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Crystallization of Amorphous Pd-Si Alloy during Low Temperature Annealing

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Abstract

Crystallization process of Pd-Si amorphous alloy containing about 20% silicon was investigated. It was found that the crystallization initiates in the surface region at relatively low temperatures below 250°C and the atomosphere has an appreciable effect on the process. Rate of crystal growth follows the autocatalytic type of equation rather than usual Johnson-Mehr equation. The mechanism of crystallization are explained qualitatively. It was emphasized that these facts play a decisive role for the application to the electronic devices because of their large surface to volume ratio.

1. Introduction

Amorphous alloys exhibit excellent properties which are originated in their structural and chemical homogeneity. They are in a homogeneous disordered state where no locallized disorder, such as dislocations or grain boundaries, exists. The fluctuation in chemical composition is also very small. Furthermore, it is also possible to produce mono-phase amorphous metallic materials even in the composition range where homogeneous materials can not be expected in the ordinary crystalline state. Now these excellent and promising properties in amorphous alloys are stimulating many researchers to the development of amorphous alloys to practical use.

The amorphous alloys, however, cannot be free from the intrinsic thermal instability which is characteristic in a meta-stable phase introduced by drastic methods. Therefore, one of the most important problems in the practical use of the amorphous metals is the crystallization process. Especially, as the crystallization during the relatively low temperature annealing is the most usual practice in order to secure the stabilization of the physical, chemical and other properties, considerable efforts have made by many authors.[1,2] The present report is concerned with the crystallization phenomena of Pd-Si amorphous alloys containing about 20% silicon, which was prepared by the so called splat cooling, in the temperature range below about 250°C. The main results obtained are that the crystallization initiates at the surface of the sample and the compositional change of the crystallized layer can not be detected. These

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results are considered to be very important for the application to the electronic devices, because of the decisive role played by the surface owing to the large surface to volume ratio.

2. Experimental and results

(A) Incubation time

The incubation time is estimated from the measurements of the velocity of 300KHz acoustic wave transmitted along the thin plate samples. Acoustic waves were excited and detected by the ferromagnetic metal pieces attached to the both ends of sample.

To analyse the results exactly, the three layered structure of the transmission media must be taken into account, because the crystallized layers exist at the both surfaces of sample as described below, and the sound waves have a different velocity in each layer. However, we used the results only for the detection of the incubation time here.

The pair distribution function g(r) obtained by the X-ray diffraction gives the nearest neighbor distance of 2.8 Å, which is longer by about 0.03 Å compared with those of the metastable supersaturated crystalline phase. Therefore, change of the volume, accordingly the density in the crystallization process can be neglected. Hence, the change in wave velocity shown in Fig. 1, Fig. 2 and Fig. 3 are attributable to the change in Young's modulus.

A pronounced effect of the atomosphere is observed on the incubation time. With the formation of the crystalline phase, the atoms enter the more deep potential wells, and it is easily understood that the mean strength of alloys for applied stress increases and, therefore, this method is useful for the estimation of the incubation time. The incubation time becomes shorter in the order of vacuum, argon, nitrogen atomosphere and oil immersion. The effects of various atomospheres may be attributed to the differences of cooling power as discussed in the discussion section.

