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Design of Amorphous Magnetic Materials for high frequency Sensors Based Upon Permalloy Characteristics

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퍼멀로이 특성을 기초로 한 고주파 센서에 사용되는 비정질 자성재료의 개발

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초 록

급속히 발전하고 있는 EPS 기술에 사용되고 있는 조화센서의 제조에 대해 연구하였다.

연구의 중점은 기본적으로 EPS 시스템에 사용되는 센서물질의 자성적 특성에 두었다. 조화 센서로서 사용되기 위한 주요 특징으로는 자기 이방성이 거의 0인 특서에서 기이나는 B-H곡선에서의 비선형성이다. 이와 관련하여 높은 신호를 발생하기 위한 자벽의 움직임과 자장열처리에 관하여 기술하였다.

1. INTRODUCTION

A ferromagnetic amorphous CoP alloy was first reported in 1965 and splat-quenched ferromagnets with attractive soft ferromagnetic properties were reported by Duwez's group in 1966. The subsequent growth of interest in metallic glasses over the next 15 to 20 years was exponential. Amorphous alloys of magnetic interest are based either on 3-*d* transition metals (T) or on rare-earth metals (R). In the first case, the alloy can be stabilized in the amorphous state with the use of glass forming elements such as boron, phosphorus and silicon :

Examples include $Fe_{80}B_{20}$, $Fe_{40}Ni_{40}P_{14}B_{6}$, and $Co_{74}Fe_{5}B_{18}Si_{3}$ ($T_{1-x}M_{x}$, with $15<x<30$ at%, approximately).

The late transition metals (TL=Fe, Co, Ni) can be stabilized in the amorphous state by alloying with early transition metals of 4-*d* or 5-*d* type (TE=Zr, Nb, Hf) ;

Examples include $Co_{90}Zr_{10}$, $Fe_{84}Nb_{12}B_4$, and $Co_{82}Nb_{14}B_4$ ($TE_{1-x}TL_x$, with x approximately in the range 5 to 15 at%).

In terms of practical application, A need of metallic glasses grows in the field of electronic article surveillance, EAS ; the process of placing tags or markers on items to deter theft.

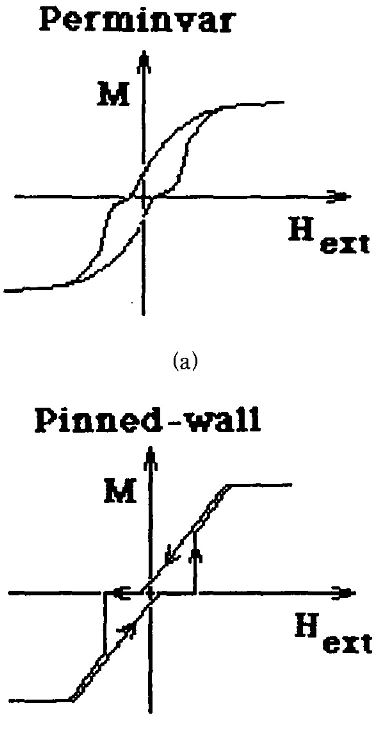
1. 1. Electronic Article Surveillance Sensors

What is needed for EAS is to set up an interrogation zone (usually defined by a magnetic dipole antenna pair) near the entrance or exit to an area to be secured. When the magnetic field in the interrogation zone is perturbed by an active tag, the system is alerted. The tags of interest here are magnetic. Magnetic tags change the characteristics of the excitation field in frequency or in time.

Frequency shifting of the excitation field is a consequence of harmonic generation. Harmonic tags multiply the drive frequency by the non-linear permeability of the tag. Materials for such tags must have very low coercivities and large, nonlinear permeabilities. Cobalt-rich, zero-magnetostriction alloys are prime candidates. In this study, a novel type of harmonic tag is designed based on the concept of domain wall pinning. By annealing a strip of soft amorphous alloy in zero field, the domain walls are stabilized in their demagnetized locations. After annealing, a small non-zero field is required to free or de-pin the walls. When this field threshold is exceeded, the walls snap to a new position with a resultant sharp change in permeability (Fig. 1).

