저자장에서 비정질 후막(Sm$_{1-x}$Pr$_x$)Fe$_2$의 자성

김 재 영

삼성 종합 기술원, 미래 기술실 수원 우체국 사서함 111호

Magnetism of Amorphous Bulk (Sm$_{1-x}$Pr$_x$)Fe$_2$ Alloys in a Low Magnetic Field

Jai-Young Kim

Technology Strategy Research Center, Sam-Sung Advanced Institufe of Technology

초   록 RFe$_2$(R=rare earth) Laves상 금속간 화합물은 10^{-3} 정도의 큰 포화 자왜 정수를 나타내고 있어, 자왜 재료의 응용 분야에서 많은 주목을 받고 있다. 그러나, 이 금속간 화합물은 결정 자기 이 방성 에너지가 크기 때문에, 큰 포화 자왜 정수를 얻기 위해서는 높은 외부 자장이 요구되어진다. 이 에 따라 저자장에서 보다 높은 자왜 정수를 얻고자 하는 연구들이 행하여 지고 있는데, 이를 위한 방 법은 RFe$_2$ Laves상 금속간 화합물중 결정 자기 이방성 부호가 각기 다른 회토류 금속의 치환 혹은 RFe$_2$ 금속간 화합물의 비정질화이다. 본 연구에서는 RFe$_2$ 금속간 화합물의 자기 이방성 에너지를 최 소화하여 저자장에서 높은 자왜 정수를 얻기 위해, 결정 자기 이방성 정수 및 자왜 정수의 부호가 각 각 반대인 SmFe$_2$와 PrFe$_2$을 합금화 한후, 비정질화하여 자왜 정수의 변화를 포함한 자성을 조사하였다.

Abstract RFe$_2$(R=rare earth) Laves Phase intermetallic compounds are one of the promising materials for magnetostrictive applications, due to large magnetostriction coefficients in the order of 10^{-3}. However, because RFe$_2$ intermetallic compounds have large magnetostriction constants as well as large magnetocrystalline anisotropy constants, a large external magnetic field is necessary to reach saturation magnetostriction. Hence researches on giant magnetostriction have been concentrated on producing materials exhibiting a high value of magnetostriction in a low magentic field. The main research trend of the giant magnetostriction to obtain the large value in the low magnetic filed, fortunately as the signs of magnetocrystalline anisotropy constans in RFe$_2$ intermetallic compounds alternate with the rare earth metals, has been to substitute the rare earth metal for others and hence to reduce the magnetocrystalline anisotropy energy. In addition, amorphous RFe$_2$ alloys have been researched. In this research, both of the methods which are substitution of the rare earth metal and amorphization in RFe$_2$ intermetallic compounds are simultaneously conducted to obtain the large magnetostriction coefficient in the low external magnetic field. Among them, SmFe$_2$ and PrFe$_2$ are selected, and amorphized in substrate-free bulk state. Magnetism in amorphous bulk (Sm$_{1-x}$Pr$_x$) Fe$_2$ alloys is investigated in the low magnetic field.

1. Introduction

It is well known that RFe$_2$(R=rare earth metal) Laves phase intermetallic compounds display giant magnetostriction at room temperature[1]. These intermetallic compounds are one of the promising materials for magnetostrictive applications, as already pointed out by A. E. Clark[2]. However, because RFe$_2$ intermetallic compounds have large magnetostriction constants as well as large magnetocrystalline constants, a large exciting magnetic field is necessary to reach saturation magnetostriction[3,4]. Hence researches on giant magnetostriction have concentrated on producing materials exhibiting a high value of magnetostriction in a low magnetic field[5,6,7]. The main research trend of the giant magnetostriction to obtain the large value in the low magnetic field has been to substitute the rare earth metal for oth-

ers in the intermetallic compounds and hence reduce the magnetocrystalline anisotropy energy in the crystalline state[8, 9]. Furthermore, the researches on amorphous REe_2 alloys which can theoretically eliminate the magnetocrystalline anisotropy have also been conducted[10, 11]

In the present work, the magnetism of the amorphous RFe_2 alloys has been investigated in more detail. Among RFe_2 intermetallic compounds, two have been selected ; $SmFe_2$ which shows a high ratio of negative magnetostriction constant to magnetocrystalline anisotropy constant and $PrFe_2$ which is not readily synthesized in the crystalline state[2] have been selected for the present research. A high rate sputtering method was adapted to prepare the substrate-free amorphous bulk alloys[12]. The substrate-free bulk samples can provide the intrinsic magnetic properties of the amorphous RFe_2 alloys.

