Research Progress of Fe-based Amorphous / Nanocrystalline Alloys

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Abstract. Fe-based amorphous/nanocrystalline soft magnetic alloys are widely used in high-tech fields such as communications and computers due to their advantages of high saturation magnetic induction, magnetic permeability, resistivity, low coercivity, and iron core loss. This article briefly introduces the preparation process of Fe-based amorphous alloys, highlights the classification and application of Fe-based amorphous/nanocrystalline materials, and the effects of various alloying elements on their organization and performance, and points out the Fe-based amorphous/nanocrystalline possible research trends of alloys.

1. Introduction
Magnetic materials are one of the most important functional materials in modern science and technology and industrial development, and play a key role in the development of electronic technology. When the ferromagnetic material is not magnetized, the orientation of the magnetic dipole is in a disordered state, so that the vector sum of the magnetic dipole is zero, so it is not magnetically macroscopic. When an external field is applied, the magnetic dipole is exposed to the external field. The internal magnetic dipoles of the material are oriented and arranged, resulting in macroscopic strong magnetism. Amorphous alloys were thought to have no macro-magnetism because of the long-range disorder of atoms. In 1960, Gubanov [1] believed through theoretical research that the energy band structure of electrons is mainly determined by the atomic short program, that is, the ferromagnetism is generated by the exchange coupling of adjacent atoms, thus predicting that the Fe-based amorphous alloy has ferromagnetism. This provides a theoretical basis for the Fe-based amorphous alloy may have ferromagnetism.

2. Preparation of Fe-based amorphous alloy
Amorphous alloy, also known as metallic glass, is usually prepared by rapid solidification metallurgy. It is a new type of metal material with excellent mechanical, physical and chemical properties of general metals and glass. Compared with crystalline materials, amorphous materials rapidly decrease the melt temperature and increase the viscosity at a higher cooling rate. During the solidification process, the melt atoms do not have enough time to arrange orderly, so the nucleation and growth of the grains are suppressed, and the long-range disordered amorphous state is finally formed. The formation process is shown in Fig. 1. In addition, the amorphous state of the same composition has higher energy than the crystalline system, so the amorphous phase is in a metastable state. Under the influence of external conditions such as time, temperature or pressure, the amorphous material will change to the corresponding crystalline material.
In the middle of the last century, Professor Pol Duwez of California Institute of Technology first invented Au-Si amorphous alloy using liquid phase cryogenic technology, setting off the first climax of amorphous alloy research. In 1973, Maddin, Chen Heshou and others used the double-cylinder extremely cold rolling method and the single-cylinder extremely cold method to continuously prepare amorphous thin strips, realizing large-scale preparation of amorphous materials. However, the formation of amorphous alloys requires a large critical cooling rate (>104 K/s). The amorphous products formed are mostly thin ribbons or filaments, which limits the application and research of amorphous materials. Until the end of 1989, Professor A. Inoue [2] proposed the three principles of Inoue. Through the design of the alloy composition, the complexity of the alloy composition and the viscosity of the melt were improved, which ultimately improved the glass forming ability of the alloy. Since then, a series of amorphous alloys such as Fe-based, Co-based, Ni-based, Cu-based, Ti-based, Zr-based have been developed. Among them, Fe-based amorphous alloys have excellent soft magnetic properties. Compared with crystalline alloys, their higher permeability and resistivity greatly reduce the loss and weight of the transformer core. Amorphous alloys are widely used in power conversion and other fields [2].

3. Fe-based amorphous/nanocrystalline alloy materials
Fe-based amorphous/nanocrystalline soft magnetic alloys are based on amorphous alloys as precursors. A soft magnetic alloy with a two-phase composite structure of nanocrystalline phase and amorphous phase is obtained by an appropriate heat treatment method. It has more excellent soft magnetic properties. Taking Finemet alloy as an example, the process of alloy nanocrystallization is shown in Fig. 2. The study found that the soft magnetic properties of Fe-based nanocrystals are mainly affected by magnetic interaction. In order to achieve optimal soft magnetic properties, the grain size of the material is required to be as small as possible. In addition, in the nanocrystalline soft magnetic material, the amorphous phase has a positive magnetostriction coefficient, and the nanocrystalline magnetostriction coefficient is negative. The generation of nano-grains effectively reduces the magnetostriction coefficient of the material. When the magnetostriction coefficient $\lambda_s \approx 0$, the material has excellent resistance to stress sensitivity and high magnetic permeability, which can effectively improve the soft magnetic properties of the material [3].
In 1988, Japan Yoshizawa [4] et al. added a small amount of Cu and Nb to Fe-Si-B amorphous alloy, and obtained FeSiBNbCu alloy after crystallization annealing. Its excellent soft magnetic properties and special organizational structure have aroused widespread concern from scholars at home and abroad. Since the end of the last century, domestic and foreign universities, enterprises and research institutions have increased the research achievements on the composition design, structure, soft magnetic properties, preparation technology and production applications of Fe-based amorphous nanocrystalline alloys year by year.

3.1. Classification
So far, in the research of iron-based nanocrystalline alloys, the more mature composition system is mainly divided into three categories: Fe-M-Si-Cu-B (M=Nb, Cr, V, W), commercial grade Finemet; Fe-MB (M=Zr, Hf, Nb, Ta), commercial grade Nanoperm; (Fe, Co)-MB (M=Zr, Hf, Nb), commercial grade Hitperm. Their soft magnetic properties are shown in Table 1.

