

Effects of Mn and Ni Addition on High Frequency Magnetic Properties of Fe-based Amorphous Alloys

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The influence of Mn and Ni addition on high frequency magnetic properties of Fe-based amorphous alloys was investigated. The coercivity H_c decreases and the permeability μ' increases dramatically by adding Mn, but the effect on magnetic losses is not obvious. The magnetic loss is discussed in terms of hysteresis, eddy current, and anomalous loss. It was also found that the resistance to oxidation for FeMnSiB alloys is much higher than that of Fe-based alloys without Mn. Thus excellent soft magnetic properties can be obtained through annealing without protective gas, which is of significance to industrial production.

1. Introduction.

To improve soft magnetic properties of Fe-Si-B system amorphous alloys, several investigations on the effect of the addition of other elements have been reported. Of these, the addition of Mn appeared to be interest for their anti-ferromagnetic interactions and improvement of some magnetic properties.

A detailed study on amorphous $Fe_{73.7}Mn_{2.3}Si_{14}B_{10}$ alloy was firstly reported in 1981 (1) and then alloys of $Fe_{82-x}Mn_xSi_5B_{13}$ series were investigated in 1977, the result of which indicates that the H_c and high frequency magnetic losses may be reduced by adding Mn element (2).

A much more exciting result was given by S. Murakami and H. Okumura in 1989 (3) presenting the effective permeability ($f=1kHz$) up to 1.5×10^4 and the magnetic loss ($f=100kHz$, $B=0.3T$) about 1/5 that of FeSiB series alloys by adding Mn into Fe-based alloys. Meanwhile, another conclusion was drawn from our work in 1989 that after proper heat treatment excellent soft magnetic properties such as high remanence B_r and low losses could be obtained in alloys containing Mn and Ni (4).

In order to further our study on Mn containing alloys systematically, three series of Fe-based alloys with varied Mn contents as well as small amounts of Ni were investigated in regard to high frequency magnetic properties.

2. Experimentals

The compositions of the amorphous alloys presented are listed in Table 1 which were confirmed by chemical analysis.

Samples studied here were liquid-quenched by single roller technique and then annealed at temperatures, ranging from 400°C to 480°C at intervals of 20°C for 1 hour. The AC magnetic properties were measured by means of B-H Analyser under the condition of sin B, and DC properties by a B-H Curve Tracer. The saturation magnetization σ_s , the curie temperature T_c and the crystallization temperature T_x were

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determined from the σ_s -temperature curve measured with a Vibrating Sample Magnetometer. The electric resistivity was determined by conventional 4 terminals method. The X-ray diffraction measurements of certain samples were performed to confirm the amorphous state.

Table1 : Composition of FeMnSiB amorphous alloys in present study (at%)

No.	Fe	Mn	Si	B	Ni
1#	78	0	12	10	0
2#	75.5	2.5	12	10	0
3#	75	3	12	10	0
4#	74.5	3.5	12	10	0
5#	73	5	12	10	0
6#	81	0	8	11	0
8#	75	6	8	11	0
9#	73.5	7.5	8	11	0
10#	73	8	8	11	0
11#	75	2	8	11	4
12#	75	4	8	11	2
13#	75	4.5	8	11	1.5

