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Observation of phosphorus segregation onto the free surface of an amorphous $Fe_{44}Ni_{36}P_{14}B_6$ alloy

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Phosphorus segregation to the free surface of an amorphous $Fe_{44}Ni_{36}P_{14}B_6$ alloy during annealing in the temperature range 180 to 300° C has been studied by Auger electron spectroscopy. The phosphorus concentration increased with annealing temperature with an abrupt change appearing at about 250° C. At 276° C the phosphorus Peak Height Ratio on the surface was three times as high as that of a sputtered surface. A step-heating scheme has been employed to observe the surface segregation of phosphorus in the temperature range 25 to 290° C. On heating, the segregation behaviour can be correlated with a degradation in toughness properties . It is concluded that the segregation of phosphorus onto the free surface of this amorphous alloy is an indication of some local atomic migration processes, for example clustering, occurring inside the bulk.

1. Introduction

The mechanical properties of amorphous alloys with the general composition of $(Fe, Ni)_{80}(P, B)_{20}$ have been studied extensively in the last few years. These alloys, if rapidly quenched during their preparation, are extremely strong but can still deform plastically on bending without fracturing. The stability of these metal glasses and the influence of composition on their stability have been discussed by many authors [1–4]. The atomic mobility in the amorphous state is expected to scale roughly as T/T_g, where T_g is the glass transition temperature. However, many of the metal–metalloid glasses undergo a catastrophic loss of ductility during low temperature annealing. For example, the metglass $Fe_{40}Ni_{40}P_{14}B_6$, which is quite ductile in the as-quenched state, becomes brittle after only 2 h at 100° C whereas no crystallization is detectable until about 370° C. The origins of this embrittlement are controversial. Walter *et al.* [5] claimed that it is a consequence of clustering of metalloid atoms and have shown that the fracture surfaces of phosphorus-containing glasses are enriched in phosphorus after 2 h annealing at 325 and 350° C. Phosphorus would appear to be the worst element in this respect since the thermo-stability of this metglas improved as phosphorus is progressively replaced by boron. Chen [6], on the other hand, has argued that there exists no fast diffusive process for metalloids and that the embrittlement is the result of a very fine scale phase separation. Both the above hypotheses involve the atom motion either in a longer or a shorter range. It is well established that, phosphorus is a surface active element and it will be enriched on the free surface when annealed at the particular temperature where atom motion may occur.

The purpose of this work is to study the surface segregation of phosphorus in an $Fe_{44}Ni_{36}P_{14}B_6$ alloy at various temperatures and to relate this segregation behaviour to the clustering of phosphorus atoms in this alloy and its possible embrittlement.

2. Experimental procedure

The samples used for Auger analysis were 0.08 mm thick ribbons prepared by rapid quenching. The composition of the alloy was approximately, in atomic per cent, 36Ni, 44Fe, 14P, 6B. The samples

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were degreased and then mounted on the specimen stage where the samples can be heated to 800° C. X-ray diffraction did not show any signs of crystallization before or after Auger analysis.

For the analysis of the ribbon surface, a conventional Auger electron spectrometer (AES) with a cylindrical mirror analyser and a coaxial electron gun was used. The electron gun had a beam size of 0.2 mm and was operated at 2 kV and 5 μA. The experiment was carried out under a vacuum of 2.6×10^{-7} Pa or better. In order to remove the surface contamination and to obtain element depth profiles, an ion gun was used working at 500 V to 2 kV, the beam current was 6 μA under 6.6×10^{-3} Pa argon atmosphere. An iron–constantan thermocouple was attached to the sample to measure the heating temperature. The surface composition of the amorphous alloy was determined by measuring the Auger peak height ratio (*PHR*) of any element with respect to the basic element iron. Although this measurement does not give the absolute amount of surface coverage, it does reflect the relative change of an element on the surface. The Auger peaks chosen to calculate the PHR in this work are 703 eV for iron, 848 eV for nickel, 120 eV for phosphorus and 179 eV for boron.

Before starting the diffusion measurements, all samples were cleaned by ion sputtering to remove the surface oxide layer or other contamination until a steady state of surface composition was reached which is believed to approximate to the bulk composition. The sample was heated as quickly as possible to a predetermined temperature and the Auger spectrum recorded. When the segregation has reached a stable level, the sample was cooled down and sputtered once more to remove any segregation. The above process was repeated at a different temperature after each run.

