<sup>5+</sup> state peak. Because of no definitive oxidation of underlying alloy by air exposure after immersion, the increase in the oxidized phosphorus by air exposure results from oxidation of elemental phosphorus on the topmost surface of the spontaneously passivated film.

The formation of elemental phosphorus on the topmost surface of the spontaneously passivated film occurs within a few second by immersion. The XPS analysis of amorphous

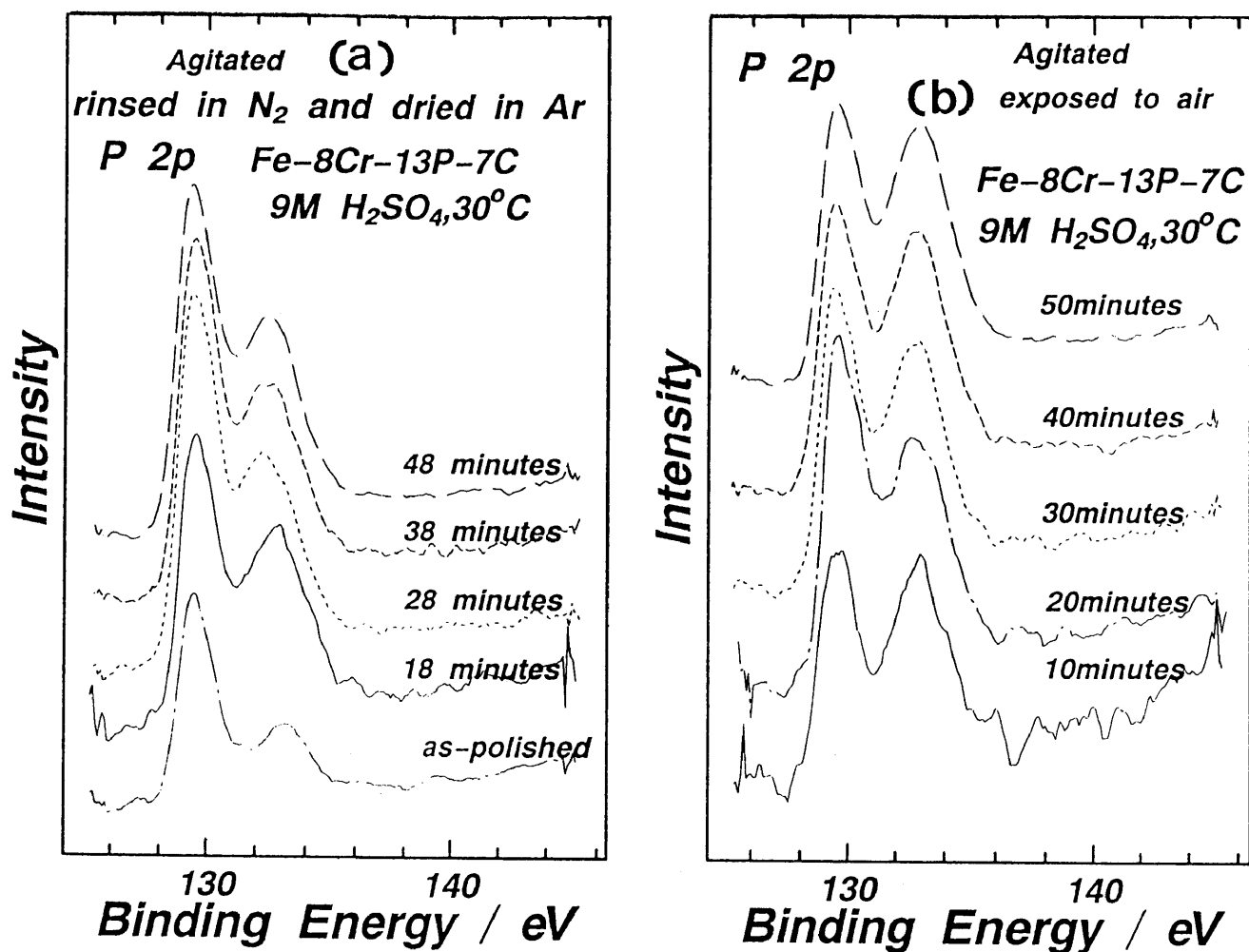


Fig. 10 Change in the P 2p spectrum for amorphous Fe-8Cr-13P-7C alloy specimen immersed in stirred 9 M H<sub>2</sub>SO<sub>4</sub> open to air at 30°C<sup>(1)</sup>.

(a) XPS measurements were carried out without intentional air exposure of specimens after immersion.

(b) XPS measurements were carried out for the specimens washed and dried in air after immersion.

Ni-10Ta-20P alloy in 12 M HCl at 30°C reveals that the formation of elemental phosphorus at only 1 sec after immersion, being accompanied by sharp ennoblement of the open circuit potential.

