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Embrittlement of Fe,Ni,Co Amorphous Alloys Containing Metalloid Elements by Crystallization*

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Synopsis

The ductile-brittle transition behavior for several metal-metalloid amorphous alloys (Pd-Si, Fe-P-C, Fe-Si-B, Ni-Si-B, Co-Si-B) has been examined as functions of the aging time and temperature below 500°C and the relationship between embrittlement and crystallization process has been discussed. The tendency for embrittlement by the isothermal aging differs depending on the composition of amorphous alloys. Pd-, Ni- and Co-based alloys remain ductile until the precipitation of the MS-I or MS-II phases. On the other hand, Fe-based alloys become completely brittle at the incipient stage of crystallization. The reason why only Fe-based alloys become brittle prior to the appearance of the MS-I or MS-II phases may be due to the internal strain generated by the nucleation of a fine body-centered cubic crystal in amorphous structure.

I. Introduction

Fe- and Co-based amorphous alloys with Si and B\(^{(1-3)}\) form easily amorphous phase in wide composition ranges, and exhibit excellent mechanical and magnetic properties as well as higher crystallization temperature as compared with those of the amorphous alloys containing P, C and/or B.\(^{(4,5)}\) Owing to these advantages the practical application of X-Si-B (X: Fe, Co, Ni) amorphous alloys as a type of soft-magnetic material has been anticipated in Japan at present\(^{(6,7)}\). However, the excellent characteristics of these amorphous alloys disappear after crystallization. Therefore, the crystallization behavior of amorphous alloys has been one of the most important research subjects.


The present authors\(^{(8,9,10,11)}\) have studied previously the crystallization process and the temperature-time-transformation (T-T-T) relation of various metal-metalloid amorphous alloys. They have shown that there exists an immutable process in the transition from amorphous to equilibrium phase, and pointed out\(^{(10)}\) that the aging treatment at fairly lower temperatures than the crystallization temperature brings significant changes in various properties of amorphous alloys. For instance, the iron-based amorphous alloys become rapidly brittle with a catastrophic loss of ductility at the incipient stage of crystallization. However, the relationship between embrittlement tendency and crystallization process and the influence of composition on embrittlement are left unknown. The purpose of the present work is to examine the ductile-brittle behavior of several amorphous alloys by isothermal aging and to discuss the relationship between this result and the crystallization process.

II. Experimental

Specimens used in the present work are the metal-metalloid alloys of Pd\(_{80}\)Si\(_{20}\)^{*}, Fe\(_{80}\)P\(_{13}\)C\(_{7}\), Fe\(_{78}\)Si\(_{10}\)B\(_{12}\), Ni\(_{73}\)Si\(_{9}\)B\(_{17}\) and Co\(_{70}\)Si\(_{15}\)B\(_{10}\). Electrolytic pure metals (Fe, Ni, Co), paradium (99.99 wt%), silicon (99.999 wt%), boron (99 wt%), red phosphorus and white cast iron were used as raw materials. Their mixtures were melted in argon atmosphere using the Tammann furance. The melts were sucked into a quartz tube of about 3 mm in inner diameter and then solidified in air. Ribbon specimens of 2~3 mm width and 0.04~0.05 mm thickness were prepared from these master alloys by using roller quenching apparatus. The cooling rate was sufficiently high to produce amorphous samples. The structure was confirmed by X-ray diffraction and transmission electron microscopy.

Mechanical properties and the crystallization temperature \(T_x\) of these amorphous alloys obtained from earlier works\(^{(8,11)}\) are listed in Table 1. Also, the characteristics of phases at each stages of the crystallization process for these amorphous alloys are represented in Table 2.\(^{(9,10,11)}\) The compositions of specimens were obtained by chemical analyses. Hardness was measured by a Vickers microhardness tester with a 50 g load. Crystallization behavior of the alloys was obtained from a differential thermal analysis (DTA) using 8.33\(\times\)10^{-2} °C/s scan.

