Annealing Temperature Dependence of A-C Magnetic Losses and Microhardness in Fe-TM-B (TM = Fe, Mo, W, Mo-W) Alloys Obtained by Electroless Plating

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Annealing temperature dependence of some physical properties in Fe-TM-B (where TM = Fe, Mo, W, Mo-W) alloy deposits obtained by electroless plating have been studied. The magnetic losses of Fe-Mo-B and Fe-Mo-W-B deposits depend strongly on the physical phase composition of the deposits and their content, as well as annealing temperature. The microhardness of the alloy deposits reaches peak values when the annealing temperature is 400 °C, which is relative to the crystallization process and type and number of crystallization precipitant phases.

Amorphous Fe-based alloy deposits have both strength and mechanical tenacity and excellent soft magnetic properties. After suitable heat treatment, these properties of the deposits will show further improvement. There are many reports on Ni/Co-based alloy deposits and these alloy deposits have been widely applied in many industries because of their excellent physical properties.[1-3] Reports of Fe-based alloy deposits are few compared with those for Ni/Co-based deposits. The main reason is that the electroactivity function of chemical deposition for Fe is too weak; only by adding electrodeposition function that a metal couple produces can chemical deposition function be observed. Until now, there have been only Fe-P, Fe-TM-B (where TM = Fe, Me, W) as well as Fe-containing alloy, deposit reports.[4-11] The reports of physical properties for these alloy deposits are very few. We have already described bath stability, composition dependence of some physical properties and the differential scanning calorimetry (DSC) of Fe-TM-B alloy deposits.[12-15] In the current study, the effect of annealing temperature dependence of a-c magnetic losses and microhardness in such alloy deposits was investigated.

Experimental Procedure

The Fe-TM-B (TM = Fe, Me, W, Mo-W) alloy deposits were obtained in an alkaline bath and by electroless reduction with potassium borohydride. Some basic solutions containing sodium citrate or sodium potassium tartrate as the complexing agents were determined. The results indicated that sodium potassium tartrate was the most appropriate. The composition of the solutions was fixed at 90 g/L sodium potassium tartrate, 20 g/L ferrous sulfate, 20 g/L sodium hydroxide, 40 g/L sodium molybdate and/or sodium tungstate for TM = Mo and/or W, for best bath stability. The composition was changed with varied potassium borohydride concentration. The operating temperature was controlled at 40 °C, using a water bath. The substrates used were copper and steel sheets (when studying microhardness), 1.5 x 1.5 cm. To obtain deposition, it was necessary for the copper or steel sheet to be in contact with an aluminum sheet. The composition of the samples was determined by chemical analysis. The structure of the deposits was examined by X-ray diffractometer (XRD). The isothermal annealing of the films was done in a vacuum heat treatment furnace with fixed temperature for one hr. The microhardness of the deposits was determined by horizontal metallurgical microscope. The a-c magnetic losses were measured by an a-c mutual inductance bridge.[16]

Results and Discussion

A-C Magnetic Losses

The table shows the composition and structure for the Fe-TM-B deposits. It can be seen that the formation of amorphous structure ranges from 18.0 to 27.4 at pct boron for Fe-B, from 6.6 to 30.0 at pct boron for Fe-Mo-B, and from 9.8 to 27.3 at pct boron for Fe-Mo-W-B alloy deposits. But Fe-W-B deposits do not form an amorphous structure in the composition range studied. Thus, it can be seen that molybdenum facilitates the formation of amorphous structures, but tungsten makes difficult the formation of such structures for Fe-based deposits.

To study the law of structure change and a-c magnetic losses for electroless Fe-Mo-W-B amorphous alloy deposits after heat treatment, the alloys having high glass formability were annealed at high temperature. The as-plated samples were annealed at successively higher temperatures: 300, 400, 500 and 600 °C, respectively, and kept at heat for one hr. Figure 1 indicates the changes in losses in the course of a four-step anneal conducted at successively increasing temperature for Fe-Mo-W-B alloy deposits, together with Fe-Mo-B amorphous alloy deposits.[17] It can be seen that the alloys that possess higher glass formability all have lower losses in the first two-step anneal (300 and 400 °C).

The results of XRD patterns show that atoms first incur structure relaxation, then start to appear partly crystallized.[13] The amorphous component of the deposits can still exist—α-Fe, Fe_3B and $(Mo, W)_2B$ phases appeared in Fe-Mo-W-B deposits and α-Fe and Mo_2B phases arose in Fe-Mo-B deposits,[7] but the diffraction peak for all is not strong. The higher losses occur in the last two-step anneal (500 and 600 °C). The results of XRD patterns show that full crystallization happened except that the original crystallization phases, Fe_2B, (Mo, W)B and Fe_2(MO, W) again arose in Fe-Mo-W-

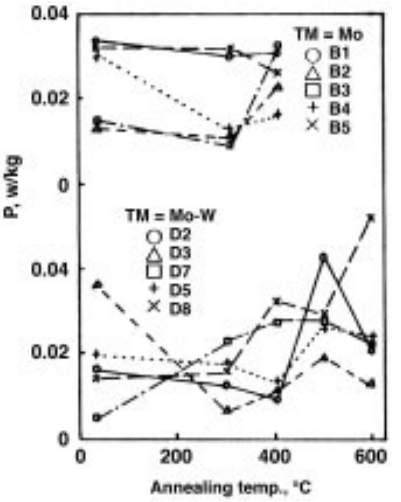

Fig. 1—A-C magnetic losses P for Fe-TM-B (TM = Mo, Mo-W) deposits vs. annealing temperature Ta.