A step heating regime was also employed to heat the sample from one temperature directly to a higher one in order to minimize segregation taking place during the thermal cycle. Auger peaks of certain elements were recorded after 10 min at this temperature and a *PHR* against temperature obtained.

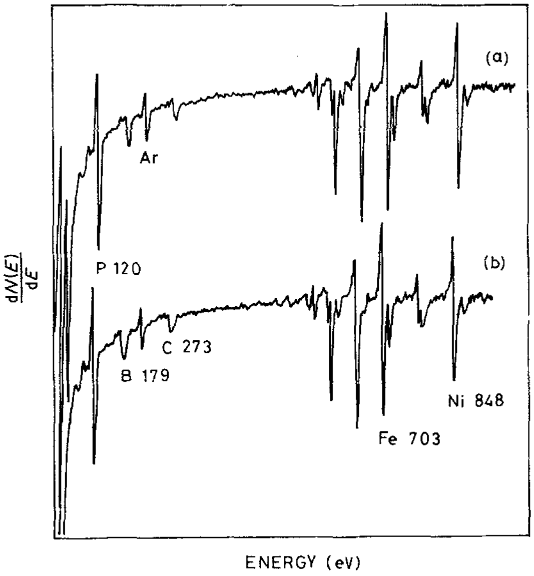

Figure 1 Auger spectra of the sputtered cleaning surface of amorphous $Fe_{44}Ni_{36}P_{14}B_6$ (a) before annealing and (b) after several cycles at different temperatures.

3. Experimental results

An Auger spectrum of the sputtering cleaned surface of the original FeNiPB sample is shown in Fig. 1a. Besides the four constitutional elements, iron, nickel, phosphorus and boron, carbon and sulphur were also obtained, which are believed to arise from surface adsorption and the amorphous alloy preparation process. After heating and sputtering at different temperatures for several cycles the surface was cleaned again by sputtering. No change in the Auger spectrum can be detected (Fig. 1b), implying that there is an insignificant loss of phosphorus from the bulk so that the sample can be reused even after many cycles of heating and sputtering. Spectra taken from different areas of the same sample after 2 h of heating at 276° C are almost identical, implying that the surface composition is roughly homogeneous from area to area. Figs. 2a and b are examples of the variation of surface composition as a function of heating time at 183 and 276° C respectively. Phosphorus is the predominant segregating element to the free surface of this amorphous alloy. For annealing at 183° C, the phosphorus concentration increases monotonically with heating time reaching a maximum *PHR* of about 1.4. For 276° C annealing, the phosphorus concentration on the free surface increased very rapidly until the maximum *PHR* of about 3.0 was reached. The other elements remained approximately constant. Fig. 3 shows the variation of phosphorus *PHR* with heating temperature for a period long enough to reach the steady state (the maximum *PHR*). As heating was progressed up to about 240° C the phosphorus concentration increased dramatically but the other

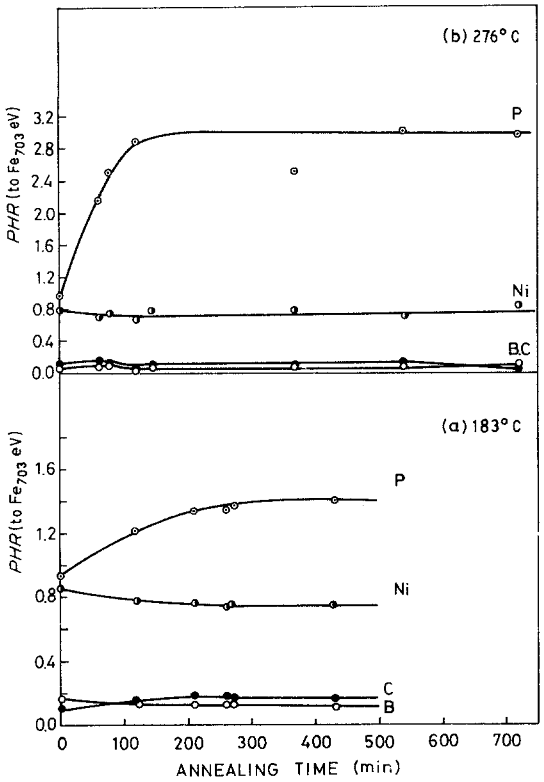

Figure 2 Representative plots of *PHR* against time (a) at 183° C, (b) 276° C.