The ductile-brittle behavior during isothermal aging was tested for the specimens annealed for various times at various temperatures in evacuated silica capsules. The degree of ductility was determined by measuring the radius of

\* Composition of alloys is expressed in at% unless otherwise stated.


Table 1. Mechanical properties and crystallization temperature for several amorphous alloys.

<table>
<thead>
<tr>
<th>Alloy system</th>
<th>Vickers hardness (DPN)</th>
<th>Fracture strength $\times 10^2$(MPa)</th>
<th>Young's modulus $\times 10^4$(MPa)</th>
<th>Crystallization temperature, $T_x$ (°C, $8.33 \times 10^{-4}$C/s)</th>
<th>Critical fracture temperature, $T_f$ (°C, $\times 6$ks)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$<em>{80}$Si$</em>{20}$</td>
<td>325</td>
<td>13</td>
<td>67</td>
<td>380</td>
<td>330</td>
</tr>
<tr>
<td>Fe$<em>{60}$P$</em>{13}$C$_7$</td>
<td>760</td>
<td>30</td>
<td>122</td>
<td>410</td>
<td>290</td>
</tr>
<tr>
<td>Ni$<em>{72}$Si$</em>{18}$B$_{10}$</td>
<td>860</td>
<td>26</td>
<td>79</td>
<td>468</td>
<td>450</td>
</tr>
<tr>
<td>Ni$<em>{72}$Si$</em>{18}$P$_{12}$</td>
<td>840</td>
<td>24</td>
<td>71</td>
<td>464</td>
<td>430</td>
</tr>
<tr>
<td>Co$<em>{72}$Si$</em>{18}$B$_{10}$</td>
<td>910</td>
<td>29</td>
<td>95</td>
<td>480</td>
<td>460</td>
</tr>
<tr>
<td>Co$<em>{72}$Si$</em>{18}$B$_{12}$</td>
<td>915</td>
<td>22</td>
<td>84</td>
<td>412</td>
<td>—</td>
</tr>
<tr>
<td>Fe$<em>{72}$Si$</em>{18}$B$_{12}$</td>
<td>910</td>
<td>32</td>
<td>85</td>
<td>505</td>
<td>310</td>
</tr>
</tbody>
</table>

$T_x$: Crystallization temperature, at which the exothermic peak begins to appear at a scanning rate of $8.33 \times 10^{-4}$C/s.

$T_f$: Temperature at the critical fracture strain $\varepsilon_f=1$ for the aging time of 6 ks.

Table 2. Characteristics of phases at four stages of crystallization process for several amorphous alloys.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Pd$<em>{80}$Si$</em>{20}$</th>
<th>Fe$<em>{60}$P$</em>{13}$C$_7$</th>
<th>Fe$<em>{72}$Si$</em>{18}$B$_{12}$</th>
<th>Co$<em>{72}$Si$</em>{18}$B$_{10}$</th>
<th>Ni$<em>{17}$Si$</em>{18}$B$_{17}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS</td>
<td>fcc</td>
<td>bcc</td>
<td>bcc</td>
<td>hcp (a=2.496A)</td>
<td>fcc (a=3.508A)</td>
</tr>
<tr>
<td></td>
<td>(a=3.921A)</td>
<td>(a=2.861A)</td>
<td>(a=2.848A)</td>
<td>(c=4.041A)</td>
<td></td>
</tr>
<tr>
<td>MS-I</td>
<td>fcc</td>
<td>bcc</td>
<td>bcc</td>
<td>hcp (a=2.51A)</td>
<td>fcc (a=3.52A)</td>
</tr>
<tr>
<td></td>
<td>(a=3.89A)</td>
<td>(a=2.87A)</td>
<td>(a=2.87A)</td>
<td>(c=4.07A)</td>
<td></td>
</tr>
<tr>
<td>MS-II</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Complex ordered phase ?)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ST</td>
<td>Pd, Pd$_3$Si</td>
<td>Fe, Fe$_2$C</td>
<td>Fe, Fe$_2$Si</td>
<td>Co, Co$_2$B</td>
<td>Ni, Ni$_2$B</td>
</tr>
<tr>
<td></td>
<td>Fe$_4$P</td>
<td>Fe$_2$B</td>
<td>Fe$_2$Si</td>
<td>Co$_3$Si</td>
<td>Ni$_2$Si</td>
</tr>
</tbody>
</table>