2. EXPERIMENT

A number of soft magnetic materials can be used as the precursor to the marker material. Usable materials are amorphous transition metal-metalloid compositions which include transition metals comprising Co and Fe with the total transition metal content 60 to 80 atomic percent and various combinations of metalloid contents (B and Si). These precursor amorphous alloys (general formula Co_{95}-$xFe_5(BSi)x$) were made by planar flow casting at the Metglas Products Division of Allied-Signal Corporation. How to determine the composition of amorphous materials will be given in the discussion section.



(a)

(b)

Fig. 1. M-H loops for (a) Typical Perminvar loop. (b) Devised pinned wall loop

Initial compositions were verified by chemical analysis with Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and electron probe microanalysis (EPMA). These ribbons are characterized by near-zero magnetostriction ($\lambda_s < 1 \times 10^{-6}$) and high dc permeability in the as-cast state. Differential scanning calorimetry indicates that the onset of crystallization occurs at 465℃ and maximum peak appears at 535℃.

Ribbons with a cross section of 20㎛×3mm were cut to a length of 40mm. Samples were then first annealed under various time (3min.-7hrs.), temperature (250℃~420℃) and atmosphere in the presence of a 60 Oe longitudinal magnetic field that saturated them along their length. Maximum annealing temperature was well below the crystallization temperature, 465℃. In this experiment, the second annealing was performed at temperature as low as 320℃ in a field free environment after the first annealing was done with a 60 Oe longitudinal field.

The field induced anisotropy was measured by hysteresis loop tracing after the first annealing. After the second annealing, the wall pinning force (average of left and right pinning force) vs. annealing time for different annealing temperature was measured by hysteresis loop tracing with a drive field of 1.5 Oe at 10 Hz. For the frequency domain analysis, the material was driven by a 73 Hz excitation from 0 to 2 Oe. The output level of the pick-up voltage at 1.5, 2.5, 3.5 and 8 kHz with a band width of 600 Hz was measured.

3. RESULTS AND DISCUSSION

3. 1. Determination of Composition of Amorphous Ribbons with Suitable Magnetic Properties for Sensors

3. 1. 1. Advantages of Amorphous Alloys over Other Crystalline Alloys

Amorphous metallic alloys lack long-range atomic order and consequently exhibit many characteristics important for a variety of high frequency sensor applications. Some of their attractive technical characteristics are listed below.

1) High electrical resistivity for a metallic alloy (100~200μΩcm) due to electron scattering from atomic disorder. High resistivity is important in suppressing eddy currents during high-frequency magnetization reversal.

2) No macroscopic magnetocrystalline anisotropy (residual anisotropies typically amount to 10J/m^3 for 3d-based alloys but can approach 10^{7}J/m^3 for certain rare-earth containing alloys). Hence magnetization rotation is relatively easy. Anisotropy fields, H_K, of a few Oersteds are readily achieved.

3) No microstructural discontinuities (grain boundaries or precipitates) on which either magnetic domain walls or mechanical dislocations can be pinned. Hence magnetization by wall motion is relatively easy. Coercive fields, H_C, of a few milli-Oersteds are readily achieved.

As a result, ferromagnetic metallic glasses based on 3d transition (T) metals are generally good 'soft' magnetic sensor materials with both low dc hysteresis loss and low eddy current dissipation. In addition, they are characterized by high elastic modulus (i.e. they resist plastic deformation) and, for certain compositions, they show good corrosion resistance. These characteristics combined with the fact that metallic glasses can be economically mass fabricated in thin gauges, has led to broad commercial interest for sensor application.

Consequently, when the highest permeability is required in case of harmonic sensor application, the amorphous cobalt rich alloys represent an attractive alternative to conventional 78% Ni permalloy. One advantage they have over permalloy is their much higher hardness. This is important in sensor applications. In fact, the high yield strength of amorphous metallic alloys generally makes them much more resistant to plastic deformation and slip-induced anisotropy than crystalline alloys.