elements remained unchanged. Beyond 300° C such an observation cannot be made in this way because phosphorus segregation is too fast to be monitored by Auger measurement. In order to avoid this shortcoming, a step-heating scheme was employed. The sample was kept at a lower temperature for 10 min and the peak heights of phosphorus and iron were measured, then the sample was brought up to a somewhat higher temperature and the peak heights of phosphorus and iron were measured again. This process was repeated until a predetermined temperature was reached. The heating time was not necessarily 10 min, it could be longer or shorter depending on the segregation rate of the elements under observation.

In Fig. 3, curve (b) is a plot of phosphorus concentration (*PHR*) against heating temperature, but in this case the phosphorus segregation at the surface is the value accumulated from all the temperatures at which the sample has been subjected to before reaching this measured temperature, i.e. this is an integral curve. Compared with the steady state curve (a), the step-heating curve has a similar shape above 200° C but the temperature at which the *PHR* changes rapidly is delayed about 40° C. Moreover, there is a small but noticeable rise in phosphorus segregation at 80 to 100° C.

After reaching the steady state at 276° C, the sample was ion-sputtered and the phosphorus concentration–depth profile is shown in Fig. 4. The sputtering conditions are: Ar$^+$ energy 800 eV and beam current 6 μA. The phosphorus concentration decreased rapidly to the level before heating, implying that phosphorus segregation at the free surface is largely concentrated on the few outer-

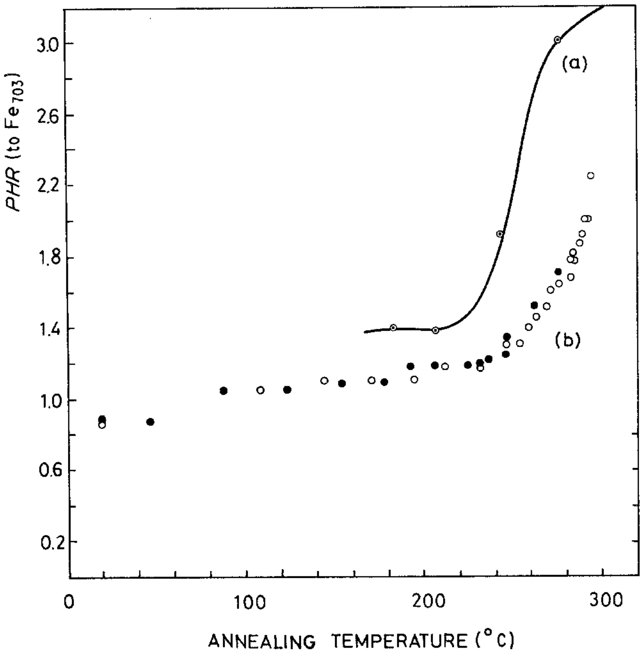

Figure 3 The variation of phosphorus *PHR* against annealing temperature. (a) *PHR* in the steady state at each temperature. (b) Integral *PHR* of the step-heated sample.

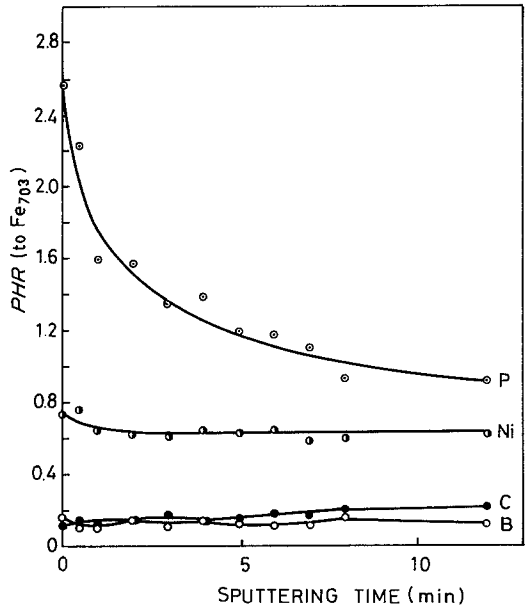

Figure 4 Phosphorus concentration–depth profile of the amorphous $Fe_{44}Ni_{36}P_{14}B_6$ alloy after reaching the steady state at 276° C.

most atom-layers. Nickel decreased slightly owing presumably to preferential sputtering. The other elements showed no appreciable changes.