3. Results and Discussion

(1) Effects of composition on magnetic properties

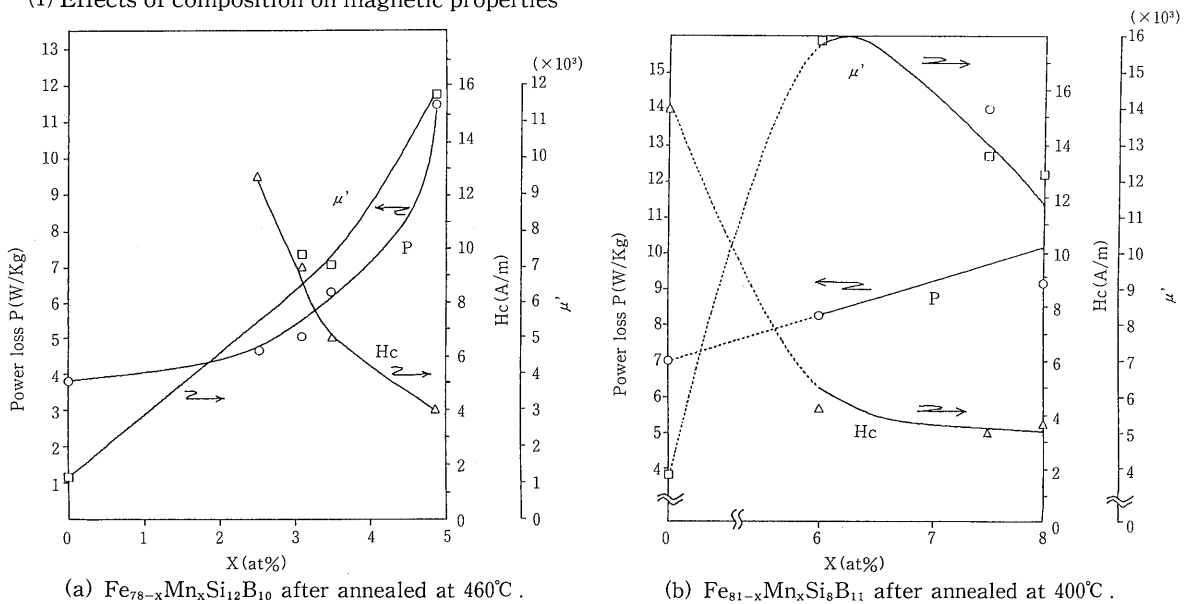


Fig.1 Variation of magnetic losses (0.1T, 50kHz), μ' and H_c of annealed FeMnSiB system alloys with Mn content.

Fig.1 shows the composition dependence of magnetic properties annealed at optimum temperature for first (1-5#) and second (6-10#) series of amorphous alloys, respectively. Both the permeability μ' at 1kHz with a driving field of 0.8A/m and the magnetic losses at 50kHz and 0.1T under the magnetizing condition of $\sin B$ were measured. From these figures, it is evident that by adding Mn H_c decreases and μ' increases significantly due to the decrease of λ_s as was studied by S. Murakami(3). However, there appears to be no obvious effect of Mn addition on magnetic losses, which will be discussed later. Moreover, it can be seen

from Fig. 1 that the lower magnetic losses were obtained in the first group of alloys (1-5#) with the Si+B content of 22at%. The lowest value is 3.61w/kg for $\text{Fe}_{74.5}\text{Mn}_{3.5}\text{Si}_{12}\text{B}_{10}$ which is much lower than that of ordinary Fe-Si-B alloys and high μ' was obtained for $\text{Fe}_{75}\text{Mn}_3\text{Si}_{12}\text{B}_{10}$ as shown in Fig. 1. It suggests that the amount of Si+B plays an important role in reducing the high frequency magnetic losses.

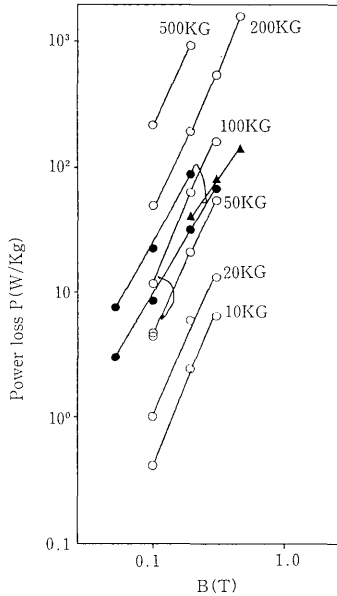


Fig. 2 Frequence dependence of magnetic losses at 0.1~0.3T for $\text{Fe}_{74.5}\text{Mn}_{3.5}\text{Si}_{12}\text{B}_{10}$ (○), and of Metglas 2605S (●), (from the Catalogue of Allied Corp.) and Finemet (5)(▲)