3. 1. 2 Factors Affecting Sensor Application

1) Magnetic Moments and Curie Temperatures

Fig. 2 below shows the variation of saturation moment per transition metal (TM) atom (4.2 K) as a function of TM content for amorphous alloys based on boron, $TM_{80}B_{20}$, and on phosphorus, $TM_{80}P_{20}$. The variation of magnetic moment in crystalline alloys is shown as a dotted line for reference.

Reasonably strong magnetization can be obtained in a variety of amorphous alloys based on iron, cobalt and/or nickel. The reduced moments of amorphous alloys compared to crystalline alloys are due to the presence of the metalloid (M) atoms, B, P, Si, etc., which are needed to stabilize the glassy state.

Changes in magnetization and Curie temperature with M atom content are generally weaker than changes with TM concentration. The saturation moment and Curie temperature vary as the TM/M ratio deviates from 80/20. The moments for Fe and Co-base glasses and the T_C for Co-base glasses all increase as M-content decreases ; T_C for Fe base glasses decreases as M content decreases. In this study, amorphous materials with compositions of $Co_{80-x}T_x(BSi)_{20}$ are selected in compromise between magnetic moment and other magnetic properties such as crystalline anisotropy and magnetostriction.

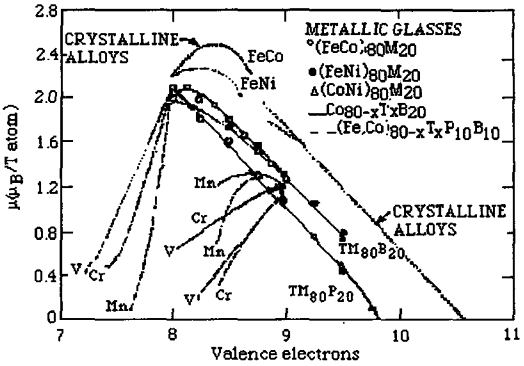


Fig. 2. Variation of magnetic moment per transition metal atom in crystalline and amorphous alloys as a function of number of valence electrons. Valence electron concentrations of 8, 9 and 10 correspond to Fe, Co (or $Fe_{0.5}Ni_{0.5}$) and Ni, respectively. The data for crystalline materials are referred to as the Slater-Pauling curve.

2) Magnetic Characteristics of Permalloys

The iron nickel alloys most often used in harmonic sensor application are found between 9.5 and 10 valence electrons per atom where the moment is just less than one Bohr magneton per atom. Magnetic iron-nickel alloys are generally called Permalloys®. This registered trademark has become a generic term for nickel-iron alloys. There are three major compositions of technical interest :

1) 78% nickel permalloys (Supermalloy®, Mu-metal Hi-mu 80® etc) and
2) 65% nickel permalloys (A Alloy®, 1040 Alloy®).

3) 50% nickel permalloy (Deltamax®).

These permalloys are of prime charactersistics for high order harmonic applications due to the fact that magnetostriction and magnetocrystalline anisotropy both pass through zero near this composition. See Fig. 3, below. These alloys are used where the highest initial permeability is required. The 65% nickel permalloys show a strong response to field annealing while maintaining $K_1 \approx 0$. What makes the 50% nickel permalloys important is their higher flux density (B_S=1.6 T) as well as their responsiveness to field annealing which gives a very square loop which is the prerequisite for harmonic sensor application. Thus, we should consider the magnetic characteristics of permalloys for the successful design of amorphous sensors.

3) Magnetostriction

The most significant contribution to the macroscopic anisotropy in 3d-base metallic glasses is due to internal stresses. The ternary diagram in Fig. 4 shows the compositional variation of magnetostriction over a field of Fe-Co-Ni-base amorphous alloys. What we see is that the magnetostriction is of order 30×10^{-6} for iron rich glasses and drops to zero with cobalt additions near an Fe/Co of approximately 4/76. This ratio is close to the Fe/Co ratio for zero magnetostriction in crystalline alloys. Zero magnetostriction ternary compositions are found along the solid line. The data in this figure are not strongly dependent on the type of metalloid used in the alloy.