##### 5. Role of Phosphorus in Amorphous Alloys

It is generally characterized that an increase in the phosphorus content of amorphous metal-metalloid alloys leads to increase in both oxygen and proton reduction and to decrease in anodic activity for dissolution. When the open circuit potential exceeds the passivation potential of the alloy, passivation spontaneously occurs forming a passive film in which the phosphorus content is rather low. In general, the open circuit potential of spontaneously passivated alloys continues to increase for a long period of time due to enhancement of the protectiveness of the film. When the open circuit potential exceeds about 300 mV(SCE) in acidic

solutions, elemental phosphorus is no longer stable and is oxidized mostly to phosphate. Accordingly, unless the resultant phosphate is stable in the given environment, phosphate dissolves into solution, and the passive oxyhydroxide film is detected by XPS.

##### 6. Role of Phosphorus in Crystalline Alloys

Phosphorus contained in amorphous single phase alloys affects beneficially for spontaneous passivation by enhancing the cathodic activity and decreasing the anodic activity. Phosphorus contained in crystalline alloys act similarly to that in amorphous alloys, but the effect is often significantly detrimental from the corrosion point of view.

When different amounts of phosphorus are added to chromium an interesting result was obtained<sup>(12)</sup>. Figs. 11 and 12 show corrosion rates and change in open circuit potentials of Cr-P alloys in 47% HF. Because chromium is not stable in

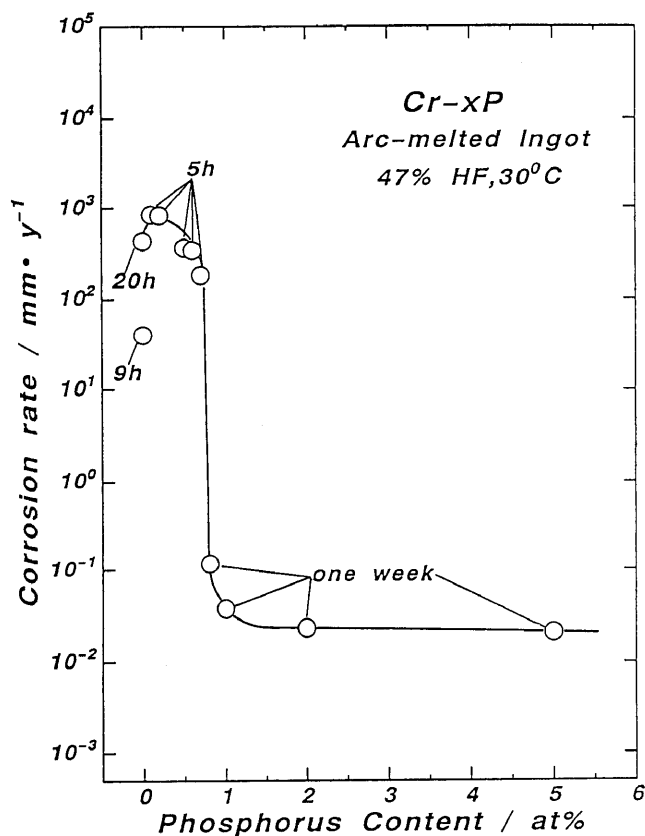


Fig. 11 Corrosion rates of arc-melted Cr-P alloys measured in 47% HF at 30°C as a function of phosphorus content of alloy<sup>12)</sup>.

this aggressive environment, the air-formed film is broken and the open circuit potential decreases. Surface roughening during immersion results in the increase in the corrosion rate with time. Phosphorus contained in the Cr-P alloys forms  $\text{Cr}_3\text{P}$  phase at grain boundaries. The  $\text{Cr}_3\text{P}$  phase has a very high activity for cathodic oxygen reduction. The addition of small amounts of phosphorus such as less than 0.8 at% increases the corrosion rate because phosphorus enhances the cathodic activity in spite of the fact that the alloys are in the active region. However, when a sufficient amount of phosphorus is added such as 0.8 at% or more, the enhancement of cathodic activity becomes high enough to ennoble the open circuit potential to the passive region of chromium, and hence spontaneous passivation occurs.

The  $\text{Cr}_3\text{P}$  phase is significantly stable in this strong acid. As shown in Fig. 13, immersion of a low phosphorus alloy gives rise to dissolution of bcc Cr grains leaving the  $\text{Cr}_3\text{P}$  phase present at grain boundaries. A large amount of precipitation of the  $\text{Cr}_3\text{P}$  phase at grain boundaries leads to grain boundary degradation, and hence it is impossible to add a large amount of phosphorus to conventional alloys for enhancement of passivation of the matrix phase by cathodic activation. A small amount of phosphorus addition to

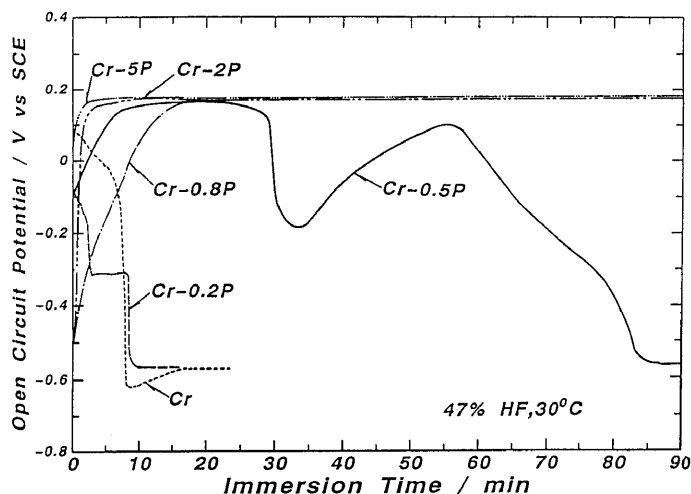


Fig. 12 Change in open circuit potentials of arc-melted Cr-P alloys measured in 47% HF at 30°C as a function of time of immersion<sup>12)</sup>.