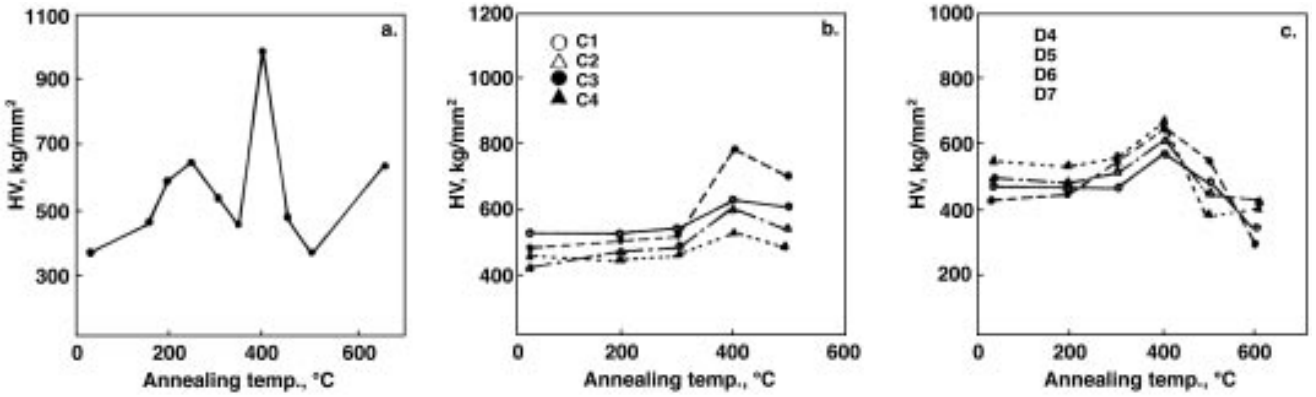

Fig. 2—Microhardness HV for Fe-TM-B (TM = Fe, W, Mo-W) deposits vs. annealing temperature Ta: (a) TM-Fe (b) TM-W (c) TM-Mo-W.

B deposits, and the Fe_3B crystallization peak appeared in Fe-Mo-B deposits. As these results indicate, a two-step process of crystallization was observed for Fe-Mo-W-B and Fe-Mo-B amorphous alloy deposits. The significant ways of decreasing magnetic losses for electroless Fe-Mo-W-B alloy deposits are, on the one hand, that the deposit conditions must be rationally controlled to obtain deposits having higher glass formability, and on the other hand, the best anneal technology must be adopted.

Microhardness

The structure changes because of structure relaxation and crystallization processes when the alloy deposits are heat treated. The microhardness of the deposits may increase further during heat treatment. Figure 2 shows the microhardness as a function of annealing temperature for electroless Fe-TM-B alloy deposits after isothermal annealing for one hr. It can be seen from (a) that the increase of microhardness is a result of structural relaxation at lower temperature for Fe-B deposits annealed below 250 °C;[5] at higher temperature, 250-350 °C, the relaxation of the internal stresses and coagulation of boride particles result in decrease of microhardness. At 400 °C, a very high microhardness appears as a result of the dispersion hardening resulting from formation of the Fe_3B phase. When the temperature is higher than 400 °C, the sample crystallizes perfectly in its equilibrium structure which removes the hardening effect resulting from the structural changes or precipitation during crystallization. The microhardness then decreases rapidly, but increases again because of forming a second precipitant α-Fe phase during annealing at 550 °C for one hr. From Figs. 2b and 2c, a law similar to that mentioned above exists for the results of Fe-W-B and Fe-Mo-W-B alloy deposits. When the temperature is lower than 300 °C, the microhardness of the deposits increases slowly or decreases slightly with increasing temperature because of structural relaxation At higher temperature, 300-400 °C, the microhardness of the deposits increases rapidly with increasing temperature and appears the greatest at 400 °C, for example, after annealing at this temperature. The microhardness of the deposits $Fe_{90.2}W_{3.5}B_{6.3}$ and $Fe_{63.7}Mo_{12.1}W_{1.3}B_{22.9}$ is 773 and 644 kg/mm², respectively. When the annealing temperature is higher than 400 °C, the microhardness of the deposits shows a tendency to decrease. In fact, the change in microhardness at different annealing temperatures is caused by the change of deposit structure. It can be seen from the X-ray patterns of Fig. 3 for $Fe_{85.6}W_{2.5}B_{11.9}$ deposits isothermally annealed for one hr that the deposits have precipitated α-Fe, W_2B (slightly) and Fe_3B phases when the annealing temperature was lower than 400 °C. It is clear that α-Fe is a strengthening phase; other substable state phases show scattered state distribution in α-Fe solid solution, which makes it obtain strength, and the microhardness rises rapidly. It can also be seen from Fig. 3 that the strength of the α-Fe peak is larger at the annealing temperature of 400 °C than at 300 and 470 °C, which means this deposit appears stronger and is identical with the results of Fig. 2. Similar results can be seen from the $Fe_{71.9}Mo_{17.7}W_{0.6}B_{9.8}$ deposit X-ray pattern in Fig. 4. The results are similar to those reported by Zhang[18] and Liu.[19] Thus, it can be seen that the crystallization law of these alloy systems shows little difference, so that the effect of alloying on crystallization is not obvious, which causes basically similar change in microhardness vs. annealing temperature in the coating. It is identical with Fe-Si-B and Fe-W-Si-B alloys obtained by rapid quenching.[20]