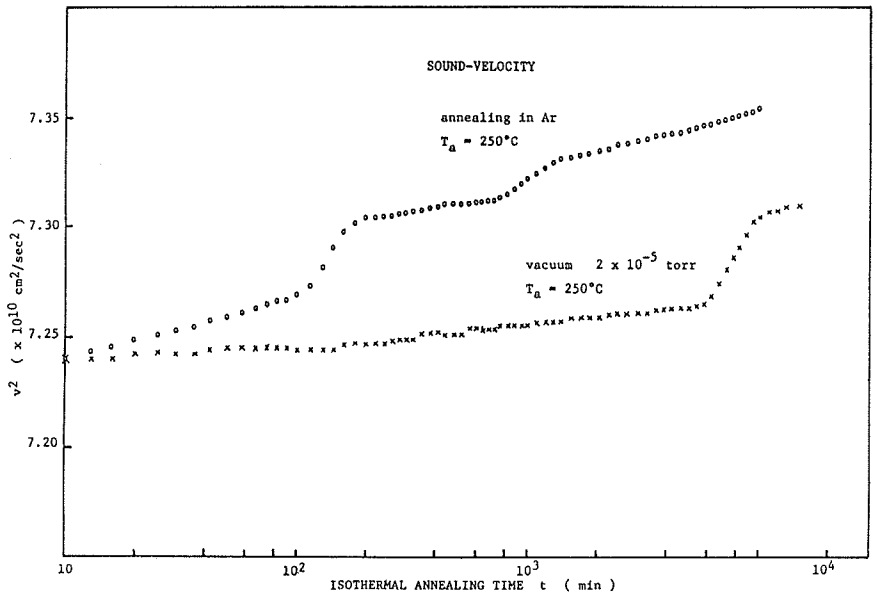

Fig. 1

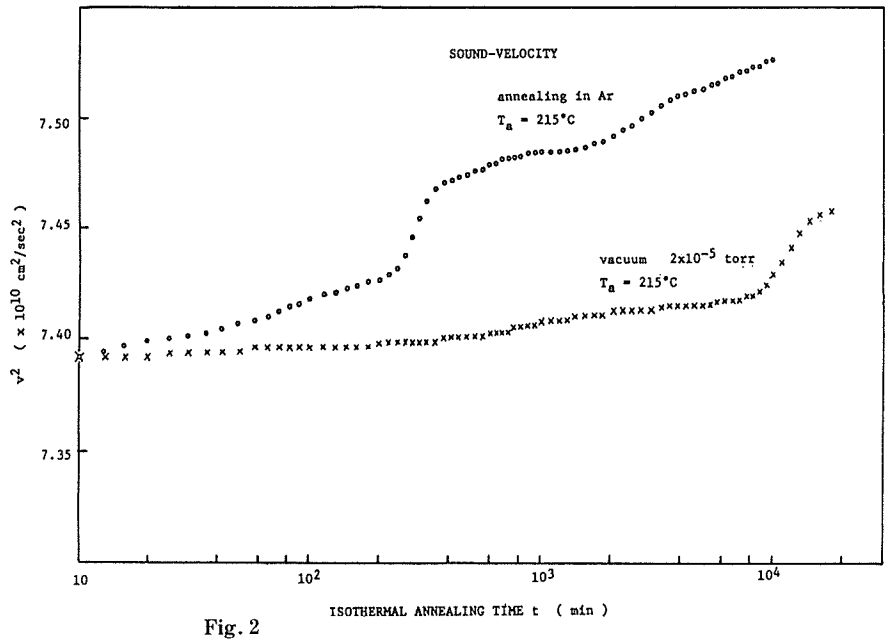

Fig. 2

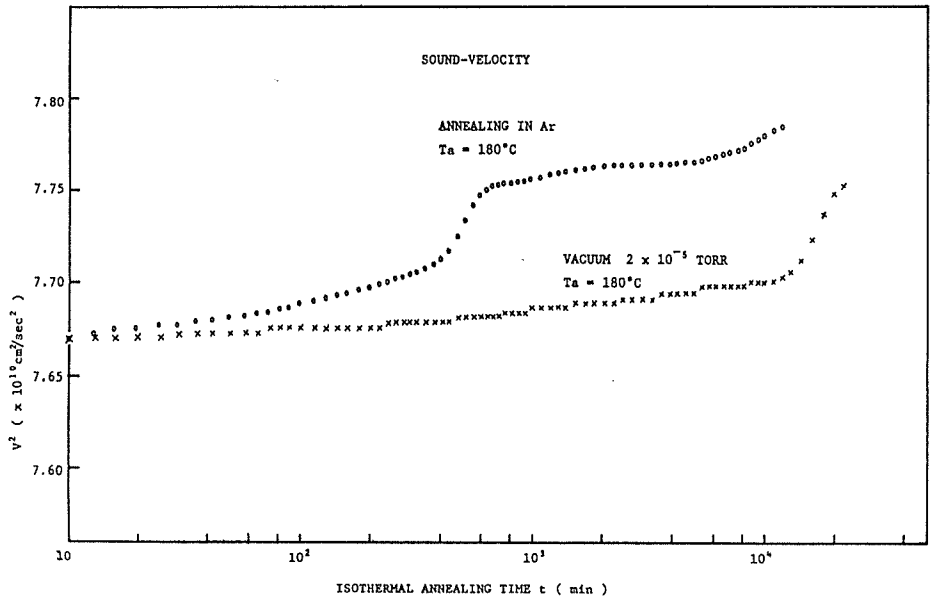

Fig. 1. 2. 3. The change of sound velocity with annealing time.