2. Experiments

Alloy targets were prepared by arc melting in an Ar gas atmosphere. Amorphous bulk specimens of $(Sm_{1-x}Pr_x)$ Fe_2 alloys in the form of a disk with 15mm diameter and 0.3mm thickness were deposited on Cu substrates in the Ar pressure of 4×10^{-2} Torr, using a high rate DC -triode sputtering apparatus[12]. The Cu substrates were then dissolved by a mixture of chromium troixide and sulfuric acid solution at 350K for 24hours to obtain as-deposited substrate-free specimens.

The as-deposited specimens were examined by X-ray diffraction (XRD) using Fe $K\alpha$ radiation at room temperature to confirm their amorphous states. Measurements of Curie (T_C) and crystallization (T_X) temperatures were carried out by means of a magnetic balance under a heating rate of 10℃/min. and the magnetic field of 5kOe. Magnetization parallel to the samples'planes and magnetostriction (λ II $-\lambda$ I) curves were measured at room temperature using a vibrating sample magnetome-
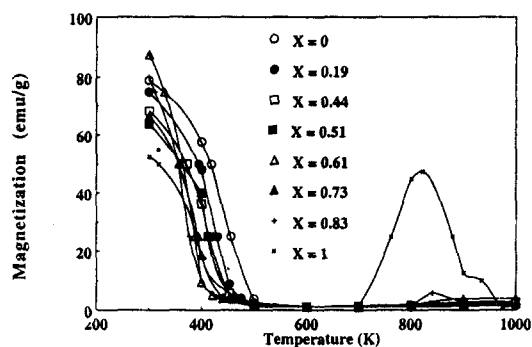

Fig. 1. Change of magnetization with respect to temperature in heat-treated amorphous $(Sm_{1-x}Pr_x)Fe_2$ alloys

ter (VSM) and a conventional strain gauge method with a precision of 10^{-6}, respectively. λ II and λ I denote the magnetostriction coefficients parallel and perpendicular, respectively to a magnetic field.

Heat treatment was performed in order to release the internal stress and to homogenize the amorphous states in the amorphous $(Sm_{1-x}Pr_x)Fe_2$ alloys, at 523K for 3hours in 2×10^{-6} Torr. After the heat treatment, the amorphous states of specimens were also confirmed by XRD.

3. Results and discussion

As-deposited and heat-treated amorphous $(Sm_{1-x}Pr_x)Fe_2$ alloys were confirmed their crystallographic states by means of XRD at room temperature. Their diffracted patterns by XRD showed broad peaks to prove amorphous states in the $(Sm_{1-x}Pr_x)$ Fe_2 alloys.

Fig. 1 shows the changes of magnetization under the magnetic field of 5 kOe with respect to temperature in the amorphous $(Sm_{1-x}Pr_x)$ Fe_2 alloys after heat treatment. On the figure, the magnetization of the amorphous alloys decreases with the increase of the temperature and disappears above 400K. These zero magnetization temperatures are defined as Curie temperature (T_C)[13] of the heat-treated amorphous alloys. When the temperature is further increased, the magnetization appears again around 700K. The appearance of the magneti-
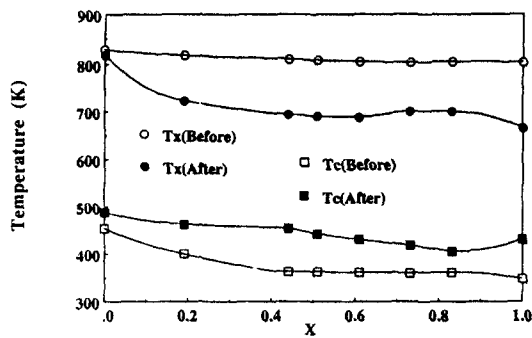
Fig. 2. Curie(Tc) and crystallization. (Tx) temperatures of amorphous (Sm₁₋ₓPrₓ)Fe₂ alloys before and after heat treatment with respect to the fraction of the Pr component
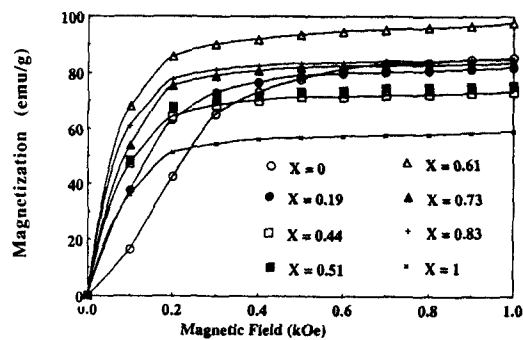

