Amorphous forming ability of Co- X (X =Cr, Mo, W) magnetic thin films

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Co- X (X =Cr, Mo, W) magnetic thin films were prepared by using DC magnetron sputtering, and their structures were examined by using X-ray diffraction (XRD). The amorphous forming ability (AFA) of the three alloy systems was discussed based on thermodynamic calculation and experiments. The results show that the Co-Mo thin films exhibit the largest AFA among them, and the Co-W thin films are condition-dependent amorphous while the Co-Cr thin films are hard to be amorphous, which is consistent with the thermodynamic calculation. The difference in AFA for the alloys of these three systems is finally ascribed to three main factors: differences in electronegativity, electron density and atomic size between Co and X elements.

KEY WORDS Amorphous forming ability; Co-Cr; Co-Mo; Co-W

1 Introduction

Cobalt- and iron-base amorphous magnetic alloys have been paid much attention due to their super high permeability, low magnetic loss, low intrinsic coercivity and etc, and thus have many applications in the fields of magnetic sensors, power transformers, and so on^[1,2]. Much effort has been focused to exploit new amorphous magnetic alloys through the conventional trial-and-error method, following the general empirical principles: (1) negative heat of mixing, (2) large atomic size difference, and (3) multicomponent alloy system^[3].

Amorphous magnetic thin films are one of interesting topics among them, which show a particularly potential application in magnetic recording head with high saturation magnetization, low coercivity and low magnetostriction, such as Co-Zr-Ta amorphous films^[1]. So far, however, it has not been well understood the nature of amorphization mechanism of materials^[4]. Our previous study showed that the amorphization of Co-Mo thin films is strongly related to both the enthalpy of formation and sputtering processing. Low deposition rate and high working pressure facilitate the amorphization of the Co-Mo thin films^[5]. Since Cr, Mo, W are important elements to improve comprehensive properties of Fe- and

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Co-base amorphous magnetic materials and they also belong to the same transition column (VIB)^[6], a comparison study on amorphous forming ability (AFA) of the Co- X (X =Cr, Mo, W) thin films is expected not only to clarify their contribution to amorphization, but also further to clarify the generality of amorphization of magnetic thin films under sputtering condition.

In this study, the AFA of Cr, Mo, W with Co was thermodynamically calculated and experimentally examined, and then the difference in AFA was discussed to make it clear the origin of amorphization mechanism of the Co-base thin films by sputtering.

2 Experimental

All the thin films (about 100 nm) were deposited by dc magnetron sputtering on surface-oxidized silicon substrates at either RT or 300 °C after the chamber was vacuumed to less than 5×10^{-5} Pa. The working Ar pressure was 0.2 Pa except where we noted in the paper. The compositions of thin films were measured by scanning electron microscope with an energy disperse spectrum of X-ray (SEM-EDX), and calibrated by several standard samples. The structures of thin films were examined by X-ray diffraction (XRD) with $\text{CuK}\alpha$ irradiation at 40 kV and 40 mA. Transmission electron microscopy (TEM) analysis was conducted on Hitachi H800 electron microscope with an operation voltage of 200 kV. TEM foil was prepared as follows: a disc (Co-20.9 at. pct W thin film deposited at RT and 0.2 Pa) of about 3 mm in diameter was mechanically ground from the Si substrate to about 40 μm thick, further dimpled to about 5–10 μm using Gatan-Nissen dimple grinder, finally ion milled to get a hole by Gatan ion miller (Model 691).

3 Results

Since Co-rich Co- X thin films are composed of two phases in competition under the sputtering conditions in this study, that is, hexagonal closed packed (hcp) and amorphous phases, the prediction on amorphization and the amorphous composition range can be done by thermodynamic calculation through comparing the enthalpy of formation of the two structures, based on Miedema's semiempirical model^[7]. For the hcp solid solution, its enthalpy (ΔH_{SS}) is consisted of three contributions, that is^[7],

$$\Delta H_{\text{SS}} = \Delta H_{\text{SS}}^{\text{chem}} + \Delta H_{\text{SS}}^{\text{el}} + \Delta H_{\text{SS}}^{\text{str}} \approx \Delta H_{\text{SS}}^{\text{chem}} + \Delta H_{\text{SS}}^{\text{el}} \quad (1)$$

where $\Delta H_{\text{SS}}^{\text{chem}}$, $\Delta H_{\text{SS}}^{\text{el}}$, $\Delta H_{\text{SS}}^{\text{str}}$ are the chemical, elastic and structural contributions to the total enthalpy of the hcp phase. Since the structural contribution is usually considered to have a minor effect in determining the amorphous forming composition range^[8], as an approximation, this contribution is not considered in this study. For the Co- X binary alloy systems, then,

$$\Delta H_{\text{SS}}^{\text{chem}} = C_{\text{Co}}C_X(C_X^{\text{S}}\Delta H_{\text{CoinX}}^{\text{sol}} + C_{\text{Co}}^{\text{S}}\Delta H_{\text{XinCo}}^{\text{sol}}) \quad (2)$$

$$\Delta H_{\text{SS}}^{\text{el}} = C_{\text{Co}}C_X(C_X E_{\text{CoinX}} + C_{\text{Co}} E_{\text{XinCo}}) \quad (3)$$

where C_X (X =Cr, Mo, W) is the atomic fraction of elements X , and C_X^{S} is the surface fraction of which the Co and X elements are in contact^[7]. ΔH^{sol} is the enthalpy of solution, and E is the elastic mismatch energy. Both of them are tabulated in Ref.[7].