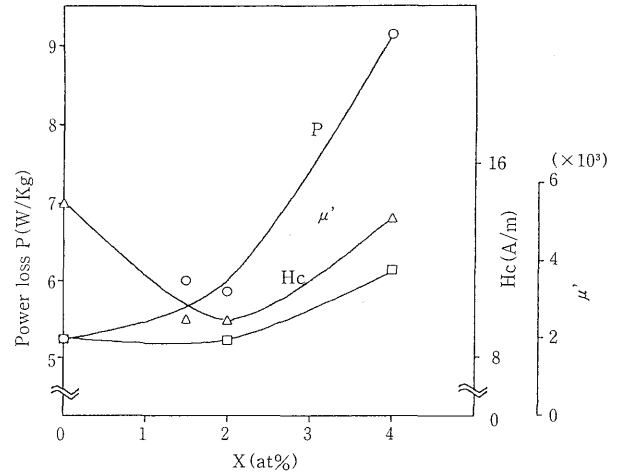


Fig. 3 Variation of the magnetic losses (0.1T, 50 kHz), μ' and H_c of $\text{Fe}_{75}\text{Mn}_{8-x}\text{Ni}_x\text{Si}_8\text{B}_{11}$ alloys with Ni content after annealing at 440°C

Fig.2 presents the frequency dependence of magnetic losses for $\text{Fe}_{74.5}\text{Mn}_{3.5}\text{Si}_{12}\text{B}_{10}$ and the data for Metglas 2605S3, 2605SM as well as Finemet for comparison. It is known that the loss of FeMnSiB alloys is lower than that of 2605SM, 2605S3 and close to that of Finemet though μ' is not so high as for the latter. Nevertheless, from the view of their lower cost and simple annealing procedure without protective gas, the FeMnSiB alloys can be selected as the candidate for high frequency uses on an industrial scale.

Based on our previous work and the fact that Mn often exists with Ni as raw material, the influence of Ni addition on magnetic properties was also investigated. Fig. 3 gives the variation of magnetic properties as a function of Ni content for the third group of alloys (8, 13, 12, 11#). It seems that there is no obvious effect on high frequency properties by adding Ni.

The optimum magnetic properties of alloys studied are summarized in Table 2.

Table2 : Opimum magnetic properties of certain Fe-Mn-Si-B system alloys

item No.	composition (at%)	μ' ($\times 10^4$)	P (W/Kg)	B_{10} (T)	σ_s (emu/g)	T_c (°C)	T_x (°C)
3#	$\text{Fe}_{7.5}\text{Mn}_3\text{Si}_{12}\text{B}_{10}$	0.73	4.91	1.29	160	363	535
4#	$\text{Fe}_{74.5}\text{Mn}_{3.5}\text{Si}_{12}\text{B}_{10}$	0.26	3.61	1.25	159	351	550
8#	$\text{Fe}_{7.5}\text{Mn}_6\text{Si}_8\text{B}_{11}$	1.59	8.16	1.07	130	230	495

(2) Discussion on magnetic losses

The experimental results show that even for alloy without Mn (1 #) the magnetic losses are also very low, which seems to be contrary to previous results(1)(2)(3). It is well known that the magnetic losses can usually be divided into three parts, i.e hysteresis loss, eddy current loss and anomalous loss. So, the losses of FeMnSiB amorphous alloys presented here are discussed as below in regard to these three parts of losses.

a. Hysteresis loss

Our previous work presented that Mn addition has the effect of reducing low frequency magnetic losses owing to the decrease of H_c (4) while the hysteresis loss is the dominant part in low frequency losses. Besides, Fig. 4 gives the comparison between DC. B-H loop and 50kHz AC. B-H loop for alloys 1-5#. Obviously, the Mn addition can reduce the hysteresis loss which is proportional to the area of the B-H loop but not the total high frequency magnetic losses.