Fig. 3. Room temperature magnetization curves of heat-treated amorphous (Sm₁₋ₓ Prₓ)Fe₂ alloys in a low magnetic field

zation is caused by the formation of crystalline state in the amorphous matrix, and the temperatures at which it occurs are defined to be crystallization temperatures (Tx) of the amorphous alloys[14].

Tc and Tx of the amorphous (Sm₁₋ₓ Prₓ)Fe₂ alloys before and after heat treatment are plotted with respect to the fraction of Pr in Fig. 2. Tc and Tx of the amorphous alloys increase and decrease, respectively after the heat treatment. It is deduced that the amorphous alloys acquire thermal energy by the heat treatment and convert to structure-relaxed amorphous states. Since the structure-relaxed amorphous states are close to a crystalline states of low free energy, they display lower Tx and higher Tc than those of as-deposited amorphous

states.

Room temperature magnetization curves of the heat-treated amorphous (Sm₁₋ₓ Prₓ)Fe₂ alloys in a low magnetic field are illustrated on Fig. 3. These curves are the first parts of the hysteresis loops so that the magnetic fields are only increasing. Slopes of the curves on the figure increase with increasing substitution of Pr until X=0.61, but decrease with further increasing the substitution of Pr, except for X= 0.83. Since slope of the magnetization curve is expressed by susceptibility in magnetization process which is inversely proportional to magnetic anisotropy energy (K$_M$)[15], the changes in the slopes represent those in K$_M$ of the amorphous alloys. As Sm atoms are substituted for Pr atoms, K$_M$ in Sm-rich and Pr-rich regions of the amorphous alloys is decreased and increased, respectively. Because magnetocrystalline anisotropy energy (K$_{MC}$) is theoretically eliminated in amorphous state[10,11], magnetoelastic anisotropy energy (K$_{ME}$) is predominant factor in K$_M$ under the condition of unchanged magnetostatic energy (K$_{MS}$) and expressed as follows,

$$K_{ME} = -\frac{3}{2}(\lambda II - \lambda I)\sigma \qquad (1)$$

K$_{ME}$: magnetoelastic anisotropy energy
($\lambda II - \lambda I$) : Magnetostriction coefficient
σ : Stress state

Since K$_{ME}$ is the product of magnetostriction and stress in the amorphous alloys, it is necessary to understand variation of the manetostriction in terms of Pr atoms substitution. As Sm atoms are substituted for Pr atoms in the amorphous alloys, magnetostriction coefficients are decreased in negative sign of Sm rich region until X=0.61, converted at the minimum value of X=0.61 and increased in positive sign of Pr rich region, which will be verified on Fig. 8. Under the base of change in the magnetostriction coefficient, K$_{ME}$ in the amorphous alloys decreases until X=0.61 and then increase with the further increase of Pr
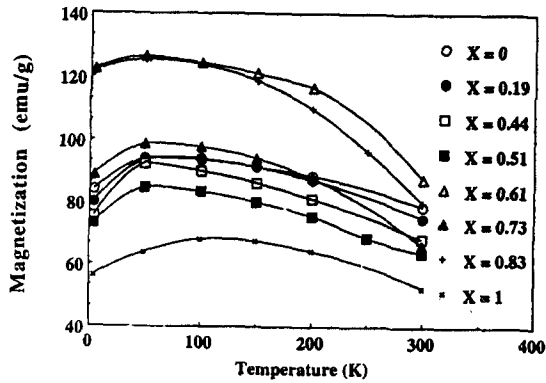
Fig. 4. Variation of magnetization in heat-treated amorphous (Sm₁₋ₓ Prₓ)Fe₂ alloys from 4.2K to room temperature
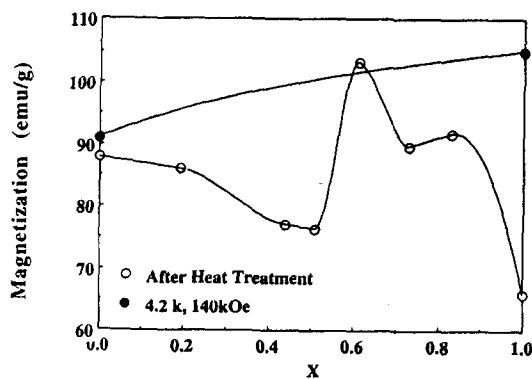