There are also important λ_S=0 compositions in the (FeCoNi)Zr system (no metalloids).

Because of the technological importance of low magnetostriction, extensive efforts have been made to reduce the magnetostriction of amorphous alloys based on iron. Iron has a higher saturation magnetization and is more abundant in nature compared to cobalt; magnetostriction of $Fe_{80}B_{20}$ is approximately 32×10^{-6} at ambient temperature. Room temperature magnetostriction of iron-base glasses was shown to scale with M^2 so that λ_S=0 could only be approached with a

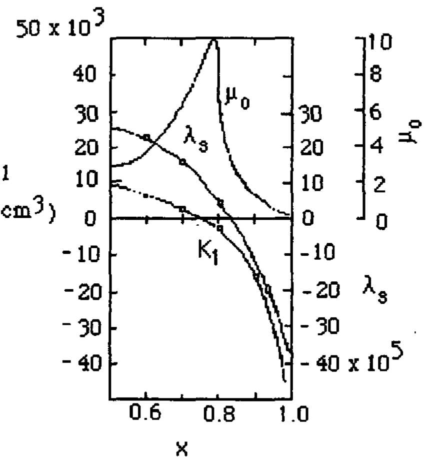


Fig. 3. Crystal anisotropy K_1, saturation magnetostriction λ_S, and initial permeability μ_0 for $Ni_x Fe_{1-x}$ alloys (after Bozorth).

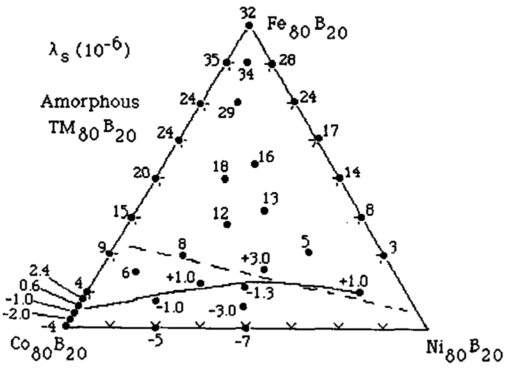


Fig. 4. Saturation magnetostriction at room temperature for amorphous alloys $(Fe\text{-}Co\text{-}Ni)_{80}B_{20}$. Solid line shows course of zero magnetostriction compositions and dashed line shows predictions based on split-band model.

loss of magnetization. Nevertheless, it has been found that for certain TE substitutions for Fe, the coefficient of M^2 can be quite small and $\lambda_S < 5 \times 10^{-6}$ can be achieved while retaining reasonable values of magnetization. In these Fe-TE-metalloid alloys the decreased room temperature magnetostriction is due partially to the suppressed Curie temperature.

Because the magnetocrystalline anisotropy of amorphous alloys is zero, most soft properties are controlled by stress-induced anisotropy and hence scale with the magnetostriction coefficient. Fig. 5 below shows how the coercivity in amorphous CoFeB alloys reaches a minimum near the composition where λ_S is zero.

As the Fe/Co ratio is varied, λ_S goes from positive (Fe-rich) to negative (Co-rich). Where $\lambda_S \approx 0$, H_c reaches a minimum. Such zero magnetostriction alloys are important for some of the same reasons that make the crystalline permalloy composition important: low coercivity, high permea bility, ease of magnetization. Consequently, $Co_{80}B_{20}$composition is most suitable for harmonic sensor application.

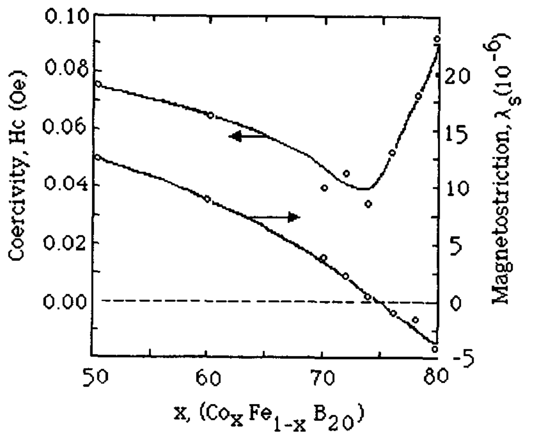


Fig. 5. Coercivity and magnetostriction in amorphous Co-rich alloys.

