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EFFECT OF METALLOIDAL ELEMENTS ON STRENGTH AND THERMAL STABILITY OF IRON-BASE GLASSES

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1. Introduction - It has been well known that several iron-base glasses possess a high fracture strength with sufficient ductility and toughness. The compositional factors play an important role in determining the strength of the glasses. Several works have investigated the effect of metallic elements on the mechanical properties of iron-base glasses (1,2).

Iron-base glasses often lose ductility upon annealing near or below crystallization temperatures. In particular, those containing phosphorus embrittle well below the crystallization temperature (3,4).

This work reported herein has been undertaken to clarify the role of metalloidal elements (B, C, Si, P and Ge) on the strength and embrittlement behavior of iron-base glasses.

2. Experimental - The single roller method was applied to the preparation of glassy alloy ribbons of about 2 mm in width and 20 μm in thickness. This technique consists of impinging a stream of melt onto the outer surface of steel disc rotating at a high speed (50 m/sec). The glassy alloys prepared were Fe_{100-x-y}^{ix}N_xY_y (x=1 or P, N=B, C, Si, P or Ge) and their structure were confirmed by X-ray analysis. The microhardness was measured with a Vickers-Diamond indenter using a load of 100 g. The crystallization temperature was measured using a differential thermal analyzer with a heating rate of 5 K/min. In order to evaluate the mechanical stability of iron glasses, the strain for fracture (λ_f) of ribbon was measured by bending method reported by Luborsky et al. (3). The embrittlement temperature T_B was defined as the annealing temperature for a given annealing time after which the specimen lost ductility at room temperature (λ_f = 1).

3. Results and Discussion - Figs. 1 and 2 show the glass forming regions of Fe_{100-x-y}^{ix}N_xY_y alloys.
Fig. 3. Microhardness of Fe$_{80}$B$_{20}$-$_N$ glasses as a function of metalloid content.

Fig. 4 Microhardness of Fe$_{80}$P$_{20}$-$_N$ glasses as a function of metalloid content.

prepared by a single roller method, where $N$ is B, C, Si, P or Ge. The estimated cooling rate was of the order of the $10^6$ K/sec. Figs. 3 to 5 show the microhardness of Fe$_{80}$P$_{20}$-$_N$, Fe$_{80}$B$_{20}$-$_N$, Fe$_{85}$-$_B$$_{15}$_N and Fe$_{85}$-$_P$$_{15}$_N alloys, respectively. The average change in microhardness with the concentration of 1 at.$\%$ metalloid, $dH_V/dX$, is evaluated from these data because the hardness changes in almost linear manner with the concentration of metalloids. The hardness equation obtained by using the least-squares analysis is expressed by

$$H_V (kg/mm^2) = 580 + 24(at.\%B) + 17(at.\%C) + 11(at.\%P) + 6(at.\%Si) + 4(at.\%Ge).$$

The average deviation of calculated hardness from the measured value is $\pm 20$ kg/mm$^2$. From this equation, the apparent hardness of pure iron glass is estimated to be 580 kg/mm$^2$. This equation is applicable to estimation of hardness for the binary and ternary iron-base glasses.

The $dH_V/dX$ of each metalloid is plotted against its valence in Fig. 6(a). Boron belonging to group IIIA has the largest $dH_V/dX$. This suggests that the bond may be formed by overlap of s-p orbitals of the metalloid atom and s-p-d orbital of the iron atom. According to Hume-Rothery (5), the average outer electron concentration is customarily used as a measure of the valence of that element. The hardness of iron-base glasses is plotted against the $e/a$ in Fig. 7, where average electron concentration for any alloy is taken as the weighted means according to the atomic percentage of elements. Values reported by Davis (2) are also included in that figure.
Fig. 6. $dH/dX$ plotted against the valence of metalloids (a), and against the atomic radii of metalloids (b).

As shown in Fig. 5, the e/a has a significant effect on the hardness with an increase in the valence of metalloids decreasing the bond strength between iron and metalloid. The $dH/dX$ of metalloids such as C, Si, and Ge that belong to the same group IVA decreases with increasing the atomic diameter in the order of C, Si, and Ge as shown in Fig. 6(b). Here, the radius of respective metalloid in the tetrahedral covalent structure is used (6). Hume-Rothery has suggested that the s-p hybrid overlap in metalloids becomes increasingly difficult with increasing atomic size of the elements in the order of C, Si, and Ge. The data for B and P included in Fig. 5(b) show some deviation from the relation. This implies that both valence and atomic size of metalloids play the important role in the hardness of glasses.

The embrittlement temperatures $T_B$ for 2 hrs annealing of Fe$_{80}$B$_{20-x}$X$_x$ alloys (N=C, Si, P or Ge) are shown in Fig. 8. Replacing B with about 3 at.% Si or C slightly increases $T_B$, then decreases it until a minimum around 6 at.% Si or C. Further replacing again increases $T_B$. Any replacement of B with Ge and P decreases $T_B$. The $T_B$ for 2 hrs annealing of Fe$_{80}$P$_{20-x}$X$_x$ alloys are shown in Fig. 9. Replacing P with 2-4 at.% B, C or Si significantly increases $T_B$. With further increase in B, C or Si content, $T_B$ of these glasses decreases and attains a minimum.
Fig. 10. Composition dependence of $T_x$ and $T_B$ (2 mins anneals) for Fe$_{80}$B$_{20}$-X$_x$ glassy alloys.

$550 \text{ K around equi-atomic content of metalloids.}$ In order to clarify the correlation between embrittlement process and crystallization process of the glassy iron-base alloys, the crystallization temperature $T_x$ is compared with the $T_B$. The initiation time for crystallization by isothermal annealing $t$ is estimated from the isochronal crystallization temperature $T_x$ by using $t = (T_x/\alpha)k/E$ (7), where $\alpha$ is the constant heating rate, $E$ the activation energy for crystallization and $k$ the Boltzmann constant.

When $T_x$ is about 700 K at 5 K/min and $E$ is about 70 Kcal/min, the $t$ value corresponding to 5 K/min is estimated to be about 2 mins. The $T_x$ and $T_B$ (2 mins anneals) of Fe$_{80}$B$_{20}$-X$_x$ and Fe$_{80}$P$_{20}$-X$_x$ alloys are shown in Figs. 10 and 11 respectively. With the exception of replacing B of the Fe-B glass with P, the replacement of either B or P with small content of about 3 at.% second metalloid increases $T_B$ apparently resulting from the increase in thermal stability, i.e. the increase of $T_x$. With further increase in the second metalloid content, $T_B$ decreases and becomes lower than $T_x$ with the exception of Fe-B-C alloys.

Should this embrittlement prior to crystallization is due to atomic clustering some what analogous phase separation as suggested by Chen (4), the embrittlement behavior of metallic glasses would be determined by two factors: the bonding characteristics of metalloids which affect the tendency to phase separation, and the mechanical properties of separating phase. Admixture of two kind of metalloids, which possess the different bonding characteristics to iron, causes embrittlement prior to the crystallization for alloys such as Fe-B-Si, Fe-B-P and Fe-P-C.

References