(B) Rate of crystallization

The rate of crystallization is measured by the X-ray diffraction method, the principle of which is based on the difference in the penetration depth of X-ray with the incident angle. As shown in Fig. 4 the diffraction peaks characteristic to the crystalline phase appear in the superposition on those of the amorphous phase after a certain annealing time. The height of these peaks is the approximate measure of the rate of crystal growth process. Fig. 4 shows the diffraction pattern of CuKα characteristic X-ray. As the penetration depth of CuKα into the

Pd-Si alloy is about a few μm, this result gives information about the surface region. It is interesting to note that the reflection from the (200) plane is a linear function of the annealing time.

Fig. 5. shows the crystallized fraction in the surface region. It is very interesting that the crystallization initiates at the surface region in every case. However, no appreciable compo-

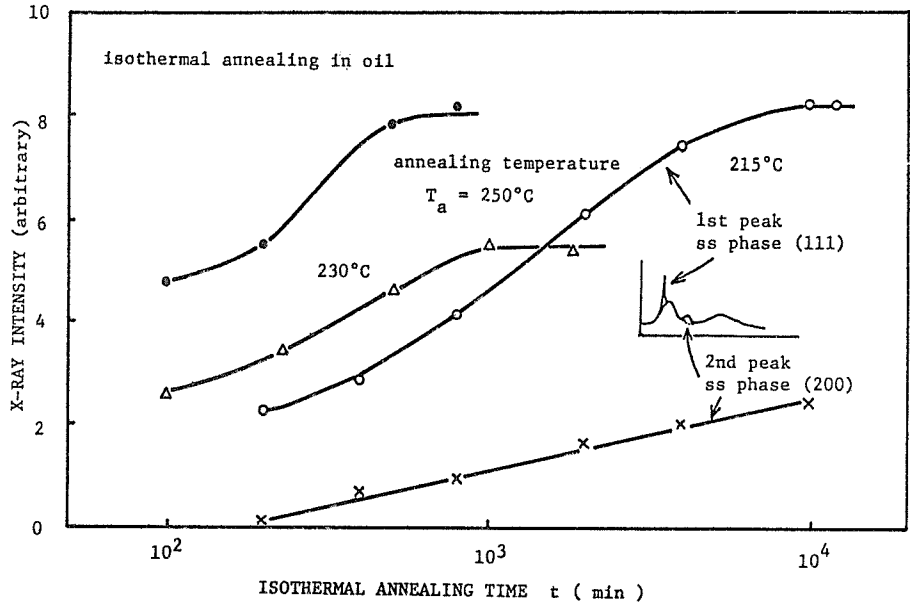

Fig. 4 Intensity of reflacted X-ray beam from crystallized part of specimens.

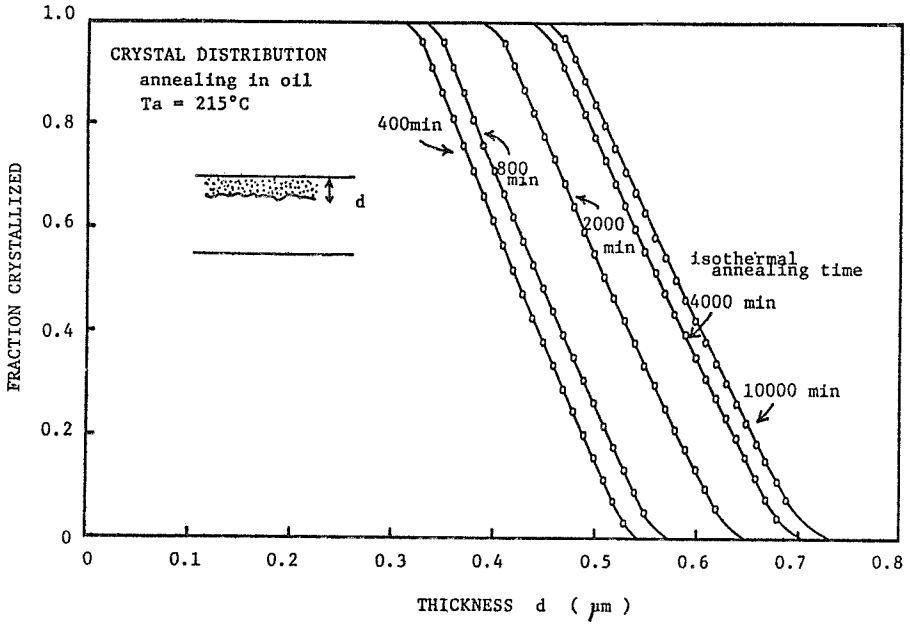

Fig. 5 Crystallized fraction at surface region.

sitional change was detected by means of the X-ray micro-analysis. The crystallized parts are assumed to be present in the form of dispersed small particles. In order to obtain information from the interior, the characteristic MoKα ray was used, but no change was detected in the present temperature range. At the higher temperatures above about 250°C, no preferential