The phosphorus concentrations (*PHR*) after 2 h annealing at various temperatures are shown in Fig. 5 as a function of heating temperature, and the fracture toughness curve was replotted from the data given by Ast and Krenisky [3]. It is obvious that the behaviour of phosphorus segregation to the free surface is closely related to the change of the fracture toughness of this alloy, both changing abruptly within the same temperature range. The phosphorus concentrations (*PHR*) on the free surface after heating for 10 min are shown in Fig. 6 as a function of heating temperature (a), together with a curve (b) drawn from the work of Williams and Egami [4] showing the ductile–brittle transition temperature varying with the annealing temperature. These two curves have almost the same tendency. However, more work is required before this correlation can be confirmed and extended to other amorphous alloys.

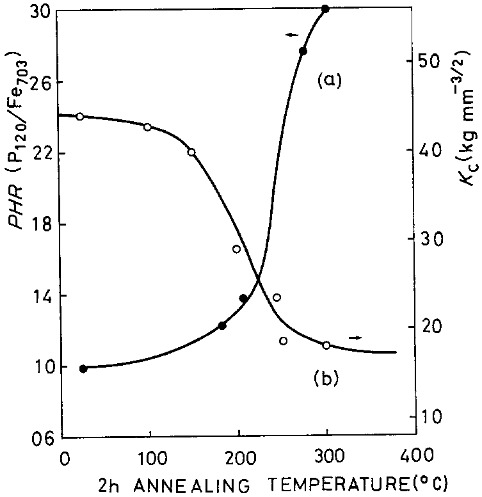

Figure 5 Phosphorus *PHR* after 2 h annealing at various temperatures (a); the fracture toughness against 2 h annealing temperature (b) replotted from Ast and Krenisky [3].

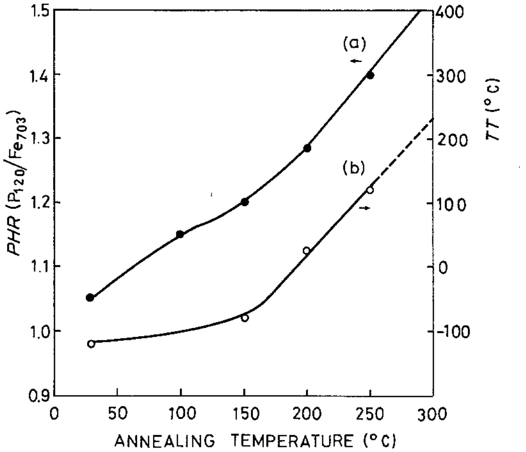

Figure 6 The phosphorus concentration (*PHR*) on the surface after ten min annealing at various temperatures (a); and the ductile–brittle transition temperature (TT) against 15 min annealing temperature (b) drawn from Williams and Egami [4].

4. Discussion

The study of the segregation of solute atoms to the free surface in alloys or nominally pure metals is an important application of AES. Not only is it used to obtain fundamental information about the thermodynamics of surfaces in multicomponent systems, but it is also essential in the study of the adsorption of impurities which affect surface-controlled reactions, as well as in the study of interactions between solutes which promote or retard the types of solute segregation leading to embrittlement of steels. In connection with the latter, it is the goal of a number of investigators [7–9] to gain information about grain-boundary segregation from studies of segregation at the free surface. This indirect approach is necessary whenever it is impossible or impractical to produce intergranular fractures in ultrahigh vacuum. It also has the advantage that segregation occurs faster and generally to a higher degree at free surfaces than at grain boundaries. If a particular segregation phenomenon is not observed on the free surface, it will possibly not be observed at the grain boundary. However, the amorphous alloys which are super-saturated metastable solutions have no grain boundaries. Where do the solute atoms go when the sample is heated to a temperature at which they are mobile? The favourable place for the solute atoms to stay is the free surface, especially for those elements which can reduce the surface energy, for example phosphorus. Walter *et al.* [5] have studied the fractured surface of the amorphous $Fe_{40}Ni_{40}P_{14}B_6$ alloy after 2 h annealing at 325 and 350° C by AES and found that phosphorus was enriched twice as much at the fractured surface as that before heating. They therefore concluded that phosphorus had segregated during annealing into discrete regions of high concentration. These regions are responsible for the embrittlement of the amorphous alloy. Hence the observation of surface segregation of the amorphous $Fe_{44}Ni_{36}P_{14}B_6$ alloy during annealing by means of AES reveals that some migration processes may take place inside the specimen before crystallization on an atomic scale. i.e. the surface segregation is an indication of atom mobility within the bulk.