Table 1. Soft magnetic properties of three main Fe-based amorphous nanocrystalline alloys.

| Grade   | Bs/T | μe/(H.m⁻¹) | Hc/(A.m⁻¹) | λs/10⁻⁶ |
|---------|------|------------|------------|---------|
| Finemet | 1.24 | 1.0×10⁵    | 0.53       | 2.1×10⁶ |
| Nanoperm| 1.63 | 2.2×10⁴    | 5.80       | -1.1×10⁶|
| Hitperm | 2.00 | 1.0×10⁴    | 9.10       | 3×10⁻⁵  |
Finemet alloy was first discovered by Yoshizawa et al. Its typical composition is Fe<sub>73.5</sub>Si<sub>13.5</sub>B<sub>9</sub>Nb<sub>3</sub>Cu, which is the most widely studied and applied iron-based nanocrystalline alloy at home and abroad. As shown in Fig. 2, since the Cu element is almost insoluble in the iron element in the early stage of annealing, it leads to component separation and the formation of Cu-rich clusters. Furthermore, the compositional fluctuations of elements in the matrix between clusters and α-Fe nucleation are induced [5]. During the nucleation process, the Si element in the matrix diffuses into α-Fe to form the BCC α-Fe(Si) phase. The elements of Nb and B are insoluble in α-Fe and accumulated in a large amount in the amorphous matrix, inhibiting the growth of crystal grains and improving the stability of the remaining amorphous phase [6]. In recent years, domestic and foreign research on Finemet alloys has increasingly focused on optimizing its composition [7].

Nanoperm alloy was discovered by Suzuki [8] and others in 1990, and the typical composition is Fe<sub>90</sub>Zr<sub>7</sub>B<sub>3</sub>. In 1998, Willard [9] used Co to partially replace the Fe element in the Nanoperm alloy to obtain a new type of Hitperm-type iron-based nanocrystalline alloy. The typical alloy composition is Fe<sub>44</sub>Co<sub>44</sub>Zr<sub>7</sub>B<sub>4</sub>Cu. The addition of Co element increases the Curie temperature of the alloy, but as the Co content increases, the coercive force and cost of the alloy also increase. Compared with Finemet alloy, Nanoperm alloy has higher saturation magnetic induction intensity, Hitperm's high temperature application performance is more outstanding. However, the alloy components of the two contain more easily oxidizable elements such as Zr, Nb, Hf, and the temperature of the melting and casting belt is higher, which hinders the production and application of these two alloys [10].

3.2. Application
At present, soft magnetic amorphous/nanocrystalline alloy materials have been widely used in distribution transformers, transformers, reactors and other devices, and the application fields involve power supplies, switching power supplies, instrumentation, automotive electronics, industrial and mining/petroleum, solar energy, etc. Chinese scholars have become an important force in the research of Fe-based amorphous/nanocrystalline alloys with high saturation magnetic induction strength, and have achieved many important results [11-14].

4. Effect of alloying elements on Fe-based amorphous/nanocrystalline alloys

4.1. Co element
The amorphous phase has a positive magnetostriction coefficient, and the nanocrystalline phase has an opposite magnetostriction coefficient. With the addition of Co element, the volume fraction of nanocrystalline phase increases. The alloy can obtain more nanocrystalline grains at a low annealing temperature, the magnetostriction coefficient is reduced, and excellent soft magnetic properties are obtained. However, when the Co content exceeds 40 at%, as the Co content increases, the Curie temperature of the alloy decreases, the coercivity increases, and the soft magnetic properties deteriorate rapidly [15]. In addition, the addition of Co element in the Fe-based nanocrystalline alloy is also beneficial to improve the glass forming ability of the alloy.

4.2. Si and B elements
Compared with Zr-based and Mg-based alloys, the glass-forming ability of iron-based alloys is weaker. The addition of Si and B elements can effectively improve the glass-forming ability of Fe-based amorphous, and the strong amorphous forming ability of B element is 5 times that of Si element [16]. In addition, FeCuNbSiB alloys with Si contents of 13.5 at% and 16.5 at% have similar soft magnetic properties before annealing. After annealing, with the precipitation of α-Fe grains, the magnetostriction coefficient of the alloy decreased significantly. The higher the Si content, the smaller the magnetostriction coefficient and the better the soft magnetic properties [17].
4.3 Nb element
The addition of Nb element can suppress the growth of the crystalline phase and stabilize the residual amorphous matrix [18]. The study found that Nb element can increase the precipitation temperature difference between the primary and secondary phases of the alloy. During the annealing process, the possibility of precipitation of secondary phases such as Fe₂B is reduced. However, when the content of Nb element in Fe-based nanocrystalline alloy exceeds 3 at%, as the content of Nb element increases, the saturation magnetic induction intensity of the alloy decreases. It has no obvious effect on refining the grain size and widening the precipitation temperature range of the two crystalline phases [19].

5. Conclusion
Fe-based amorphous/nanocrystalline alloys have excellent soft magnetic properties and are industrially produced. It has gradually replaced traditional soft magnetic materials such as silicon steel and ferrite and is widely used in various industries. It will play an increasingly important role in the high-tech field in the future. Although more and more scholars at home and abroad have been engaged in the research of Fe-based amorphous/ nanocrystalline alloys in recent years and have achieved remarkable results, there are still many shortcomings. The research can focus on the development of new added elements, increase the content of Fe in the alloy, and improve the soft magnetic properties of the alloy while reducing costs. In addition, improving the preparation process and heat treatment process of the iron-based amorphous/nanocrystal is also crucial.

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