Fig. 5. Dependence of the magnetization on substitution of Pr in heat-treated amorphous (Sm₁₋ₓ Prₓ)Fe₂ alloys.

substitution. The changes of K_M originated by the those of K_{ME} also decrease and increase as the magnetostriction coefficients are negative in Sm rich region and positive in Pr rich region, respectively. This leads to the increase and decrease of the slopes of the curves in Smrich and Pr rich regions, respectively. Comparison of K_{ME} between SmFe₂ and PrFe₂ alloys, the former and the latter have the preferential direction parallel and perpendicular to the smaple's plane. This leads to the fact that the amorphous PrFe₂ with the positive magnetostriction is harder to be magnetized parallel to the sample's plane than the amorphous SmFe₂ with the negative magnetostriction. When SmFe₂ which has a negative K_{MC} is sub-

stituted by PrFe₂ which has a positive K_{MC}, the localized K_{MC} in the short range order[16] of the amorphous(Sm₁₋ₓPrₓ)Fe₂ alloys would compensate each other at X=0.83. The minimum K_{MC} which reduces K_M results in the increase of the slope at X=0.83 in the amorphous alloys.

Variations of magnetization in the heat-treated amorphous (Sm₁₋ₓPrₓ)Fe₂ alloys from liquid helium temperature (4.2K) to room temperature are shown on Fig. 4. The magnetization was measured at 5kOe, which was not sufficient to reach the saturation magnetization at the low temperature. In the low temperature range, the magnetization of X=0.61 and X=0.83 is quite large but that of X=1 is comparatively small. Under the consideration of unsaturated states in the low temperature, K_M of the amorphous alloys is small and large at X=0.61 and X=0.83, and X=1, respectively. The reductions of the magnetic anisotropy energy at X=0.61 and X=0.83 is originated by the reduction of K_{ME} and K_{MC}, respectively in short range order of the amorphous state, which is well coincided with result of the slopes in the curves on Fig. 3. The preferential perpendicular magnetic anisotropy at X=1 displays the smallest magnetization under the magnetic field of 5kOe.

Dependence of the magnetization of the heat-treated amorphous (Sm₁₋ₓPrₓ)Fe₂ alloys on the amount of Pr substitution measured at room temperature and 16kOe is shown in Fig. 5. The magnetization of the amorphous Sm Fe₂[17] and PrFe₂[18] obtained at 4.2K and 140kOe is also indicated by the closed circles. Since the amorphous SmFe₂ and PrFe₂ alloys are ferri[19] and ferro[17] magnetism, respectively, the magnetization of the former is smaller than that of the latter. The magnetization of the amorphous SmFe₂ measured at 16kOe is close to that obtained at 4.2K and 140kOe, but the magnetization of the amorphous PrFe₂ measured at 16kOe is much lower than that obtained at 4.2K and 140kOe. This means that
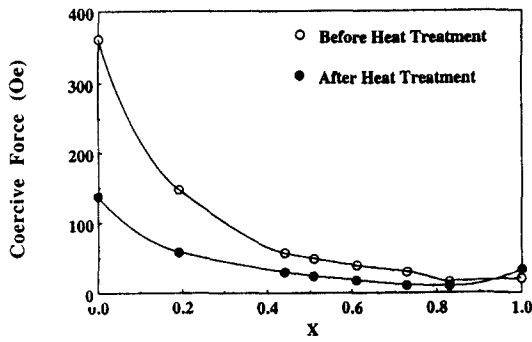
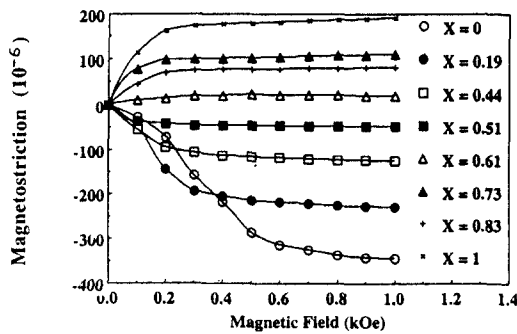Fig. 6. Coercive force (H_c) before and after heat-treated amorphous (Sm₁₋ₓ Prₓ)Fe₂ alloys