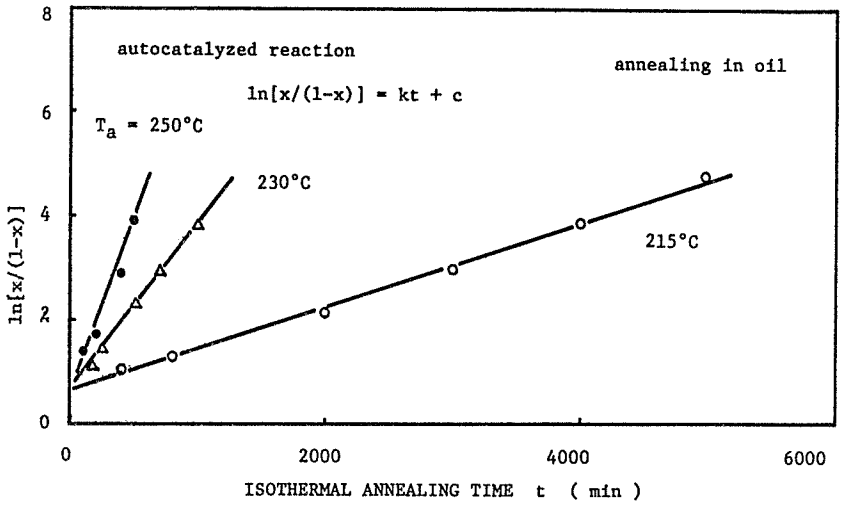

Fig. 6 Rate of crystallization process, accorging to autocatalitic mechanism.

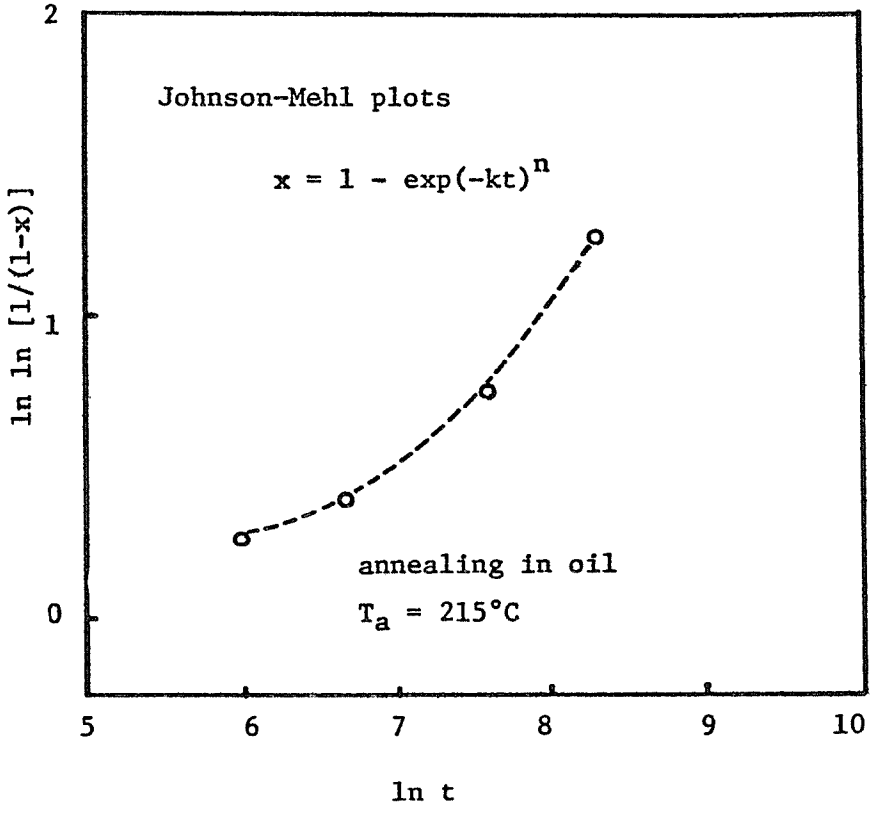

Fig. 7 Rate of crystallization process, according to Johnson-Mehl mechanism.

crystallization at the surface was detected.