In the case of the amorphous phase, the elastic and structural contributions to the total enthalpy are avoided out. However, in addition to a chemical contribution similar as the Eq.(2) but modified by Weeber^[9], there is also a topological term $\Delta H_{\text{am}}^{\text{T}}$ due to the character of the relative disordering in an amorphous phase^[8]. Then the total enthalpy of an amorphous phase Co- X , ΔH_{am} , is given as follows,

$$\Delta H_{\text{am}} = \Delta H_{\text{am}}^{\text{chem}} + \Delta H_{\text{am}}^{\text{T}} \quad (4)$$

$$\Delta H_{\text{am}}^{\text{chem}} = C_{\text{Co}}C_X(C_{\text{Co}}^{\text{S}}\Delta H_{\text{XinCo}}^{\text{sol}} + C_X^{\text{S}}\Delta H_{\text{CoInX}}^{\text{sol}})[1 + 5(C_{\text{Co}}^{\text{S}}C_X^{\text{S}})^2] \quad (5)$$

$$\Delta H_{\text{am}}^{\text{T}} = 3.5(C_{\text{Co}}T_{\text{Co}}^{\text{m}} + C_XT_X^{\text{m}}) \quad (6)$$

where T_X^{m} is the melting point of Cr, Mo or W. The enthalpies of formation for both Co- X hcp and amorphous phases are thus constructed, as shown in Fig.1.

The calculation predicts that the transition compositions from hcp to amorphous are about 18.7 at. pct Mo and 17.1 at. pct W for the Co-Mo and Co-W alloys at RT, respectively. For the Co-Mo thin films, this prediction has been well confirmed by experiments in our recent work^[5]. In this study, a series of Co-W thin films were deposited at RT and their structures were determined, as shown in Fig.2a. The structure dependency on alloy composition is similar as that of Co-Mo thin films, and the transition composition is about

Fig.1 Formation enthalpies of the three alloy systems at RT, calculated by using Miedemas model: (a) Co-Cr, (b) Co-Mo, (c) Co-W.

Fig.2 XRD patterns of the Co-W and Co-Cr thin films (all in at. pct) deposited at RT and 0.2 Pa, where the diffraction peaks of the hcp structured Co-Cr(W), (10.0), (00.2) and (10.1) peaks are clearly observed: (a) Co-W thin films; (b) Co-Cr thin films.

19 at. pct W, which is also consistent with our calculation. In contrast, the formation enthalpy of the Co-Cr hcp phase is always lower than that of the amorphous one, suggesting that it be very hard for Co-Cr thin films to be amorphous. Indeed, amorphous Co-Cr thin films were not detected in either previous studies^[10,11] or present study, as shown in Fig.2b. In order to further confirm the amorphous structure of Co-W thin films, Co-20.9 at. pct W sample was examined by TEM, as shown in Fig.3. A typical amorphous structure was observed in bright field image, and selected area electron diffraction was further clarified that the Co-20.9 at. pct W thin film was of amorphous when it was deposited at 0.2 Pa and RT. The good agreement between the calculation and the experiments implies the amorphization of Co-X thin films has a strong relation with their formation enthalpy.

Fig.3 TEM observation of Co-20.9 at. pct W thin film deposited at 0.2 Pa and RT, showing a typical amorphous structure.

4 Discussion

Both the calculation and the experiments above show that it is easy to be amorphous for Co-Mo and Co-W thin films but hard for the Co-Cr thin films. However, it is still difficult to compare the difference in AFA between the Co-Mo and Co-W thin films since they exhibit similar amorphous forming ability from both the calculation and the deposition at RT. In this case, a series of Co-X thin films were deposited at 300 °C. The Co-Cr thin films are still of hcp structure but the Co-Mo thin films become amorphous when the transition composition is larger than about 23 at. pct Mo^[5]. For the Co-W thin films, however, no amorphous structure is detected up to about 24 at. pct, and all the films have very high diffraction intensity of the Co(00.2) peak, as shown in Fig.4a. In other words, the high substrate temperature obviously enhances the crystallization of Co-W thin films, completely different from that deposited at RT. The abnormality of non-amorphization of Co-W thin films deposited at high substrate temperatures suggests that Co-Mo thin films

Fig.4 XRD patterns of the Co-X ($X=\text{Cr, Mo, W}$) thin films deposited at 300 °C: (a) films deposited at 0.2 Pa, (b) effect of the working pressure.

have larger AFA than either Co-W or Co-Cr thin films.