4) Magnetic Anisotropy

Clearly, magnetic anisotropy of crystalline origin is not a factor in amorphous alloys. However, the ease of difficulty of reaching saturation in a given direction is also affected by sample shape and by field-induced or strain-induced atomic ordering. These factors still operate in non-crystalline materials. In the process of fabricating an amorphous material, or in post-fabrication processing (e.g., field or stress annealing), or because of internal stresses, or the shape of the sample itself, a macroscopic anisotropy of magnetization may be superimposed on the essentially isotropic amorphous material characterized by K_0. A uniaxial shape or strain gives rise to a uniaxial magnetic anisotropy.

5) Field Induced anisotropy

It is possible to alter the technical properties of a metallic glass by field annealing. Amorphous alloys with compositions of $Co_{80-X}T_X(BSi)_{20}$, which is chosen along with various soft mangnetic properties, respond very well to magnetic field heat treatments so loops with a variety of shapes can be achieved. Dramatic magnetic domains in amorphous ribbons annealed in longitudinal and transverse fields illustrate the magnetic consequences of field annealing.

When a magnetic material is heated below its Curie temperature but high enough for short-range atomic mobility, the local structure has lower energy for certain atomic orderings relative to the direction of the local magnetization. With time, the thermal motion of the atoms will result in a slight biasing of the local structure toward this magnetically more stable atomic order (Fig.6).

Upon cooling, this direction of magnetization is frozen in, or stabilized to the extent that local ordering took place. If a field is applied during the annealing process, then the magnetization may exhibit a long-range orientational order that will result in local atomic rearrangements that have a long-range orientational correlation with the magnetization direction. Upon cooling, the magnetization of the sample will have a tendency to orient in the direction it had during the annealing process. The enhanced atomic mobility in the amorphous state allows for pair ordering in certain cases at relatively low temperatures compared to crystalline alloys. The role of the metalloids in this process should clearly be important because of their high mobility and strong chemical interaction with the T metals. If they assume a non-random orientational distribution around the T sites, they may favor magnetization in a particular direction.

Field induced anisotropy obtained in this study is given in Fig. 7.

3. 2. Domains and Technical Magnetic Properties of Amorphous Alloys

Samples of finite shape generally break into magnetic domains, regions in which the magnetization is saturated, generally along an easy axis. Domains are separated by domain walls, surfaces across which the direction of magnetization changes significantly. Domain walls typically have widths of 10 to 300nm for hard and soft magnetic materials, respectively. When domains are present, the net magnetization can be changed without rotating the domain magnetization, M_d, if the domain walls can be moved. A

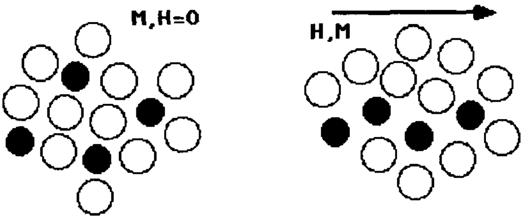
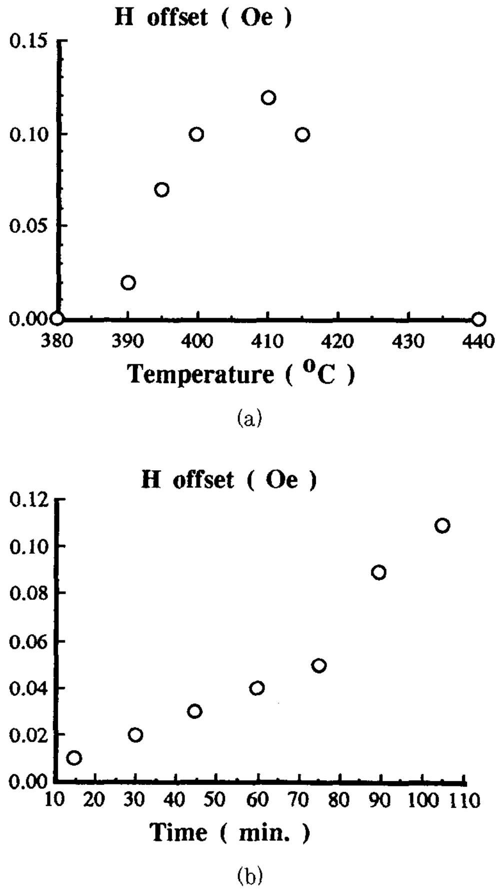


