Research Status and Development Trend of Cu-Zr- Based Amorphous Alloys

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Keywords: Cu-Zr, Morphous alloy, Adding element, Mechanical properties, Corrosion resistance.

Abstract. Firstly, the Cu-Zr-based amorphous alloy, which is a type of material with a broad application prospects, was introduced, as well as the research status and progress at domestic and foreign were summarized from the aspects of alloy system, their properties and applications in this paper. Secondly, the properties of Cu-Zr-based amorphous alloys, such as mechanical properties and corrosion resistance, and the effect of adding elements on the ones were focally discussed. Finally, the existing problems of the Cu-Zr-based amorphous alloys were briefly described and their development trends were proposed.

Introduction

Since Au-Si\textsuperscript{[1]} amorphous alloy was prepared in the United States in the 1960s, the researchers found that the amorphous alloy has a special structure and more some excellent properties such as high strength, hardness and fracture toughness, compared to crystalline materials, so it was considered as a new material with significant application potential, furthermore, amorphous alloys had become a new focus of domestic and foreign in material research field since the 1980s\textsuperscript{[2-5]}. Because the Cu-based amorphous alloy holds a relatively low price with a widely application in the engineering field and the Zr-based amorphous alloy possess a higher strength, elastic modulus, hardness and so on, their preparation technologies and properties had been further improved by the researcher in recent ten years\textsuperscript{[4-6]}. Therefore, the Cu-Zr-based amorphous alloys have been received a special attention and is a focus of research in the field of amorphous alloys.

The role of Alloying Elements in Cu-Zr-based Amorphous Alloy System

At present, adding elements is simple in process and low in cost among various methods to improve the properties of amorphous alloys\textsuperscript{[7-10]}, which can also change the microstructure of the alloy in essence, so it has been received a particularly extensive research. The reduced glass transition temperature, super-cooled liquid phase area and melting point of the alloy are affected by adding and changing the content of the alloying elements, as well as it can change the GFA and mechanical properties of the alloy and so on. So far, the Cu-Zr-Al, Cu-Zr-Ce, Cu-Zr-Gd, Cu-Zr-Y, Cu-Zr-Al-Ag, Cu-Zr-Al-Gd, Cu-Zr-Al-Y, Cu-Zr-Ti-Ni and other basic alloy systems have been studied.

Non-metallic Elements

Hydrogen is a non-metallic element when it was added into the Zr\textsubscript{55}Cu\textsubscript{30}Ni\textsubscript{15}Al\textsubscript{10} amorphous alloy to improve the GFA\textsuperscript{[11]}, the strengthening effect is very excellent. Because the atomic radius of hydrogen is a very small and formed a negative mixing enthalpy with other four component, which would cause a lot of atomic size mismatch degrees and form a new atoms, so it would inhibit the formation of crystal phase, increase the effective atomic stacking structure, reduce the liquidus temperature \( T_l \) and improve the stability of liquid phase. Therefore, it was beneficial to improve the GFA of Zr\textsubscript{55}Cu\textsubscript{30}Ni\textsubscript{15}Al\textsubscript{10} alloy.

When a small amount of P/B were added into the Zr\textsubscript{71}Fe\textsubscript{15}Cu\textsubscript{14} alloy\textsuperscript{[12]}, the bonding force between the atoms of the alloy was greater. During the solidification process, it was difficult that diffusion between the atoms and it was easier to form bulk amorphous alloy. With P content
increasing, the compressive fracture strength of the alloy gradually rises. When P content was 4%, the alloy possessed the highest fracture strength with value of 618MPa. The addition of B can significantly improve the mechanical properties of the alloy. With the addition of B increasing, the fracture strength of the alloy firstly decreases and then increases. When P content was 5%, the alloy possesses the largest fracture strength with value of 1398MPa.

Minor Si affects the GFA and corrosion resistance of Cu-Zr-Al alloy\(^{[13]}\), with the content of Si increasing from 0.5 to 1%, the super-cooled liquid phase area of Cu\(_{49}\)Zr\(_{45}\)Al\(_6\) amorphous alloy increased, indicating the GFA of Cu\(_{49}\)Zr\(_{45}\)Al\(_6\) alloy was improved. At the same time, with Si content increasing, the corrosion rate of amorphous alloy decreases and the corrosion resistance increases.