In order to further clarify this point, according to our recent work that the high pressure promotes the amorphization of the Co-Mo thin films^[5], Co-22 at. pct W thin films were deposited at various pressures at 300 °C, as shown in Fig.4b. High pressure restrains the orientation of Co(10.0) and seems to enhance the orientation of Co(00.2), but fails to promote the amorphization, as compared with the amorphous Co-21 at. pct Mo thin film deposited at 1.3 Pa. In short, these experiments clearly show the AFA of Co-*X* thin films decreases in sequence: Co-Mo>Co-W>>Co-Cr.

It should be noted that Cr, Mo and W are in the VIB column and atomic size difference between *X* (*X*=Cr, Mo, W) and Co is Co-Cr (~0%)<<Co-Mo (8.8%)<Co-W (9.6%)^[12], but the Co-Mo thin films show the largest AFA among these three alloy thin films. In the previous literature of liquid quenching induced amorphization of binary alloys, the two dissimilar atoms in the liquid are combined more tightly and then it is more difficult for the atoms to move cooperatively, finally the crystallization is hindered if the effect of atomic size is dominant and this size difference is large^[13]. But in this study, the atomic size difference between Co and W is larger than that between Co and Mo^[12], while the Co-W thin films have less AFA. It would imply the atomic size difference effect is at least not the sole factor to control the amorphization of Co-*X* thin films.

Another important factor to control the amorphization is, as we discussed above, the enthalpy of formation. By the calculation in Fig.1, the formation enthalpy of the amorphous phase of the Co-Mo alloys decreases drastically with Mo content, especially for the alloy compositions higher than the transition composition. In contrast, it is not for the Co-W alloys which keep almost no change. Since the negative enthalpy of mixing is favorable to be amorphous^[3], the fact of difference in the formation enthalpy dependency of Mo(W) content may qualitatively illustrate the AFA difference between the two alloy systems, but hardly give a clear map on AFA difference among different Co-*X* alloys. In other words, the amorphous forming composition range could be predicted for a given alloy system through the enthalpy of formation dependency of composition, but it is not sufficient to compare the AFA difference among different alloy systems.

There have been several attempts to predicts AFA up to date^[4,13], among which the work by Zhang *et al.* proposed a simple empirical criterion by constructing a two-dimensional phase diagram, considering the electronegativity and electron density, rather than the enthalpy of formation, based on Miedema's model^[13]. They introduced two coordinates $Y=|\Delta\phi/\Delta n_{ws}^{1/3}|$ and $Z=|\Delta R/R_{Co}|$, where ϕ is the chemical potential (or electronegativity) and n_{ws} the electron density at the boundary of the Weinger-Seitz atomic cell^[7], R is the atomic radius for *X* or Co elements. They summarized all the published alloy systems on amorphization and found that the regions of amorphous and non-amorphous alloy systems can thus be empirically separated by one curve:

$$Y = 2.52Z^{-1/4} \quad (7)$$

According to the Miedema's model, the value of *Y* is related to the enthalpy of formation. The large *Y* value means a strong short-range interaction between the two dissimilar atoms and a stable atomic configuration of the dissimilar elements, and thus it makes hard to crystallize. The same thing happens for the effect of *Z* value, as we discussed above. They used this method to justify the AFA of different binary transition-transition

metal amorphous alloys prepared by mechanically alloying, and found the accuracy is as high as about 86%^[13].

By the same token, we constructed this phase diagram containing the three kinds of the Co-X alloy systems, as shown in Fig.5. In this figure, it can be easy to find that the $|\Delta\phi/\Delta n_{ws}^{1/3}|$ value necessary for amorphization is low if the atomic size difference is large, and vice versa. The Co-Mo and Co-W alloys locate in the amorphous region while the Co-Cr alloys in the non-amorphous region, well consistent with our experiments and also thermodynamic calculation above. But the fact that the Co-W alloys are very close to the critical curve owing to lower $|\Delta\phi/\Delta n_{ws}^{1/3}|$ implies the weaker AFA than the Co-Mo alloys which are far from the critical curve. In other words, the strongest AFA of the Co-Mo alloys are owing to the effects of both $|\Delta\phi/\Delta n_{ws}^{1/3}|$ and the atomic size difference. Accordingly, Co-Mo-base alloys would be a new kind of amorphous magnetic materials with high AFA by further appropriate alloying, but more experiments should be welcome.

5 Conclusions

The Co-W magnetic thin films with a W content larger than 19 at. pct W can be amorphous when deposited at RT, but are of hcp structure at high substrate temperatures. The Co-Cr thin films are hard to be amorphous. Among Co-X (X=Cr, Mo, W) thin films, the Co-Mo thin films have the strongest amorphous forming ability, which is clarified to be due to the contributions of the differences in electronegativity, electron density and atomic size between Co and Cr (Mo, W).

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Fig.5 Comparison in the amorphous forming ability in the three alloys systems, and it means higher amorphous forming ability for the data far from the empirical curve $Y=2.52Z^{-1/4}$. It can thus be concluded the AFA sequence in these three alloy systems is as follows: Co-Mo>Co-W>>Co-Cr, which is well consistent with the experiments in this study.