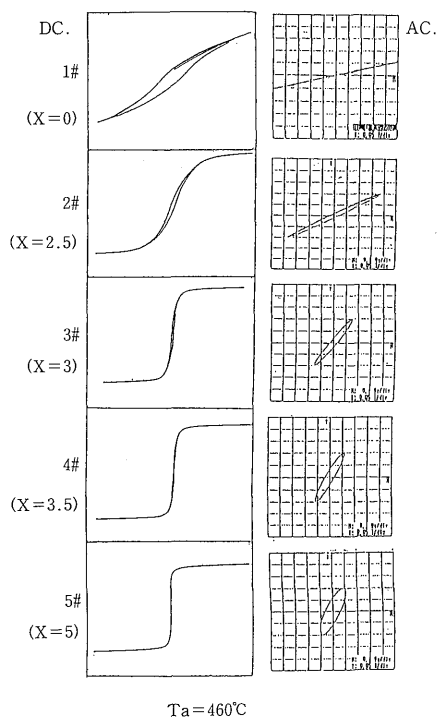


Fig. 4 Comparison between DC. B-H loop and AC. B-H loop for $\text{Fe}_{78-x}\text{Mn}_x\text{Si}_{12}\text{B}_{10}$ after annealed at 460°C

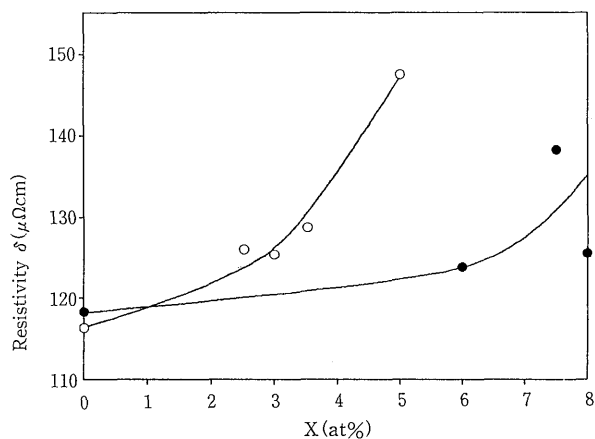


Fig. 5 Dependence of resistivity on Mn content for $\text{Fe}_{78-x}\text{Mn}_x\text{Si}_{12}\text{B}_{10}$ (○) and $\text{Fe}_{81-x}\text{Mn}_x\text{Si}_8\text{B}_{11}$ (●).

b. Eddy current loss

It is well known that the eddy current loss is nearly in inverse proportion to the resistivity of the alloys. Fig. 5 shows the dependence of resistivity on Mn content for $\text{Fe}_{78-x}\text{Mn}_x\text{Si}_{12}\text{B}_{10}$ and $\text{Fe}_{81-x}\text{Mn}_x\text{Si}_8\text{B}_{11}$, which suggests that resistivity increases with the Mn content. Therefore this part of loss should be reduced by adding Mn.

c. Anomalous loss

From experimental measurements it has been shown(6) that the anomalous loss is responsible for 90-99 per cent of the total magnetic loss of amorphous materials at higher frequencies. In general, there are mainly two approaches in improving the high frequency magnetic losses of Fe-based amorphous alloys. (1) A few of alloy elements are added into the alloys to decrease the magnetostriction λ_s , (2) The heat treatment at certain temperature was used to control the degree of partial crystallization(7).

In order to make clear which factor is dominant in anomalous loss at high frequencies, the structure of the samples was detected by X-ray diffraction. Fig. 6 shows the X-ray diffraction patterns for $\text{Fe}_{78-x}\text{Mn}_x\text{Si}_{12}\text{B}_{10}$ after annealed at 460°C alloys. Obviously, the initiation of crystallization appears in only $\text{Fe}_{78}\text{Si}_{12}\text{B}_{10}$ alloy after annealing.