Fig. 6. Schematic representation of short range order in a binary alloy. Left, no applied field and no net magnetization. Right, magnetization ordered under influence of field.



(a)

(b)

Fig. 7. (a) Field annealing response of $Co_{74.26}Fe_{4.74}Si_{2.1}B_{18.9}$ amorphous ribbon annealed for 10 min. at various temperatures.
(b) Field annealing response of $Co_{74.26}Fe_{4.74}Si_{2.1}B_{18.9}$ amorphous ribbon annealed at 380°C for various duration of time.

sample can have zero net magnetization even though the atomic moments are still aligned within domains. Domain wall motion is a strong function of microstructural features and defects having dimensions comparable to the wall width.

The technical properties of magnetic materials depend strongly on the domain structure and the behavior of the domain walls because they are at the heart of the process by which magnetic materials are magnetized and demagnetized.

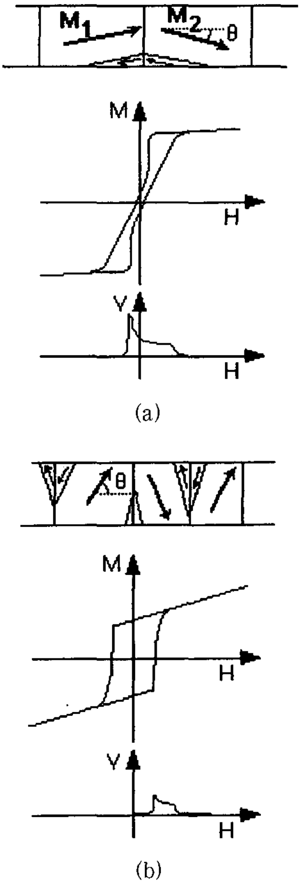
For the most part, amorphous alloys are homogeneous, i.e. there are no grains, no grain boundaries and no precipitates of any appreciable size. Because these alloys are rapidly quenched from the melt, most impurities tend to remain in solution rather than precipitating out. Thus chemical or structural inhomogeneities (except for surface roughness, pin holes and strain fields) have a scale less than 10 nm. Since the walls are wide 0.2-1.0㎛ and the defects are narrow$<$10 nm, there is little pinning of domain walls on defects in amorphous materials and H_c can be very small, the permeability can be very large.

Annealing in the absence of a field also induces a local magnetic anisotropy along the axis of the local magnetization. Thus, where a domain wall exists during annealing, it will be stabilized in that position because moving it requires rotation of the local moments from their stable orientations. Such wall pinning which was established during this study is illustrated by the B-H loop shown below on amorphous cobalt-rich alloy ribbons (Fig. 8).

4. SUMMARY

The harmonic sensor is successfully manufactured by field annealing process followed by domain wall pinning. Thus, conventional alloy sensor based on permalloy can be replaced with amorphous magnetic materials (general formula $Co_{95-x}Fe_5(BSi)_x$) which possess superior sensor qualities.

As mentioned earlier, the EAS industry is growing rapidly. In terms of improving present tags and extending present materials, it appears



(a)

(b)

Fig. 8. Schematic of domain structure, M-H loop and V-H response of harmonic tags for two cases; left, second anneal leaves M almost along ribbon axis (θ small); right, second anneal leaves M more nearly across ribbon width ($\theta \leq \pi/2$).

that the greatest opportunities exist in magnetic annealing to increase stability, signal-to-noise ratio and possibly even develop new loop characteristics for new tags.

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