**Rare Earth Elements**

It was found that rare earth elements Gd\(^{[14]}\) and Y\(^{[15]}\) have a significantly effect on the amorphous forming ability of Cu-Zr-based amorphous alloy after many years of research. In reference 16, the quaternary alloy Cu\(_{50}\),Zr\(_{12}\)Al\(_8\)Gd\(_x\) (x=0, 1, 3) with 3mm diameter was produced by the spray casting in copper mold\(^{[16]}\). When x was equal to 3, the super cooled liquid phase \(\Delta T\) reached a maximum value of 92K and the reduced glass transition temperature \(T_g\) also reached a maximum of 0.65, indicating the proper addition of Gd can obviously improve the GFA and thermal stability of the system. Gd with a large atomic radius (2.54×10\(^{-8}\)\(\mu\)m) can produces a large atomic dislocation and a large negative mixing enthalpy in the alloy system, which inhibits the formation of nucleation and is more conducive to the formation of amorphous alloy. When x was equal to 1 or 3, the compressive strength and fracture strain were 1370MPa, 1056MPa and 2.99%, 2.81%, respectively. The compressive strength of the alloy system has been clearly enhanced.

The effect of adding rare earth element Y on quaternary alloy (Cu\(_{47}\)Zr\(_{47}\)Al\(_8\))\(_{100-x}\)Co\(_x\) was studied and the samples with 7mm and 9mm diameter was produced\(^{[17]}\). The results showed: when Y content wasn’t added, Cu\(_{47}\)Zr\(_{47}\)Al\(_8\) existed a crystal phase, indicating the GFA is bad. With Y content is equal to 1%, 2% and 3%, the all samples were an amorphous phase. These results also showed that the GFA of the quaternary alloy are superior to the Cu-Zr ternary alloy.

The studies of the effect of Y on Cu-Zr-based amorphous alloy showed: a little amount of Y can increase the GFA and thermal stability of Cu-Zr-Al amorphous alloy\(^{[18]}\). For Cu\(_{50}\)Zr\(_{12}\)Al\(_8\) and Cu\(_{46}\)Zr\(_{47}\)-xAl\(_y\)Y\(_z\) (x =2 and 5) alloy, the super-cooled liquid region increases 19K and 30K, the glass transition temperature and the parameter \(\gamma\) of the two alloys rises.

**Metallic Elements**

The studies of the effect of Al on Cu\(_{60}\)Zr\(_{50}\) alloy showed: the atomic percentage of the Al was 0, 2%, 4% and 6%, the samples have a various the GFA\(^{[19]}\). The sample with little Al content will crystallize, but Al content is increased to 6%, a well amorphous structure is obtained. Whitmore, the fracture strength of the alloy increases from 1575.2MPa to 1908.6MPa, and finally decreased to 1559.3MPa with Al content increasing. This indicated that the effect of Al content on the mechanical properties of the alloy was dissimilar in different contents.

Mandal S focused on enhancing plasticity of the Cu-Zr-based amorphous alloy by adding a small amount of Ni\(^{[20]}\). The results showed: the systemic mechanical properties rise with Ni content increasing. The value of the yield stress, fracture stress, maximum stress and plastic strain of the Cu\(_{60}\)Zr\(_{25}\)Ti\(_{15}\)Ni\(_5\) amorphous sample reach to 2425MPa, 2513MPa, 2725MPa and 16ptc, respectively, which was more higher than the ones of Cu-based amorphous alloy in the reference. The author believed that the high plasticity value would be attributed to the change of free volume by the addition of Ni.

Because the price of Zn is relatively low, the relationship between the microscopic phases and properties of Cu-Zr-Zn materials was studied by Wu Dianyu\(^{[21]}\). With x increasing from 4.5% to 7% in the (Cu\(_{50}\)Zr\(_{50}\))\(_{100-x}\)Znx amorphous alloy, the volume fraction of CuZr phase decreases and a large amount of B\(_2\)-CuZr phases with memory precipitate. In other words, B\(_2\)-CuZr and amorphous phase were obtained by rapid cooling way, so the Cu-Zr-Zn amorphous composite material was obtained.
Properties of Cu-Zr-based Amorphous Alloys

Mechanical Properties

Cu-Zr-based alloys possess a higher strength and elastic modulus\(^{22-24}\). The effect of the addition of Mn and AlTiB on the mechanical properties of Al-Si-Fe-Cu-Zr amorphous alloy was studied by Yoo Hyo-Sang\(^{25}\). He found: when the as-cast billet was held at 400°C for 1 hour and then hot extruded and was annealed at 620°C, a large of equiaxed grains were observed and the grain display a skeleton structure with 1.0wt% Mn content. With the addition of Mn and AlTiB, the volume fraction of intermetallic compounds increases. For Al\(_{0.1}\)Si\(_{0.2}\)Fe\(_{0.4}\)Cu\(_{0.04}\)Zr amorphous alloy, the tensile strength increases from 100.47, 119.41 to 110.49MPa when Mn and AlTiB of 1.0wt%. The tensile strength of the extruded alloy increases to owe to that the intermetallic compounds are formed with Mn and AlTiB increasing.