Fig. 7. Variations of magnetostriction (λII$-\lambda$I) curves of heat-teated amorphous (Sm₁₋ₓ Prₓ)Fe₂ alloys with respect to substitution of Pr

although the amorphous SmFe₂ is almost saturated, the amorphous PrFe₂ is hardly satureted parallel to the samples' planes at room temperature and 16kOe. This is caused by that the amorphous SmFe₂ and PrFe₂ alloys have preferential magnetic anisotropy parallel and perpendicular, respectively to the smaples' planes, as already pointed out in Fig. 3 and 4. When the amorphous ferri-magnetic SmFe₂ is substituted by the amorphous ferro-magnetic PrFe₂ under the saturated magnetic field, the variation of the magnetization lies on the straight line between the values of the amorphous SmFe₂ and PrFe₂ alloys if only the effect of substitution is considered. However, according to the Fig. 5, the magnetizaiton of the amorphous (Sm₁₋ₓ Prₓ)Fe₂ alloys measured at 16kOe decreases until X=0.51, but abruptly

increases at X=0.61 and then decreases again with increasing substitution of Pr, except for X=0.83. Among the values, only the values of the magnetization at X=0 and X=0.61 are near to the line, the others are far from it, especially X=1. Given that the applied field is not sufficient to saturate the amorphous (Sm₁₋ₓ Prₓ)Fe₂ alloys, the amorphous alloys is hard to be magnetized as Pr is substitued for Sm. However, the magnetization of the amorphous (Sm₁₋ₓ Prₓ) Fe₂ alloys at X=0.61 and X=0.83 appears to contradict the above tendency. The former and the latter are due to the minimum K_{ME} and K_{MC}, respectively in the amorphous alloys.

Coercive force(H_c) of the amorphous(Sm₁₋ₓ Prₓ)F₂ alloys measured at 16kOe before and after heat treatment with respect to the substitution of Pr is shown in Fig. 6. As Sm atoms are substituted for Pr atoms in the as-deposited amorphous alloys, H_c is gradually reduced. After heat treatment, H_c is also generally reduced, except for PrFe₂. The reduction of H_c in the amorphous alloy is favorable for magnetostrictive application due to low loss of magnetic hysteresis energy. It is expected that the variationof H_c in the amorphous (Sm₁₋ₓ Prₓ)Fe₂ alloys with respect to the substitution is closely related to magnetic anisotropy energy, including magnetostriction and localized magnetic anisotropy. This relationship will be discussed in Fig. 9.

Fig. 7 shows magnetostriction (λII$-\lambda$I) curves of the heat-treated amorphous (Sm₁₋ₓ Prₓ)Fe² alloys in a low magnetic field. The sign of the magnetostriction in the amorphous SmFe₂ is negative and the same as that of Laves phase intermetallic compound[3]. Furthermore, its magnitude is reasonable when compared to other's experimental result[20]. The sign of the magnetostriction in the amorphous PrFe₂ is positive and equals to that calculated using Steven's equation[21]. This value is also reasonable compared to others[22]. The above similarity of the amorphous structure to the
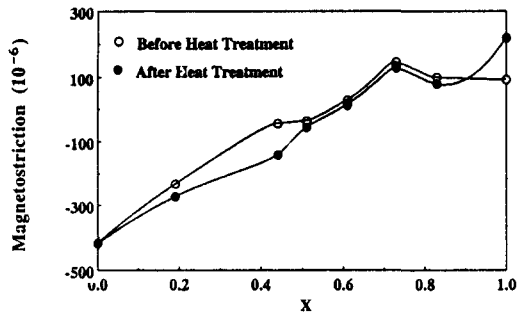
Fig. 8. Magnetostriction (λII−λI) measured at 8kOe before and after heat treatment in amorphous (Sm₁₋ₓ Prₓ)Fe₂ alloys
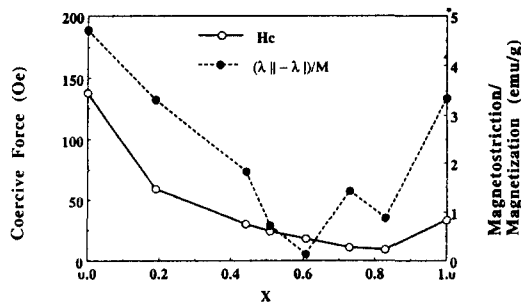

