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ARTICLE

Effects of Cu Content on Microstructures and Mechanical Properties of Ti-Ni-Based Amorphous Composites

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Abstract: Ti-Ni-based amorphous composite samples $(Ti_{0.5}Ni_{0.5})_{100\text{-}x}Cu_x$ with different Cu contents but the same diameter which has been prepared by the copper mold suction casting. The effect of the Cu contents (x=0, 10, 15, 20, 25, 30, 35, 40, at%) on the microstructures and mechanical properties of the amorphous composites was studied. Results show that both fracture strength and plastic strain of the alloy are very high when the copper content is x=20. Meanwhile the alloy exhibits the best comprehensive properties. As the x value increases, the glass forming ability of $(Ti_{0.5}Ni_{0.5})_{100\text{-}x}Cu_x$ alloy shows a waveform change from increasing to decreasing and then to increasing, but following an overall trend towards decreasing. The plasticity of Ti-Ni-based amorphous materials can be improved by adding Cu element in modest quantities (x≈25) to the Ti-Ni-based composites; however, adding more Cu (i.e., x>30) neither can improve the amorphous forming ability nor can enhance its strength. When x=15, the alloy has the highest breaking strength of 2440 MPa while gets the higher yield strength of 1471 MPa causing 17.15% plastic strain. The data are pretty high with respect to other amorphous systems or other alloy systems with memory of their shapes. When x=25, there is a certain increase in the alloy plastic strain with 21.35% plastic deformation.

Key words: amorphous composites; Cu content; microstructure; mechanical property

A category of substances composed of atoms and molecules in spatial arrangements that are not periodically ordered as in crystals with long-range symmetry and that retain certain ordered characteristics within only a little of interatomic spacing is known as amorphous materials[1]. Thanks to their excellent integrated properties, amorphous alloys have become a hotspot in the field of materials research[2-4]. For example, Ti-based amorphous alloys have excellent properties, such as light weight, high strength, and heat and corrosion resistance. Such amorphous alloys are playing an important role not only in civil aviation and space industries, but also in wide applications to medical apparatus and instruments, chemical, petroleum, light, metallurgy industrial sectors and so forth[5,6]. In recent decades, the researches into amorphous solids resulted in the discovery of ordered arrangements in disordered ones, and the seeking of simplexes and perfections from enormous complexities, thereby leading the new research orientation, and resulting in a lot of new concepts, ideas, methods, processes, models and theories, and material opinions[7]. Addition[8] is a method by adding metal particles or ceramic particles with high melting points to an alloy melt or alloy powder with high amorphous forming ability. It obtains the amorphous composites by a casting process or a hot pressed sintering process, while additional reinforcement phases can effectively control the amorphous matrix's plasticity and strength[9-11]. In the amorphous matrix's alloys, through adding different elements and controlling element contents added, the additional elements will greatly influence the microstructure and mechanical properties of the alloy ma-

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trix, introducing some modifications to the microstructure and mechanical properties of the alloy, such as strength, plasticity, and the like. We did the experimental research in order to study the effect of different contents of Cu element in $(Ti_{0.5}Ni_{0.5})_{100\text{-}x}Cu_x$ alloy system on the microstructure and mechanical properties of the matrix alloy. Ti-Ni-based amorphous composite materials prepared by the addition method were used in the present experiment, and their microstructure and mechanical properties were investigated as well.

1 Experiment

Element pieces with purity higher than 99.9% were used as starting materials. Ti-Ni-based amorphous composite specimens $(Ti_{0.5}Ni_{0.5})_{100\text{-}x}Cu_x$ which have different Cu contents but the same diameter were successfully prepared in the magnetic levitation melting process and the copper mold suction casting process during which the melting process of the master alloy under high purity argon protection conditions was carried out three times repeatedly. The microstructure and integrated mechanical properties of the materials were examined by X-ray diffraction (XRD), scanning electron microscope (SEM) and compression testing machine WDW-100J so as to assess the effects of the Cu contents (x=0, 10, 15, 20, 25, 30, 35, 40, at%) on the microstructure and mechanical properties of the amorphous composite materials.