Corrosion Resistance

Micro-alloying has a particularly large effect on the corrosion resistance of amorphous alloys\(^{26-28}\). The corrosion resistance of the Cu\(_{50}\)Zr\(_{50}\) amorphous alloys in 1mol/L NaOH solution is enhanced\(^{29}\) by adding micro-alloying elements. The author thought that the micro-alloying elements increase the Fermi level that are preferentially bonded to Zr and Cu, which would reduce the ionization energy of Zr and Cu, directly improved the rate of passive film formation, so the corrosion resistance of the Cu\(_{50}\)Zr\(_{50}\) amorphous alloys was enhanced by micro-alloying.

The corrosion behavior of Cu-based amorphous alloy composite in NaCl solution was studied by immersion and potentiodynamic polarization method\(^{30}\). The results showed: the Cu\(_{47.5}\)Zr\(_{47.5}\)Al\(_{5}\)Hf\(_{5}\) alloy occurred pitting corrosion in the mass fraction of 3.5% NaCl solution. When annealing for 30 min in the 623 K (lower than \(T_g\)) and 773 K (slightly higher than \(T_g\)), the self-corrosion potential increased, the corrosion current density slightly increased and the corrosion resistance didn’t change much. When Y was added to the Cu-Zr-Al amorphous alloy, the corrosion potential and corrosion current density decreased in the 3.5% NaCl solution with Y content increasing\(^{31}\).

Summary and Prospect

(1) The GFA, thermodynamic properties and mechanical properties of the Cu-Zr-based amorphous alloy are constantly enhanced with the preparation techniques steadily improving and perfecting, so the Cu-Zr-based amorphous material will be widely applied.

(2) The formation rules and theory of Cu-Zr-based amorphous alloy still need to be further studied. At present, it can be found that different components and contents of the alloy will have a significant impact on the GFA and mechanical properties. In the future, we should research on the components design and the theory of Cu-Zr-based amorphous alloy to obtain better performance.

(3) The Cu-Zr-based amorphous alloy has a higher strength but the plasticity at room temperature ductility is insufficient, which limits the application of Cu-Zr-based amorphous alloy in some particular fields, so it is necessary to that scholars would develop a Cu-Zr-based amorphous alloy with high plasticity in the future.

Acknowledgements

The authors are very grateful for the financial support being provided by the Yunnan Agricultural Foundation Projects (Grant No.2018FG001-062).

Reference

[1] Klement W, Willens RH, Duwez p. Non-crystalline Structure in Solidified Gold | [ndash] | silicon Alloys [J]. Nature, 1960, 187 (4740): 869-870.

[2] Sen P, Sarma DD, Budham RC, et al. An Electron Spectroscopic Study of the Surface Oxidation of Glassy and Crystalline Cu-zr Alloys [J]. Journal of Physics F Metal Physics, 1984, 14 (2): 565.
[3] Cussen L, Hicks, T. Magnetic Diffuse Scattering From Amorphous Cu-Zr Containing Manganese [J]. Materials Science Forum, 1988, 27-28 (missing): 261-266.

[4] Wang L, Liu J, Liu A, et al. Effect of Pouring Temperature on Microstructure and Mechanical Properties of Zr-based Amorphous Alloys [J]. Journal of Iop Conference Series: Materials Science and Engineering, 2018, 394(3): 0-32121.

[5] Liu Y, Pan J, Li L, et al. The Structural Relaxation Study of zr-cu-ni-al Metallic Glass During Heating By small-angle X-ray Scattering[J]. Applied Physics, 2019, 125(5): 292-297.

[6] Lee JG, Lee GJ, Park JJ, et al. The Corrosion behaviors of High - temperature in Pressurized Water of Zircaloy - 4 Joints Brazed with Zr - cu - -based Amorphous Filler Alloys [J]. Journal of Nuclear Materials, 2017,488 (5): 204-209.

[7] Wang Y, Zhan Z L, Yu X H, et al. Effects of trace elements on amorphous forming ability of cu-zr base alloy [J]. Transactions of Materials and Heat Treatment, 2013, 34(4): 12-16.

[8] Yang S, Zhang G Y, Z H. Effects of trace Y and La on corrosion resistance of zr-based amorphous alloys [J]. Journal of Shenyang Normal University (Natural Science Edition), 2008, 26(1): 49-52.

[9] Song H Feng, Wang Q, Fu T, et al. Effect of Nb addition on isothermal crystallization kinetics of cu-zr amorphous alloy [J]. Rare Metal Materials and Engineering, 2011, 40(12): 2131-2135.

