The Research Progress of Zr Based Amorphous Composite Materials

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Abstract: Based on the introduction and forms of the second phase the Zr based amorphous composites was classified. This paper introduced the research work of the endogenous phase-Zr based amorphous composite materials, the particles-Zr based amorphous composites, fiber-Zr based amorphous composite materials, the skeleton-Zr based amorphous composite materials, and prospected the development prospect of Zr based amorphous composites.

1. Introduction
Zr base amorphous alloys have excellent mechanical properties such as high strength, high elasticity, high toughness, high hardness, wear resistance, low thermal expansion coefficient and excellent corrosion resistance, etc [1-9], at the same time, Zr base amorphous alloy has the high glass forming ability, relatively simple preparation technology and equipment, is currently one of the research of amorphous alloy. But the alloy with low plasticity at room temperature show the typical brittle fracture, hardly happen macroscopic plastic strain, which seriously limits the application of the alloy as the engineering material, and makes its superior performance cannot get to play. The introduction of the second phase as strengthening phase to Zr base amorphous alloy to form Zr base amorphous composite material, which strengthened its room temperature plasticity and further improved other properties, also has opened up a broad application prospect for Zr base amorphous alloy applications in engineering materials.

2. The Research Progress of Zr Base Amorphous Composite Material
Based on the introduction of the second phase in Zr base amorphous alloy the Zr base amorphous composite materials can be divided into endogenous phase-Zr base amorphous composites and plus phase-Zr base amorphous composite materials, And the plus phase-Zr base amorphous composite materials can be divided into the particle-Zr base amorphous composites, the fiber-Zr base amorphous composites, skeleton - Zr base amorphous composite materials, and other.

2.1 Endogenous Phase-Zr Base Amorphous Composite Materials
By adjusting the alloy composition and process conditions, the crystallization of amorphous alloy or primary crystallization phase as the second phase was introduced into Zr base amorphous alloy, which was uniformly distributed in the alloy matrix to prevent shear zone extending and inspire the toughening effect of multiple shear bands formation. Fan et al [10-11] found Zr53Ti5Ni10Cu20Al12 and Zr60Cu20Pd10Al10 have good plasticity at room temperature, and the nanocrystalline’s exist in amorphous matrix by high resolution electron microscopy (sem), thus forming nanocrystalline-Zr base amorphous composite materials. The composite material has macroplasticity which due to stress con-
centrion near the nanocrystalline, which leads to the generation of multiple shear zone and the single shear zone’s difficulty to expand rapidly [12].

The amorphous with metastable structure have the trend of crystalline transition spontaneously in the process of heating. Therefore, by reasonable control of annealing process, some amorphous transform to nanocrystalline phase with size in a few nanometers to hundreds of microns, which evenly dispersed in the amorphous matrix to enhance the effect of matrix [13]. Q Wang, D K Wang et al [14] produced Zr base amorphous matrix composites enhanced by 10.5% vol nanocrystalline of the size of 2-10 nm by controlling the process conditions annealing treatment Zr41.2Ti13.8Cu12.5Ni10Be22.5 amorphous alloy. By study on the crystallization behavior of Zr56.6Cu17.3Ni12.5Al9.6Ti4 amorphous alloy with temperature, Xing Dawei [15] found that with the increase of annealing temperature and annealing time increases, the crystallization phase increased obviously, and the amorphous phase decreased significantly.

Meanwhile the primary crystallization phase could be separated out in the cooling process of the alloy melt by controlling the cooling rate. With the cooling process, the rest of the freezing melt into amorphous structure, forming a crystallization phase distributed evenly in the amorphous matrix of composite structure. Liu Jinmin et al [16] prepared in-situ martensite CuZr phase enhanced Zr50.5A9Ni13.05Cu27.45 amorphous alloy composite materials by using copper spray casting process. Because the large number of coherent twin boundary of martensite CuZr phase can effectively prevent localized shear band extension, prompt and initiation of multiple shear zone when deformation, in order to delay the initiation and propagation of crack. The mechanical properties of composite materials greatly improve, the compression fracture strength and strain respectively reached 2190 MPa and 8%.