Curvature at which fracture occurred in a simple bend test. The strain on the outer surface required for fracture, $\varepsilon_f$, is expressed as follows:

$$\varepsilon_f = \frac{t}{L-t}$$

where $L$ is the distance between parallel plates at fracture and $t$ is the thickness of the ribbon specimen. Thus, $\varepsilon_f=1$ means that the sample fractured just when $L=2t$. The equation (1) is applicable only in the case that the sample is bent in the form of a semicircular loop. Amorphous alloys showing a nearly complete plastic-rigid behavior remain semicircular up to fracture. The deformed structure and the fracture surface were observed by a scanning electron microscope.

III. Results

Embrittlement behavior during isothermal aging is shown in Figs. 1 to 4 for Pd$_{80}$Si$_{20}$, Fe$_{80}$P$_{15}$C$_7$, Fe$_{78}$Si$_{12}$B$_{12}$, Ni$_{70}$Si$_9$B$_{17}$, and Co$_{75}$Si$_{15}$B$_{10}$ amorphous alloys. In the figures the values of $\varepsilon_f$ are plotted against various aging times at temperatures between 300 and 450°C. Pd$_{80}$Si$_{20}$ alloy becomes rapidly brittle after about 120 ks at 300°C and about 1.8 ks at 350°C. Iron-based amorphous alloys (Fe$_{80}$P$_{15}$C$_7$ and Fe$_{78}$Si$_{12}$B$_{12}$) begin to fracture after about 6 ks at 300°C well below

Fig. 1. Change in fracture strain of several amorphous alloys by aging at 300°C.

Fig. 2. Change in fracture strain of several amorphous alloys by aging at 350°C.
the crystallization temperature, and the time for beginning of embrittlement decreases with the rise of aging temperature. On the other hand, Ni$_{75}$Si$_{15}$B$_{17}$ and Co$_{75}$Si$_{15}$B$_{10}$ amorphous alloys are less susceptible of embrittlement compared with the iron-based alloys and are no brittleness even after 3600 ks at 300°C. At 350°C, the Co-based alloy becomes brittle after about 600 ks, while the Ni-based alloy does not fracture even after 4800 ks. When heated at 400 and 450°C, these alloys become brittle after 42~48 ks and 0.6~1.2 ks, respectively. Thus, the
Photo 1. Scanning electron micrographs showing the topography on fracture plane of Fe$_{78}$Si$_{16}$B$_{12}$ amorphous alloy aged for various times at 300°C.

The embrittlement tendency of amorphous alloys by aging depends strongly on the alloy composition.

The embrittlement behavior of amorphous alloys by aging has been reported for a variety of alloy systems such as Fe-P-C$^{(10)}$, Fe-Ni-P-B$^{(13)}$, M-P-B-Al$^{(14)}$ (M: Fe, Ni, Co). Usually, amorphous alloys, if quenched rapidly enough when prepared, are extremely strong and deform plastically on bending without breaking or showing any signs of cracking. In the case of Fe-based alloys, however, they lose the ductility and fracture in a brittle manner at temperatures lower by several hundred degrees than $T_x$. Photograph 1 shows the topography on fracture planes for Fe$_{78}$Si$_{16}$B$_{12}$ amorphous alloy aged for various times at 300°C. At the aging time of 6 ks ($\epsilon_f$ = 1), the fractured surface shows a vein pattern as seen in Photo. 1(a). This vein structure becomes fine with increasing aging time as seen in the Photos. 1(b) (60 ks, $\epsilon_f$ = 0.09) and (c) (300 ks, $\epsilon_f$ = 0.05). Such a pattern appears to have occurred by the initiation of a number of small cracks followed by the connection of enlarged cracks$^{(15)}$. Therefore, these photographs show that the number of initiated cracks increases with increasing aging time and these cracks propagate under less energies. Photograph 1(d) is the fracture surface at the inner side than Photo. 1(c). A fine shell pattern which appears to have occurred by discontinuous propagation of cracks is seen. Such a feature on the

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fracture surface is very similar to those$^{(16-17)}$ on the tensile fracture surface of hydrogen-absorbed amorphous alloys.