The step-heating technique employed here is suitable for surveying the annealing characteristics of an amorphous alloy containing surface active elements. The plot of *PHR* against *T* is not a simple smooth curve (see Fig. 3b), and there are several breaks in it. These breaks indicate that several processes involving the migration of atoms were taking place one after another. The first one located at about 80° C shows that phosphorus atoms have segregated, but the level is not high. It seems that this process is completed in a short time, presumably being connected to a process involving a lower activation energy such as a short-range ordering of phosphorus atoms in this amorphous alloy. Luborsky and Walter [2] have shown that a fast embrittling process appeared at about 90° C and the degree of embrittlement is strongly temperature dependent. These two processes may be closely related. The second one, at about 250° C, near the Curie temperature, is accompanied by a very rapid rise in phosphorus segregation at the free surface. The phosphorus concentration (*PHR*) in the steady state at 276° C is three times as high as that of a cleaned surface. If this amount of phosphorus only comes from the few atom-layers at the surface, a depletion zone should be built up under the outermost layer. However, a concentration–depth curve obtained by ion milling does not show any phosphorus depletion zone (see Fig. 4), therefore the diffusion of phosphorus must have occurred throughout the specimen. A continuous heating technique may be developed with a very slow heating rate and a computerized AES recording system which will give a more detailed *PHR* against *T* curve similar to a differential scanning calorimeter run.

Generally the dominate driving force for surface segregation is the minimization of surface free energy, although the volume free energy might be important in certain cases. When atoms segregate from the bulk of a sample to the surface the kinetics of segregation are usually controlled by bulk mobility of diffusivity. From a comparison with some mechanical properties (see Figs. 5 and 6) it can be seen that the segregation not only occurred on a free surface but also inside the bulk of this amorphous alloy. The behaviour of low temperature annealing of an amorphous alloy is similar to temper embrittlement of low alloy steels. Careful measurement of free-surface segregation can be used to deduce some information about the motion of solute atoms in the bulk. However, amorphous alloys are not in an equilibrium condition and so it is not surprising that some of their properties will vary with heating. The chemical composition may be changed after many cycles of heating and sputter cleaning. Fortunately no detectable phosphorus depletion in the bulk was found after a number of cycles in the temperature range 180 to 300° C and the data were reproducible (see Figs. 2 and 3b). It is necessary to point out that the material used in this work is somewhat different in composition from that used by Ast and Krenisky [3] and Williams and Egami [4]. However, Luborsky and Walter [2] have already shown that changing the Fe/Ni ratio in $(Fe, Ni)_{80}(P, B)_{20}$ systems caused no change in the process of embrittlement.

5. Conclusions

1. Phosphorus segregation onto the free surface of an amorphous $Fe_{44}Ni_{36}P_{14}B_6$ alloys has been observed by AES after being heated to temperatures far below the crystallization temperature. The other elements remained approximately unchanged.

2. The temperature for the onset of phosphorus segregation was about 80° C, with the degree of segregation increasing with increasing temperature. At about 276° C, the steady state concentration of phosphorus on the free surface is three times as high as that before heating.

3. The phosphorus segregation occurred within the same annealing temperature range as the embrittlement of this amorphous alloy. Therefore, it is suggested that during the segregation of phosphorus to free surface of the amorphous $Fe_{44}Ni_{36}P_{14}B_6$ alloy phosphorus atoms also form discrete clusters in the bulk causing embrittlement of this alloy.

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