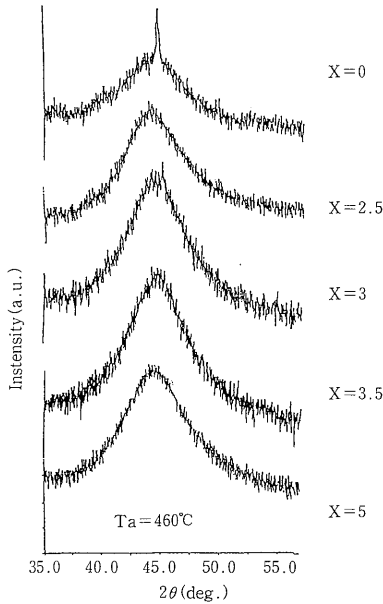


Fig. 6 X-ray diffraction patterns for $\text{Fe}_{78-x}\text{Mn}_x\text{Si}_{12}\text{B}_{10}$ after annealed at 460°C .

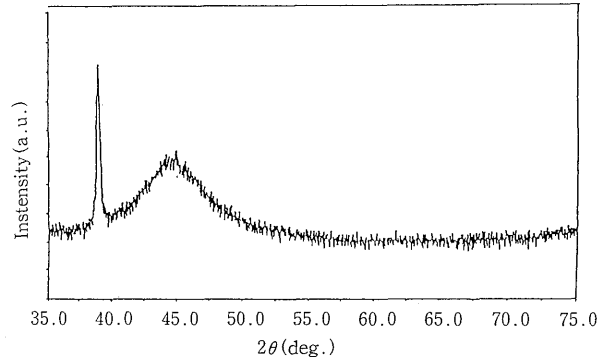


Fig. 7 X-ray diffraction pattern for $\text{Fe}_{74.5}\text{Mn}_{3.5}\text{Si}_{12}\text{B}_{10}$ alloys after annealed at 480°C .

Upon annealing, quenched-in non-uniform distributed stress can be largely eliminated. For alloy containing Mn with small λ s, the magnetostrictive-strain interaction anisotropy, and phase shift between the magnetic excitation and the resultant magnetization in the material will be decreased as the λ s decreases (8), and thus the anomalous loss should be lower as the Mn is added.

But on the other hand, as the annealing temperature increases further, the precipitation of crystalline particles will greatly affects the high frequency magnetic losses through domain refinement. In our study, after annealed at 460°C , $\text{Fe}_{78}\text{Si}_{12}\text{B}_{10}$ alloy shows the crystallized peak in X-ray diffraction pattern and much lower loss value compared with the one before crystallization while others are still in amorphous state. In addition, considering that lower losses are obtained in the first group of alloys with the Si+B amount of 22 at%, we can suppose that Si and B contents play an important role in controlling the degree of partial crystallization.

The magnetic loss for $\text{Fe}_{73.5}\text{Mn}_{3.5}\text{Si}_{12}\text{B}_{10}$ becomes very low after 480°C annealing, but the crystallization occurs as it was confirmed by X-ray diffraction (Fig. 7). So, μ' may decrease due to the influence of magnetocrystalline anisotropy as microcrystalline appears in the alloy. Consequently, by selecting appropriate composition and annealing temperature, we can either make a compromise for both relative low loss and high μ' or get some preferential magnetic properties for special uses.

(3) Results of VSM measurement

Fig. 8 shows T_c and T_x as well as σ_s of the alloys as a function of Mn content. It can be seen that the addition of Mn can increase T_x and reduce T_c so that μ' can be increased. The saturation magnetization σ_s decreases as the Mn content increases, which is in agreement with previous report (3).

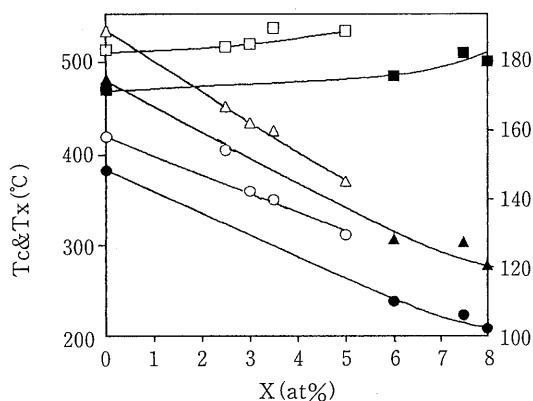


Fig. 8 T_c , T_x and σ_s vs. Mn content for $Fe_{78-x}Mn_xSi_{12}B_{10}$ (open symbol) and $Fe_{81-x}Mn_xSi_8B_{11}$ alloys (closed symbol).