IV. Discussion

1. Relationship between embrittlement behavior and crystallization process

As seen in Table 2, when the amorphous alloys containing metalloids were heated at much higher temperatures than $T_x$, the crystalline phases consist of a large amount of brittle compounds. Therefore, amorphous alloys become brittle almost invariably after crystallization. However, it has been known that the embrittlement progresses even at fairly low temperatures than the crystallization temperature for iron-based amorphous alloys. This fact is also seen in Table 1 wherein $T_f$ is compared with $T_x$. Here, $T_x$ is the temperature for the beginning of crystallization, which was measured from DTA curve at a scanning rate of 8.33 $\times$ 10$^{-2}$ °C/s, and $T_f$ is the temperature at $\varepsilon_f=1$ after 6 ks. As seen in the table, $T_f$ of Fe-based alloys is much lower than $T_x$ as compared with Co- and Ni-based alloys. From this point of view, we have examined the relationship between embrittlement behavior and crystallization process.

Figures 5 to 9 show the relation between the fracture strain and the temperature-time-transformation diagram$^{(9-11)}$ for four kinds of amorphous alloys. In the previous studies,$^{(3,8-11,18,19)}$ the present authors have found that the

![Fig. 5. Relation between fracture strain and temperature-time-transformation diagram for Pd$_{80}$Si$_{20}$ amorphous alloy.](image)

amorphous phase for many kinds of alloys crystallizes through two metastable phases (MS-I and MS-II) and finally to the stable phase by nucleation and growth mechanisms above a critical temperature, but below this temperature progressive aging gradually changes the amorphous to a single phase with the same structure as the metallic element. The crystalline structures of these metastable phases are
given in Table 2. Among these alloys, Pd$_{90}$Si$_{10}$ and Ni$_{75}$Si$_{15}$B$_{12}$ alloys remain ductile until the precipitation of MS-II phase, and Co$_{75}$Si$_{15}$B$_{12}$ alloy until MS-I phase. On the other hand, Fe$_{80}$P$_{12}$C$_7$ and Fe$_{78}$Si$_{16}$B$_{12}$ alloys become completely brittle even in the amorphous state where X-ray and electron examinations show no signs of any crystallization. That is, the precipitation of MS-II phases with complicated compound structures makes alloys brittle without exception. On the other hand, the precipitations of MS-I and SS phases with fcc structure do not take part in embrittlement as seen for Pd- and Ni-based alloys, but these phases
with hcp structure for Co-based alloy cause an embrittlement. On the contrary, Fe-based alloys become brittle even at temperatures much lower than the precipitations of these metastable phases with bcc structure. These results suggest that the embrittlement behavior is closely related to the crystalline structure of metastable phases in amorphous phase.

It has been already reported in several papers that Fe-based amorphous alloys become brittle before any detectable changes in amorphous structure. Chen\(^{(14)}\) has predicted that an embrittlement of amorphous alloys would be related to the filling of the d-shell of iron atoms. Egami \textit{et al.}\(^{(13)}\) have also pointed out that the embrittlement behavior of Fe\(_{40}\)Ni\(_{40}\)P\(_{14}\)B\(_{6}\) alloy is closely related to a change of stress relief in the alloy by aging and such a behavior may be characteristic only of ferromagnetic materials. Further, Walter \textit{et al.}\(^{(20-22)}\) have found the presence of discrete region (less than 6 nm dia) with a high phosphorus concentration on the fracture surface of Fe\(_{40}\)Ni\(_{40}\)P\(_{14}\)B\(_{6}\) alloys by Auger and small angle X-ray scattering analyses, and they have shown that the embrittlement is caused by the segregation of phosphorus and is not due to filling the d-shell of iron atoms. However, the present work clearly indicates that the presence of phosphorus is not necessary to embrittlement of amorphous alloys. Also, the Co-based alloy is not brittle prior to precipitation of any crystalline phases despite of being ferromagnetic. Therefore it is considered that several assumptions on the embrittlement are not reasonable. On this point we will be discussed later.