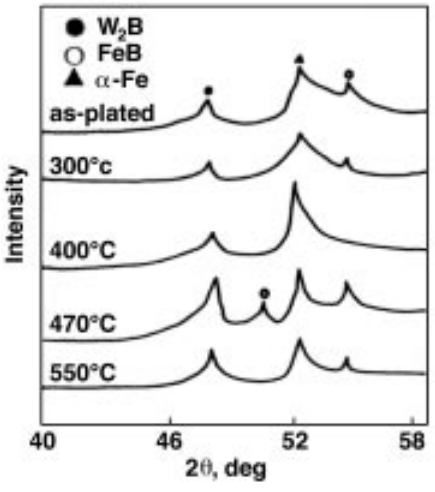

Fig. 3—XRD patterns for as-plated and annealed $Fe_{85.6}W_{2.5}B_{11.9}$ specimens at 300, 400, 470 and 550 °C, respectively, for on hr.

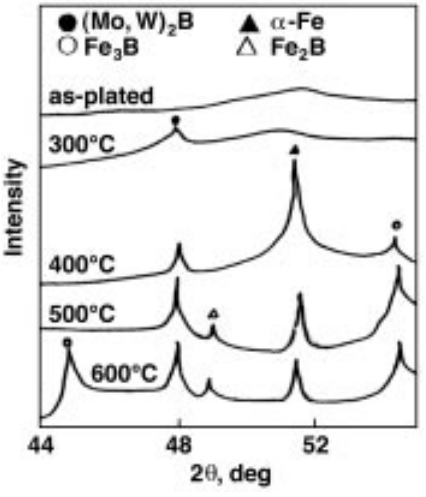

Fig. 4—XRD patterns for as-plated and annealed $Fe_{71.9}Mo_{17.7}W_{0.6}B_{9.8}$ specimens at 300, 400, 500 and 600 °C, respectively, for one hr.

Conclusions

1. The magnetic losses of Fe-Mo-W-B and Fe-Mo-B deposits depend strongly on the physical phase composition of

Composition & Structure for Fe-TM-B Deposits

Fe-B	**A1**	**A2**	**A3**	**A4**	**A5**
KBH_4,	1	3	8	15	20
B, at pct	2.2	10.6	18	24.0	27.4
Structure*	C	C	A	A	A

Fe-Mo-B	**B1**	**B2**	**B3**	**B4**	**B5**
KBH_4, g/L	2	6	10	15	20
B, at pct	6.4	10.1	14.9	23.3	30.0
Mo, at pct	18.9	16.3	14.0	13.3	11.3
Structure	A+C	A	A	A	A

Fe-W-B	**C1**	**C2**	**C3**	**C4**	**C5**
KBH_4 g/L	4	8	12	16	20
B, at pct	2.0	4.3	6.3	11.9	12.7
W, at pct	4.3	3.6	3.5	2.5	1.4
Structure	C	C	C	C	C

Fe-Mo-W-B	**D1**	**D2**	**D3**	**D4**	**D5**	**D6**	**D7**	**D8**	**D9**
KBH_4, g/L	2	6	8	9	10	11	12	15	20
B, at pct	8.8	9.8	12.5	17.7	21.6	22.2	22.9	27.3	28.3
Mo. at pct	16.7	17.7	13.5	12.8	18.2	15.2	12.1	10.0	13.5
W. at pct	0.6	0.6	0.7	1.0	1.3	1.3	1.3	Trace	Trace
Structure	C	A	A	A	A	A	A	A	C

* A-amorphous, C-crystalline

the deposits and its content, as well as the annealing temperature.

2. When the annealing temperature is lower than 300 °C, the microhardness of the deposits decreases slightly with slowly increasing temperature; in the range of 300 to 400 °C, the microhardness of the deposits increases rapidly with increasing temperature and exhibits a very high value at 400 °C. When the temperature is higher than 400 °C, the microhardness drops rapidly with increasing temperature.

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