By adding high melting point elements into Zr base amorphous alloy ,the plastic branch crystal separate out, which can inhibit the effect of shear zone rapidly expanding in the amorphous matrix, so as to make the mechanics of composite materials is improved. By adding Nb, Johnson et al developed a new alloy for Zr56.2Ti13.8Nb5.0Cu6.9Ni5.6 Be12.5, the Nb act with Zr and Ti to form the branch crystal of β-Zr(Ti),which Set on the fully amorphous matrix with volume fraction of 25%,and the size of the branch crystal is 100 microns. By adding element of Hf and Ag, Huo Juntao et al [17] prepared the bulk amorphous composite materials Zr-Cu-Al-Hf(Ag). Compressive test shows that the strength and plastic of (Zr50Cu40Al10)98Hf2 is better than Zr50Cu40Al10, the σmax is 2002MPa, the maximum plastic strainεp is 8%.The experiment confirmed that the element Hf promote the formation of branch crystal in the Zr base amorphous alloy

2.2 Particle Phase-Zr Base Amorphous Composite Materials

By adding particle phase into Zr base amorphous matrix can prevent the expansion of the shear zone, and promote the generation of fracture surface and the additional shear band, keep Zr base amorphous composite materials in high strength and high plasticity. The plus particle phase mainly includes two kinds of refractory metal particles and ceramic particles. Through the analysis of the mechanical properties of Amorphous composites reinforced by particles it’s found that: if the enhancement phase particles is toughness, compared with the system of pure amorphous composites plasticity significantly increased; if the reinforced phase is brittle particles, the plasticity increase of amorphous composites is not big, but the strength will be higher than toughness reinforced particles of amorphous composite materials. It’s because the plastic improvement mechanism of the two kind of composite materials is different [18-19]. Currently the die casting and liquid infiltration casting process are mainly adopted for preparing particle reinforced composites.

More research for plus toughness particles reinforced Zr base amorphous composites focused on such as adding metal W, Ta, Mo, Nb and TiNb [20-26]. The study found that the Zr base amorphous composites with W particle size less than 10 microns, volume fraction of 60% changed its yield stress less, and raised the plastic strain greatly, the total variable should be increased by 350%.By scanning electron microscopy (sem) in-situ tensile test combined with finite element simulation, Z. Zhu et al [24] reveals that the plastic deformation of Ta particles caused the shear zone is evenly distributed on the
substrate around the particles, which triggered an initiation and development of the secondary shear zone, and helps to improve the plasticity of Zr54Ta8Cu15.6Ni12.4Al10 amorphous composites. By microstructure observation H. Choi-Yim et al found around a certain thickness of amorphous phase was generated aroumd the enhanced phase Ta, Nb, Mo particles.

The main research for plus brittle particles reinforced Zr base amorphous composites focused on ceramic particles ZrC, SiC, WC, ZrO2, etc.[27-32]. Kato et al in 1997 prepared for the first piece of Zr base amorphous composite material, will by adding join ZrC particles into the amorphous alloy matrix Zr55Al10Ni5Cu30, and found that with the adding of ZrC particles, the young’s modulus, the tensile strength, the microhardness and the plastic strain of the composites increased significantly. Then Conner et al reported that Zr57Nb5Al10Cu15.4Ni12.6 amorphous composites reinforced by SiC, WC ceramic particles has relatively lower tensile strength than W, Ta toughness particles as strengthening phase; the WC particles reinforced amorphous composite has plastic strain ratio up to 3-5%, but the addition of SiC particles did not improve the plastic of the amorphous composite. In view of Choi-Yim and Wu on research results of reinforcement of SiC particles to amorphous matrix composites, Liu Jinmin [32] concluded that the interface microstructure changes have a significant impact on mechanical properties of the composites by studying the different content of SiC particles reinforced Zr50.5Al9Ni4.05Cu36.45 amorphous alloy composite material. The limited Interfacial reaction products ZrC can enhance the bonding strength of interface, passing stress effectively, which hinder the expanding of localized shear band, prompted multiple shear zone of initiation, help to improve the strength and plastic of the alloy. While too much interface reaction can weaken the bonding strength of interface, make the alloy crack quickly along the interface during compression deformation, characterized by brittle fracture.

2.3 Fiber-Zr Base Amorphous Composite Materials

By adding ductile metal fiber into amorphous matrix can prevent the expansion of the shear zone and promote fracture surface area, and the additional shear band to keep amorphous composite materials in high strength and high plasticity. Infiltration casting process is a used preparation methods of fiber reinforced Zr base amorphous composite materials, according to join the fiber morphology the composit material can be divided into continuous fiber reinforced and short fiber reinforced two kinds.

The main research for continuous fiber reinforced phase focused on W, Mo and Ta wire [33-48], which mainly more research on W silk as enhanced phase, its from 40-1000 microns in diameter, volume can be as high as 80%. The composite has more excellent compression performance because the W wires have good combination of matrix and the help under compression loading the formation of shear band. Conner, Cheng Huanwu et al systematically studied the mechanical behavior and fracture characteristics of the W/Zr base amorphous alloy composite materials, the results showed that with the increase of W wire volume content of the elastic modulus of the composite increased, and the compression plasticity first increases and then decreases with the increase of fiber volume content, the fracture mode of the composite with the increase of fiber content from the shear fracture to longitudinal splitting.