The growth rate of the crystalline phase, which is shown in Fig. 6. follows the autocatalitic type of rate equation, $\ln [x/(1-x)] = kt+c$, rather than the usual Johnson-Mehl equation. The usual Johnson-Mehl plot

$$x=1-\exp(-kt)^n$$

is shown in Fig. 7., which deviates apparently from the linear relationship between $\ln\ln [1/(1-x)]$ and $\ln t$, where x is the crystallized fraction, k the rate constant and n is the constant determined by the nucleation mechanism. The rate constant calculated from the experimental results shown in Fig. 6. are shown in Fig. 8., from which the following formula is obtained for the rate constant k.

$$k=1.9\times10^{13} \exp(-1.3\ \mathrm{eV}/k_0T)$$

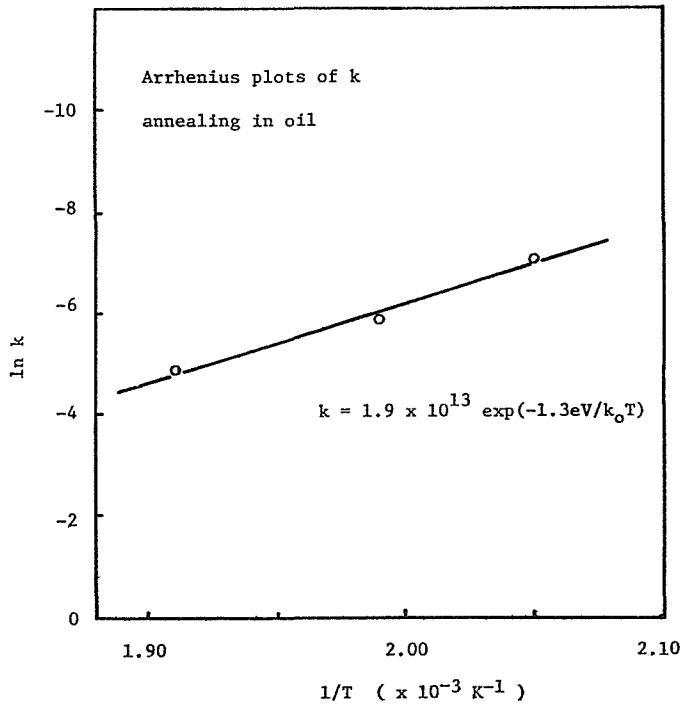

Fig. 8 Arrhenius plot for rate constant k.

3. Discussions

The observed nucleation and growth processes are highly complex and are difficult to explain quantitatively. The nucleation process is considered to be due to the thermal fluctuation. The clusters of various size (number of atoms in a cluster) are considered to exist by thermal fluctuation and they grow or annihilate thermally. Only the clusters larger than the defined critical size, which is determined by the volume and surface (interface) free energy of the cluster, act as the growing nuclei. In order to grow spontaneously for the clusters, free

energy of the clusters becomes smaller by the order of k_0T (k_0 is Boltzmann's constant) than that of the critical nuclei by adding of atoms to them.

In other cases, some of the clusters may become supercritical by local cooling ; that is, the nucleation process is athermal.

In both cases above mentioned, if the released thermal energy during the growth process of the clusters is balanced out by the dissipated heat into the atomosphere, then the steady state of growth process is established. It is considered that the time necessary for the establishment of the steady state determines the incubation time.

If the adsorption of the atomspheric constituent occurs on the surface, another influence of the atomosphere is also considered. Adsorption decreases the surface energy, and the surface of lower free energy may appear, as in the case of faceting.

After the surface is covered with the crystalline phase, the growth rate into the interior of the sample follows the autocatalitic process. This fact may be explained as follows ; the exothermic nature of the crystallization process activates the atoms thermally in the neighborhood. In this case, it is also assumed that the cooling effect of the atomosphere is important in order to maintain proper supercooling in the sample. The cooling effect is assumed to be determined by the radiation loss in the case of the vacuum, and by convection or conduction in other cases. In the case of gas atomosphere, the accomodation effect may also be taken into account. The adsorption will have a considerable effect in the case of oil immersion.

The pre-exponential factor is the order of the frequency of the thermal vibration of atoms in crystals, and the activation energy is much lower than those of the diffusion over a long range. These facts are considered to show that only the atoms in contact with the crystalline phase, which vibrate in the shallow potential wells, take part in the growth process.

4. Conclusion

The most important result obtained is that the crystallization initiates at surface during low temperature annealing and seriously affected by the atomospheric conditions.

According to a more detailed analysis,[3] crystallization at the surface region was not observed at higher temperatures of annealing than 250°C. It seems that the different crystallization mechanism operates in a higher temperature range.

Different types of crystallization mechanism were reported by various authors.[1,2] These results show that so-called amorphous alloys do not have one definite atomic arrangement but have a variety of arrangement depending on the quenching rate, the difference of composition and the amount of treatment after quenching, etc.

References

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