conventional alloys is always detrimental because the precipitation of the  $\text{Cr}_3\text{P}$  phase or segregation of phosphorus at grain boundaries results in chromium depression around grain boundaries, and chromium depression and high cathodic activity induce intergranular corrosion and intergranular stress corrosion cracking.

## 7. Conclusion

Comprehensive study of the role of phosphorus in enhancing the corrosion resistance of amorphous metal-phosphorus alloys in strong acids can be summarized as follows.

Phosphorus contained in alloys consisting of a single solid solution phase containing passivating elements is quite effective in enhancing the corrosion resistance by stimulating spontaneous passivation in strong acids. When the alloys are immersed in strong acids, initial active dissolution of the alloys results in the formation of an elemental phosphorus layer on the topmost surface. The elemental phosphorus layer is active for cathodic oxygen and proton reduction and acts as a diffusion barrier against further anodic dissolution. These functions of phosphorus lead to ennoblement of the open circuit potential and to spontaneous passivation. Passivation generally occurs by the formation of passive oxyhydroxide films under the elemental phosphorus layer. Ageing of the passive film often gives rise to further enhancement of the protectiveness of the passive film and to further ennoblement of the open circuit potential. The ennoblement of the open circuit potential results in oxidation of elemental phosphorus to phosphate and phosphate dissolves into the solution.

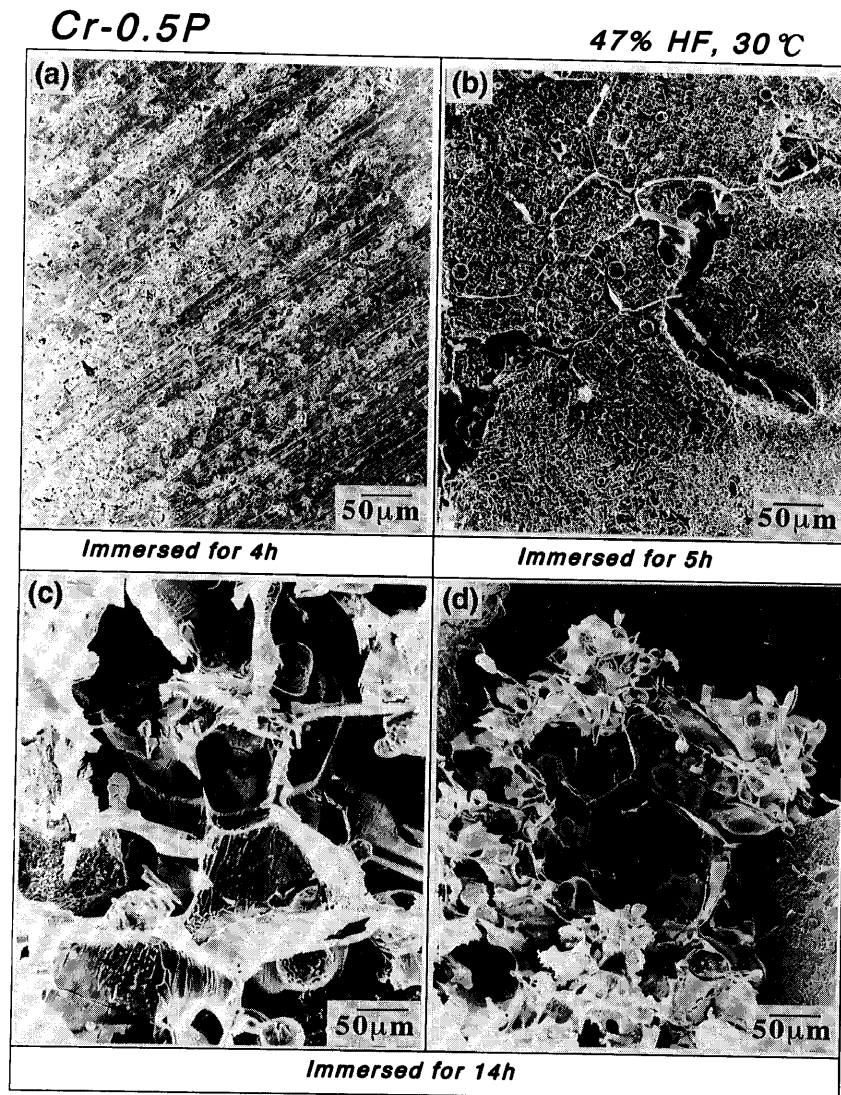


Fig. 13 SEM images of Cr-0.5P alloy after immersion in 47% HF at 30°C for 4, 5 and 14 h<sup>12)</sup>.

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