Because Zr base amorphous alloy under the action of the enhancement of the W wire can produce self-sharpening effect caused by the localized shear fracture behavior in the process of penetrating the destruction of the object, at the same time has high density, can be used to withstand the impact of structural materials such as armor-piercing core. G Rong, Lei Bo et al carried out a series of high speed penetration test on W wire/Zr base amorphous composites of, studied the self-sharpening behavior and penetration of the material. The good mechanical properties and potential defense applications of W wire reinforced Zr base amorphous composite makes it one of the most widely studied of amorphous alloy composite material.

In view of the limitations of high strength and high modulus of one-way continuous fiber reinforced amorphous composites only along the fiber direction, S T Deng, Ma Guangcai et al [49-51], added the short fiber as reinforced phase such as stainless steel capillary, carbon nanotubes to the Zr base amorphous alloy, in which the strengthen phase randomly distributed to pile arrangement, and the
composites exhibit isotropic; At the same time the introduction of the short fiber can achieve lower volume percentage to introduce more interface, so than the same volume of continuous fiber reinforced composite materials have greater compressive plastic strain. In CNTs-Zr base amorphous composite materials, along with the increase in CNTs adding quantity, the young's modulus, the shear modulus, the bulk modulus and the hardness of amorphous composites increased.

2.4 Skeleton-Zr Base Amorphous Composite Materials
The amorphous composites with endogenous phase enhancement, particles enhancement and fibers enhancement all can’t limit the expansion of the amorphous shear zone from the direction of 3d. But in the amorphous composites reinforced by skeleton, matrix and the skeleton reinforced phase interact with each other within the 3d space, which effectively reduce the stress concentration, can enhance the deformation resistance and the plastic of amorphous composites, at the same time can realize the composites’ isotropic [20]. Now the main research for skeleton-Zr base amorphous composite materials focused on W skeleton and SiC skeleton reinforced Zr base amorphous composites [52-57].

Zhang et al studied the quasi static compression performance of Zr base amorphous composites reinforced by W skeleton of 80% volume content, it is concluded that the compressive strength of the composites can be as high as 3450MPa, the fracture strain reached 50%, the strength and plasticity are far higher than that of W particles and W wire enhanced amorphous composite materials. Li et al studied the quasi-static and dynamic compression mechanical properties of the W skeleton amorphous composites in contrast, and analyzed the influence of W skeleton volume fraction on mechanical properties. they found that composite materials’ dynamic compression strength higher than quasi static, consistent with W silk reinforced amorphous composites, which shows the positive strain rate sensitive effect of composite materials; As W skeleton volume fraction increases, the pore is dense, plastic of composite material, the better.

2.5 Others
By introducing a component with large mixing enthalpy, the alloe melt with difficult miscibility gap was prepared. Under the condition of rapid solidification, melt structure is rapid freezing, thereby the two phase or multiphase amorphous composite structure was obtained. Differences in performance between different phase, can be used to extend the effective way to change the internal cracks of amorphous, so as to improve the mechanical properties of amorphous.

Sun Linlin et al [58] found that the uniform amorphous matrix separated into 2 kinds of amorphous alloy. when the typical amorphous structure material Zr48Cu36Ag8Al8 alloy kept warm at 703K for 20 min. Wang Zhongyuan et al [59] found that alloy melt liquid phase separation occurred during the solidification process when they added the Co-Cu binary metastable immiscible alloy into the Zr-Ce binary stable immiscible alloy, the Co and Cu elements respectively distributed in rich Zr and Ce in the liquid phase, and eventually rich Zr-Co and rich Ce-Cu two liquid phase were formed. Under the condition of rapid solidification, rich Zr-Co and rich Ce-Cu two liquid phase formed by the liquid-liquid separation of quaternary alloy respectively Glass changed to form the Zr and Ce based amorphous phase, eventually formed two-phase amorphous alloy composite materials.

3. Prospect
Zr base amorphous composite materials with high specific strength, specific stiffness, high hardness, high wear resistance an, corrosion resistance and other excellent physical properties would have broad in the aerospace, precision instruments and equipment manufacturing, chemical industry and other fields application prospects. Zr base amorphous alloy has similar mechanical performance parameters to human bone, and at the same time has many characteristics, such as good biocompatibility with the human body environment. So Zr base amorphous composite material could be used for the preparation of medical scalpels, artificial teeth, artificial bone and biological sensing material. Moreover, with the enhancement function of W wire, Zr base amorphous composite material has a self-sharpening effect in the in the process of penetrating the destruction of the object because of the local shear fracture
behavior in the process of deformation, that makes W fiber-Zr base amorphous composites penetrator have a great application prospect in the field of national defense.

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