Fig. 9. Relationship between coercive force(Hc), magnetization (M) at 16kOe and magnetostriction (λII−λ I) at 8kOe in heat−treated amorphous (Sm₁₋ₓ Prₓ)Fe₂ alloys

crystalline structure is related to the fact that the localized structure of the amorphous alloy is similar to structure of an intermetallic compound in the composition with the lowest free Gibb's free energy[23], and magnetic and electric properties of the amorphous alloy are usually determinded by its localized struc-ture[24] [25]. As the substitution of Sm for Pr is increased in the amorphous (Sm₁₋ₓ Prₓ)Fe₂ alloys, the changes in the slopes of the negative magentostriction curves are the same those of the magnetization curves in the Sm rich region as shown in Fig. 3. On the other hand, the slopes of the positive magnetostriction curves are opposite to those of the magnetization curves in the Pr rich region as illustrated in Fig. 3. Since the substitution of the negative magnetostriction of the amorphous SmFe₂ for the positive magnetostricion of the

amorphous PrFe₂ effectively reduces K$_{ME}$ parallel to the samples' planes, it increases the both gradients of the magnetization shown in Fig. 3 and the magnetostriction displayed in Fig. 7. However, since the amorphous PrFe₂ had preferential K$_{ME}$ perpendicular to the planes, indicated earlier in Fig. 3, 4 and 5, this substitutional effect cannot play a major role in reducing the magnetic anisotropy energy in Pr rich region. The exception for X=0.83 was amorphous structure in the discussion of Fig. 3.

Magnetostriction (λII−λI) measured at 8 kOe before and after heat treatment in the amorphous (Sm₁₋ₓ Prₓ)Fe₂ alloys is represented in Fig. 8. The values of the magnetostriction in the heat−treated amorphous SmFe₂ and PrFe₂ are −420×10⁻⁶ and 220×10⁻⁶, respectively. The sign of the magnetostriction changes near X=0.61, which displays the minimum K$_{ME}$ in the amorphous alloys, as already pointed out in Fig. 3, 4 and 5. Compared with the as−deposited magnetostriction, the heat−treated magnetostriction is more negative, except for the amorphous PrFe₂. This means that the increase of magnetostriction in the amorphous SmFe₂ with respect to applied magnetic field is greater than that in the amorphous PrFe₂[2] after the heat. treatment, and so the heat−treated magnetostriction increases in the direction of the negative sign.

The relationship between coercive force (Hc) at 16kOe, magnetization (M) at 16kOe and magnetostriction (λII−λI) at 8kOe of the heat−treated amorphous (Sm₁₋ₓ Prₓ)Fe₂ alloys is summarized in Fig. 9. The equation for the relationship[26] is as follows,

$$H_c = C(\lambda II - \lambda I \ /M) \qquad (2)$$

C : Proportional constant

The conversion of the proportional constant is mainly caused by the difference in the width of the domain wall and internal stress state[27]. The conversion of the constant and Hc in the amorphous alloys presents at X=0.61. Ferri

magnetism and preferential magnetic anisotropy parallel to the plane, and negative magnetostriction coefficient affect the width of the domain wall and internal stress state, respectively in the Sm rich region. On the other hand, Ferro magnetism and preferential magnetic anisotropy perpendicular to the plane, and positive magnetostriction in the Pr rich region also influence them. This leads to the conversion of the proportional constant at $X=0.61$. The amount of H_c in the amorphous alloys in the product of magnetostriction and inverse magnetization which are related to magnetic anisotropy energy. The minimum H_c in Sm rich and Pr rich rigions shows at the minimum K_{ME} of $X=0.61$ and K_{MC} of $X=0.83$, respectively.