2. Effect of alloy compositions on embrittlement behavior

From Figs. 5 to 9 the relation between the aging temperature ($T$) and the aging time ($t$) at a constant fracture strain ($\varepsilon_f$) is expressed as follows;

$$T = T_0 - a \cdot \log t$$

(2)

where $T_0$ is the temperature ($^\circ$C) at the constant fracture strain and the definite aging time. In the present work, $\varepsilon_f$ is 1 and $t$ is 60 s. The gradient of the linear function, $a$, is termed an embrittlement coefficient, which is a parameter of the degree of embrittlement. To evaluate the activation energy for embrittlement, the relation between the reciprocal of absolute temperature and the logarithmic time at $\varepsilon_f$=1 is plotted in Fig. 10, using the results in Figs. 1 to 4. Table 3 summarizes the embrittlement parameters ($T_0$ and $a$) at $\varepsilon_f$=1, the activation energy for embrittlement ($AH_f$) and the crystallization temperature ($Tx$) for each amorphous alloys. The value of embrittlement coefficient, $a$, is about 30 for Ni-, Pd- and Co-based alloys and it is 50~80 for Fe-based alloys. That is, the enhancement of embrittlement of Fe-based alloys is much larger than those of the other alloys. $T_0$ is nearly in proportion to $T_x$ for all alloys except for iron-based alloys.

Fig. 10. Relation between the reciprocal of absolute temperature and logarithmic time at $\varepsilon_f=1$.

Table 3. Embrittlement parameters ($T_o$ and $a$), activation energy for embrittlement ($\Delta H_f$) and crystallization temperature ($T_x$) for several amorphous alloys.

<table>
<thead>
<tr>
<th>Alloy system</th>
<th>$T_o$ (°C)</th>
<th>$a$</th>
<th>$\Delta H_f$ (kJ/mol)</th>
<th>$T_x$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_{18}$Si$<em>4$B$</em>{17}$</td>
<td>480</td>
<td>26</td>
<td>360</td>
<td>468</td>
</tr>
<tr>
<td>Pd$<em>{40}$Si$</em>{20}$</td>
<td>400</td>
<td>28</td>
<td>250</td>
<td>380</td>
</tr>
<tr>
<td>Co$<em>{13}$Si$</em>{13}$B$_{10}$</td>
<td>500</td>
<td>32</td>
<td>260</td>
<td>480</td>
</tr>
<tr>
<td>Fe$<em>{48}$P$</em>{12}$C$_7$</td>
<td>400</td>
<td>53</td>
<td>120</td>
<td>410</td>
</tr>
<tr>
<td>Fe$<em>{18}$Si$</em>{12}$B$_{12}$</td>
<td>470</td>
<td>80</td>
<td>100</td>
<td>505</td>
</tr>
</tbody>
</table>

$T=T_o-a\cdot\log t$; $T$: Aging temperature, $t$: Aging time.

$\Delta H_f$ is about 300 kJ/mol for Ni-, Pd- and Co-based alloys, while that for Fe-based alloys is about 110 kJ/mol. The former value (300 kJ/mol) agrees nearly with the activation energies (about 300~400 kJ/mol) for crystallization of MS-1 phases obtained from the $T$-$T$-$T$ diagrams. From this fact it is said again that the embrittlement of Ni-, Pd- and Co-based alloys takes place by crystallization in amorphous phase. In the case of Fe-based alloy, however, the activation energies for embrittlement are fairly low as compared with those for crystallization. This means that the embrittlement in Fe-based alloys does not take place by precipitation but by other mechanisms. The equation (2) indicates that the amorphous
alloys with a high thermal stability have a large $T_0$ and a small $a$. From this point of view it can be said that Ni- and Co-based alloys are stable against the embrittlement by aging.