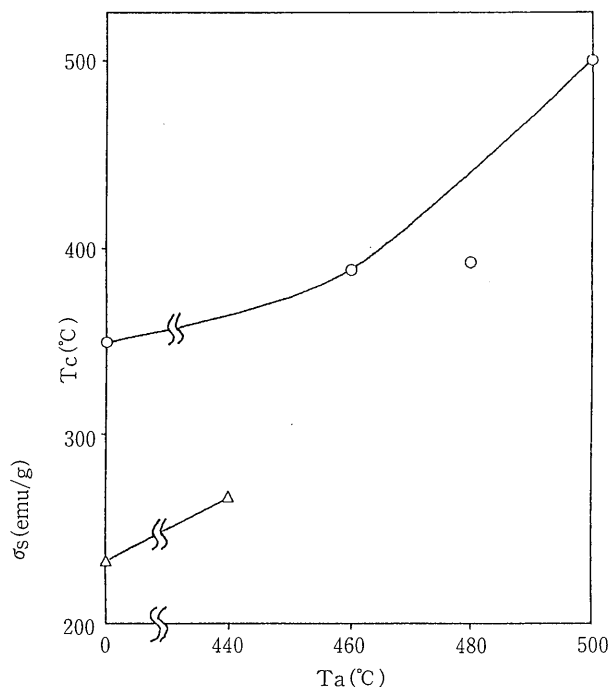


Fig. 9 Variations of T_c with annealing temperature T_a (°C) for $Fe_{74.5}Mn_{3.5}Si_{12}B_{10}$ alloys ($\circ$) and $Fe_{75}Mn_6Si_8B_{11}$ ($\triangle$).

It can be seen from Fig. 9 T_c increases with increasing the annealing temperature. This suggests that during annealing the exchange effect gets stronger due to atom rearrangement and finally T_c approaches to the value for corresponding crystalline counterpart. This phenomena implies that the ultimate result of relaxation is to reach the state of crystallization.

(4) High resistance to oxidation of FeMnSiB system alloys.

Another feature for FeMnSiB system alloys is their high resistance to oxidation. After annealed at 430°C for 1 hr in the absence of any protective gas, the FeMnSiB alloy, metglas 2605S2 and 2605SC were compared with each other in three aspects.

Firstly, in regard to color of the ribbon, the oxidation is most serious for 2605SC, the color of which is blue and black and then is the 2605S2, golden yellow, while FeMnSiB alloy presents the bright lustre as well as in cast state.

Secondly, in order to determine the extent of oxidation quantitatively, the surface oxygen content analysis was made on three kinds of alloys by a Auger Scanning Microprobe. The curve of oxygen content vs. sputtering time for Metglas 2605SC, and Metglas 2605S2 is shown in Fig. 10 (a), and that for $Fe_{75}Mn_6Si_8B_{11}$ alloy (5#) after annealing without protective gas and within protective gas for comparison is shown in Fig. 10 (b), respectively. It is obvious from the figure, that the more extent of oxidation is most serious for Metglas 2605SC; then is for 2605S2 and slight for 5# alloy containing Mn. The results of comparing two kinds of annealing conditions show that for 5# alloy the extent of oxidation is slight at 430°C no matter whether the protective gas was applied or not. The Auger data presented here are also in fair accordance with the results of surface color comparison.

Finally, the magnetic properties of alloys annealed with or without protective gas at 400°C for 2605S2 and 430°C for 5# alloy are summarized in Table 3. For 2605S2, after annealing without protective gas at 400°C, the coercivity H_c and the magnetic loss increase by nearly 100% compared with the one annealed with

protective gas. While for FeMnSiB alloy 5#, the results are almost the same no matter whether the protective gas was applied or not during annealing.