4. Conclusion

The substrate-free amophous bulk $(Sm_{1-x} Pr_x)Fe_2$ alloys were fabricated and heat-treated to investigate intrinsic magnetism. The heat treatment leaded to the decrease and increase of T_X and T_C, respectively due to the structure relaxtion in the amorphous alloys. The substitution of Sm atoms for Pr atoms in the amorphous $(Sm_{1-x} Pr_x)Fe_2$ alloys resulted in conversioins from negative to positive magnetostriction, from ferri to ferro magnetism and preferential magnetic anisotropy from parallel to perpendicular to samples' planes at $X=0.61$. These leaded to the changes in the width of magnetic domain wall and internal stress state. The minimum magnetocrystalline anisotropy in the short range of the amorphous structure showed up at $X=0.83$.

Acknowledgment

I would like to greatly appreciate to Prof. H. Fujimori at Tohoku Univ. for his kind support and encouragement during the research.

References

1. A.E. Clark and H. Belson, Phys Rev., B5, 3642 (1972)

2. A.E. Clark, Ferromagnetic Materials, Edited by E.P. Wohlfarth, Vol. 1,, chap. 7, 531 (1980)

3. C. Willams and N. Koon, Phys. Rev., B11, 4360 (1975)

4. A.E. Clrk, R. Abbundi and W.G. Gillmor, IEEE Trans. Mag., MAG-14, 542 (1978)

5. A.E. Clark, AIP Conf., Proc. 18, 1015 (1974)

6. R. Abbundi and A.E. Clark, IEEE Trans. Mag., MAG-13, 1519 (1977)

7. K. Mori, J. Cullen and A.E. Clark, IEEE Trans., MAG-19, 1967 (1983)

8. N.C. Koon, a. Schindler, C. Williams and F. Carter, J. Appl. Phys., 45, 5389 (1974)

9. A.E. Clark, R. Abbundi, O. McMaster and H. Savage, Physica 86-88B, 73 (1977)

10. A.E. Clark, Appl. Phys. Letts., 11, 642 (1973)

11. D. Foster, C. Vittoria, J. Schelleng and P. Lubitz, J. Appl. Phys., 49, 1966 (1978)

12. H. Fujimori and N.S. Kazama, SCI. REP. RITU., A-Vol. 27, No. 2 (1979)

13. S. chikazumi, Physics of Magnetism, (John Wiley & Sons, New York, 67, (1964))

14. S. Ishio, S. Takahashi, T. Miyazaki and S. Katowaki, Japanese Journal of Applied Magnetics, 13, 261 (1989)

15. M. Homma et. al., Magnetic Materals, Japan Metal Association Series 8, 106 (1977)

16. T. Egami, Amorphous Metallic Alloys, Ed. by F.E. Luborsky, Chap. 7, Butterworths, London, 100(1983)

17. K. Fukamichi and H. Komatsu, The 1884th reports of Institute for Materials Research, 251 (1989)

18. K. Fukamichi and H. Komatsu, Private Communication

19. K.H.J. Buschow, Handbook on the Physics and Chemistry of Rare-Earth, Ed. by K.A. Gschneider Jr. and L. Eyring, Elisevier Sic. Pub., 265 (1984)

20. S. Ishio and S. Kadowaki, Submitted to J. Magn. & Magn. Mater.

21. K. Steven Proc. Phys. Soc. 65, 209 (1952)
22. S. Ishio and S. Kadowaki, J. Magn. & Magn. Mater. 79, 358 (1989)
23. T. Masumoto et. al., Introduction to amorphous alloys, Agne, Tokyo, 48(1982)
24. T. Egami, Rep. Prog. Phys. 47, 1617 (1984)
25. R.P. Messmer, Amorphous Metallic Alloys, Ed. by F.E. Luborsky, Chap. 8, Butterworths, London, 114(1983)
26. R. Beckeru and W. Doring, Ferromagnetismus, Springer, Berline, 215 (1939)
27. H. Fujimori, Y. Obi, T. Masumoto and H. Saito, Mater Sci. Engng., 23, 281 (1976)