Next, we have examined the changes in the values of $T_0$ and $a$ with alloy compositions. In Fig. 11, the values for Ni-Si-B alloy system are plotted as a function of nickel content. As described above, Ni-based alloys embrittle due to the precipitation of MS-II phase. As the nickel content decreases, both of $T_0$ and $a$ increase, that is, at low temperatures the larger the amount of metalloid elements, the stronger the embrittlement tendency. Furthermore, the embrittlement behavior of (Fe$_{x}$, Ni$_{1-x}$)$_{78}$Si$_{16}$B$_{12}$ amorphous alloys has been examined in the present work. This alloy system was chosen for the investigation because the Fe- and Ni-based alloys are largely different in embrittlement characteristics. Figure 12 shows changes in $T_0$, $a$ and crystalline structure of MS-I phase as a function of Ni content. Among these alloys, the (Fe$_{0.8}$, Ni$_{0.2}$)$_{78}$Si$_{16}$B$_{12}$ alloy has the lowest $T_0$ and the highest $a$. The further replacement of Fe by Ni inhibits the degree of embrittlement. Such a composition dependence of embrittlement behavior has been recognized for (Fe, Ni)-P-B-Al amorphous alloys by Chen. He has pointed out that the embrittlement is due to an increase of mixing entropy of alloys. But the direct relationship between the mixing entropy and the embrittlement is not clarified. As is evident from the change in the crystalline structure of MS-I phase with nickel content in Fig. 12, the embrittlement is severe in the precipitation region of bcc phase. This fact indicates that the embrittlement is related to the transition from amorphous to bcc structure. The greater tendency toward
embrittlement of Fe-based amorphous alloys may be explained by the following assumption. The previous studies\textsuperscript{(23,24)} have shown that the number of atoms at the first nearest neighbor in amorphous structure is 11.5~11.8, which is near the number (12 atoms) of fcc and hcp crystals with the close-packed structure, while it is more than 8 atoms of bcc crystal. Hence the internal strain which generates by the GP zone like nucleation of a fine bcc crystal in amorphous structure is much larger than that by nucleation of fcc or hcp crystal. The increase of this internal strain seems to be the cause of catastrophic loss of ductility for Fe-based amorphous alloys. Furthermore, considering from the facts that a small increase in microhardness\textsuperscript{(20)}, stress relief\textsuperscript{(25)}, an increase in X-ray scattering intensity at small-angles\textsuperscript{(23,23)} were observed at the incipient stage of crystallization of the Fe-based amorphous alloys, it is reasonable that the internal strain generates by the nucleation of a fine bcc crystal. It is hoped that additional investigations on the embrittlement mechanism of iron-based amorphous alloys will be made in the near future.

**Summary**

The change in fracture strain of several metal-metalloid amorphous alloys (Pd-Si, Fe-P-C, Fe-Si-B, Ni-Si-B, Co-Si-B) by a bending test has been examined as functions of the aging time and the temperature below 500°C, and the relationship between the embrittlement and the crystallization process has been discussed.

1. The effect of aging on the fracture strain depends on the composition of amorphous alloys; above all, the embrittlement of the Fe-based alloys is remarkable as compared with those of other alloys.

2. The critical temperature ($T_f$) at which fracture occurs is represented by a linear logarithm function of aging time ($t$); $T_f = T_0 + a \cdot \log t$. The degree of embrittlement can be evaluated by two parameters, namely, the constant, $T_0$, and the gradient of the linear function, $a$.

3. The values of $a$ for Pd-, Ni- and Co-based alloys are small and these alloys become brittle by the precipitation of the MS-I or MS-II phases. On the other hand, Fe-based alloys have large values of $a$ and become brittle at the incipient stage of crystallization. The reason why only Fe-based alloys become brittle prior to the appearance of the MS-I or MS-II phases may be due to the internal strain generated by the nucleation of a fine body-centered cubic crystal in amorphous structure.