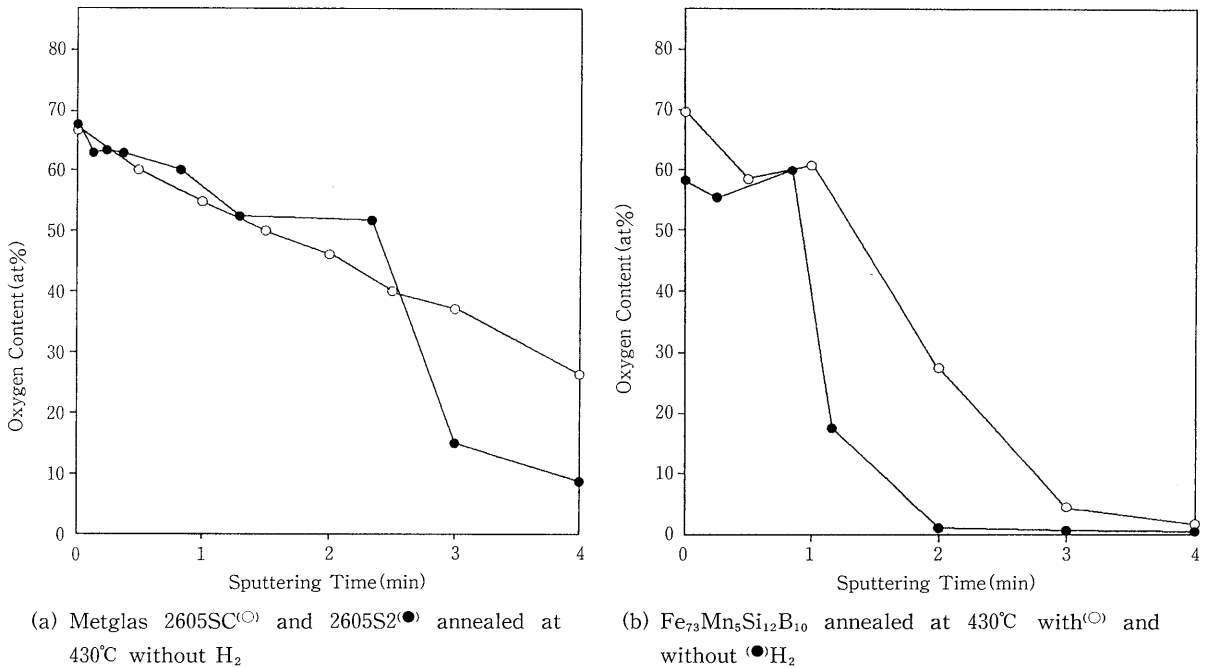


Fig.10 Variation of oxygen content for amorphous Fe-based ribbons

Table3 : Property Comparison for Fe₇₃Mn₅Si₁₂B₁₀ (5#) and 2605S2 heat-treated under different annealing conditions

No.	Annealing condition	B ₁₀ (T)	Br (T)	H _c (Oe)	μ_m ($\times 10^4$)	P _{1.0/60} (W/Kg)	P _{1.0/400} (W/Kg)	P _{0.8/8K} (W/Kg)
5 #	430°C with H ₂	1.27	1.01	0.031	18	0.087	1.5	40
	430°C without H ₂	1.28	1.0	0.028	23	0.07	1.2	32
2605S2	400°C with H ₂			0.036		0.1		
	400°C without H ₂			0.08		0.19		

4. Conclusion

The following conclusion can be drawn through above discussion.

- 1) The H_c can be reduced and μ' can increase a great deal with adding Mn element.
- 2) Although the addition of Mn has the effect on reducing high frequency magnetic losses, the loss is also affected to a large extent by partial crystallization. The proper degree of crystallization depends mainly on Si and B contents, and appropriate annealing temperature and time.
- 3) There is no obvious effect of Ni addition on high frequency magnetic properties for alloys with the Si+B amount being 7+12.
- 4) The resistance to oxidation of FeMnSyB alloys is much higher than that of Fe-based alloys without Mn.

Excellent soft magnetic properties can be obtained through annealing without protective gas.

5) Three kinds of alloys with excellent high frequency magnetic properties were obtained through our research, the data of which are summarized in Table 2.

5. Acknowledgement

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