[10] Li M Y. Effects of trace elements on aging structure and properties of Cu-Zr -(Cr) alloy [D]: Dalian university of technology, 2015.

[11] Dong F Y. Influence of liquid hydrogen on the forming ability and mechanical properties of zirconium based bulk amorphous alloys [D]: Harbin Institute of Technology, 2013.

[12] Huang W Jun. Effects of element addition on forming ability and mechanical properties of zirconium base amorphous alloy glass [D]: lanzhou university of technology, 2011.

[13] Su E L. Influence of Si elements on the amorphous forming ability and corrosion resistance of Cu-Zr-Al alloy [D]: xiangtan university, 2013.

[14] Fu HM, Wang H, Zhang H F, et al. The Effect of Gd Addition on The glass-forming Ability of Cu-Zr-Al Alloy[J]. Scripta Materialia, 2006, 55(2): 147-150.

[15] Shen Y, Xu j. Improving Plasticity and Toughness of Cu - zr - Y - al Bulk Metallic Glasses Via Compositional Tuning forward the Cuzr [J]. Journal of Materials Research, 2010, 25 (2) : 375-382.

[16] Zhang L, Luo D C, Kou S Z, et al. Effects of trace elements Gd and Nd on Cu base bulk amorphous formation ability and compression properties [J].Journal of Lanzhou University of Technology, 2017, 43(2): 13-18.

[17] Fan X H, Yang K, Li B, et al. Effect of Y on glass formation ability and mechanical properties of cu-based amorphous alloys [J]. Journal of Xi'an Technological University, 2014, 34(2): 146-151.

[18] Yue L, Liu Y, Xie K. Glass Forming Ability and Crystallization Kinetics of Cu - zr - al - (Y, Ag) Amorphous Alloy [J]. Journal of Wuhan University of Technology - mater. Sci. Ed., 2018, 33 (4): 938-945.

[19] Wang D. Study on mechanical properties of cu-zr base amorphous alloy [D]: xi'an university of technology, 2016.

[20] Mandal, S Kailath AJ. Enhanced Plasticity of Cu - zr - ti Bulk Metallic Glass and Its the Correlation with Fragility [J]. I have the Materials and the Transactions. A, 2019, 50 (1): 199-208.

[21] Wu D Y. Study on the formation and properties of cu-zr-zn amorphous materials and their composites [D]: Northwest polytechnical university, 2016.
[22] Hong K, Wu L, Jiang W et al. Study on high temperature tensile creep of cu-zr amorphous alloy thin strip [J]. Materials Reports, 2018, 32(24): 4309-4313, 4323.

[23] Li W. Study on microstructure and properties of cu-zr matrix bulk amorphous composites [D]: Hunan University, 2010.

[24] Hang Zhenghua, Feng Yingying, Li Fang. Microstructure evolution and shear band proliferation induced by trace Nb addition in cu-zr-ti-based amorphous alloy [J]. Hot Working Technology, 2019, 48(8): 84-87.

[25] Yoo HS, Kim YH, Lee SH, et al. Effect of Mn and Al-trib Addition and Heat treatment on the Microstructures and Mechanical Properties of al-si-fe-cu-zr Alloy[J]. J Nanosci Nanotechnol, 2018, 18(9):6249-6252.

[26] Wang Y, Liu Z L, et al. Microstructure and corrosion resistance of hot rolled Cr and Ni microalloyed high strength weathering steels [J]. Journal of Chinese Society for Corrosion and Protection, 2018, 38(1): 39-46.

[27] Zhou M, Gan P Y, Deng H H, et al. Research status and development trend of microalloyed aluminum alloy containing scandium [J]. Materials China, 2018, 37(2): 154-160.

[28] Yang XH, Nie XP, Jiang JZ. Ti Microalloying Effect on Corrosion Resistance and Thermal Stability of Cu45zr48al7 Bulk Metallic Glass[J]. Advanced Materials Research, 2012, 490-495(5): 3868-3873.

[29] Liu J F. Research on corrosion resistance of cu-zr based amorphous alloy based on Fermi level [D]: Lanzhou University of Technology, 2018.

[30] Zhang Z Y, Tang J N, Yu J, et al. Corrosion behavior of cu-based amorphous alloy composites in NaCl solution [J]. Journal of Chinese Society for Corrosion and Protection, 2018, 38(5): 478-486.

[31] Liu Y, Wang Y F, Xiao L J, et al. Effects of Y Alloying on Thermal Stability and Corrosion Resistance of cu-zr-al Metallic Glass[J]. Advanced Materials Research, 2013, 850-851(5): 62-65.