2 Results and Discussion

2.1 XRD analysis on $(Ti_{0.5}Ni_{0.5})_{100\text{-}x}Cu_x$ alloy system

The composition of $(Ti_{0.5}Ni_{0.5})_{100\text{-}x}Cu_x$ alloy specimens was analyzed by XRD and the results are shown in Fig.1. The trend towards forming amorphous diffuse peaks is seen from the XRD pattern over the range of 2θ=40°~50°. As can be seen from the XRD detection results, different crystal phases are precipitated. It can be seen that those components ranging from x=0, 10, 15, 20, 25 are amorphous matrix composites, and the main precipitated phases are austenitic phase B2-Ti(Ni, Cu) and martensitic phase B19'-Ti(Ni, Cu), in which B2-Ti(Ni, Cu)'s structure is related to the plasticity and B19'-Ti(Ni, Cu)'s structure is related to the strength. These peaks are superimposed on the diffuse scattering peaks. It appears that sharp crystal diffraction peaks are given at around x=30, 35 and 2θ=40°~70°. As the trend of the diffuse scattering peaks disappearing, a crystal structure is created, while the precipitated crystal phases are martensite phase of B19'-Ti(Ni, Cu) and brittle Ni_3Ti intermetallic compound phase. The diffuse scattering peaks appear when x=40 and a new phase $CuNiTi_2$ precipitates at the same time. As can be seen from the pattern, the amorphous forming ability of $(Ti_{0.5}Ni_{0.5})_{100\text{-}x}Cu_x$ amorphous composite materials is the strongest at x=15. However, the amorphous forming ability of $(Ti_{0.5}Ni_{0.5})_{100\text{-}x}Cu_x$ amorphous composite materials decreases drastically at x=30, which is contributed to the precipitation of the crystal phase. But in turn, if increasing the content of Cu (x=40) continually, glass-forming ability of $(Ti_{0.5}Ni_{0.5})_{100\text{-}x}Cu_x$ amorphous composite materials increases. Overall, however, with the increasing of the content of Cu, the glass-forming ability of $(Ti_{0.5}Ni_{0.5})_{100\text{-}x}Cu_x$ amorphous composite materials will show a waveform change from increasing to decreasing and then to increasing, while their plasticity also presents a changing curve first upwards and then downwards.

2.2 Microstructure of $(Ti_{0.5}Ni_{0.5})_{100\text{-}x}Cu_x$ alloy systems

As can be seen from Fig.2, a substantial amorphous structure results from the direct contact with the outer wall of copper mold so as to different cooling rates of the rod sample during the cooling process. The cooling rate decreases gradually from surface to center, resulting in different contents of crystal phases. As can be seen by comparison with the figure, a dense structure in Fig.2a above shows that a large amount of dense structure amorphous phases are formed on the surface of the sample at a fast cooling rate; the dendrites and acicular martensite phases can be observed clearly from Fig.2b, which are related to the strength of the alloy materials. With the increase in annealing temperatures, the dendrites grow up gradually, whereas acicular martensite phases decrease. Finally, a large amount of austenite phases could be seen in the central part of the specimen because of a small cooling rate, producing a crystalline structure.

2.3 Mechanical properties of $(Ti_{0.5}Ni_{0.5})_{100\text{-}x}Cu_x$ alloy system

Table 1 represents the statistics on the yield strength (σ_s), fracture strength (σ_f) and plastic strain (ε_p) according to Fig.3. From Fig.1 and Fig.3, it may be concluded that the

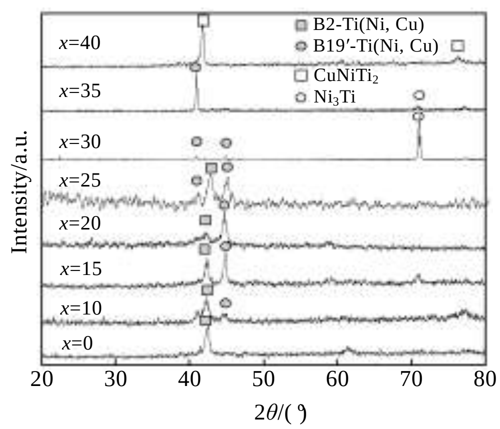

Fig.1 XRD patterns of as-cast $(Ti_{0.5}Ni_{0.5})_{100\text{-}x}Cu_x$ specimens

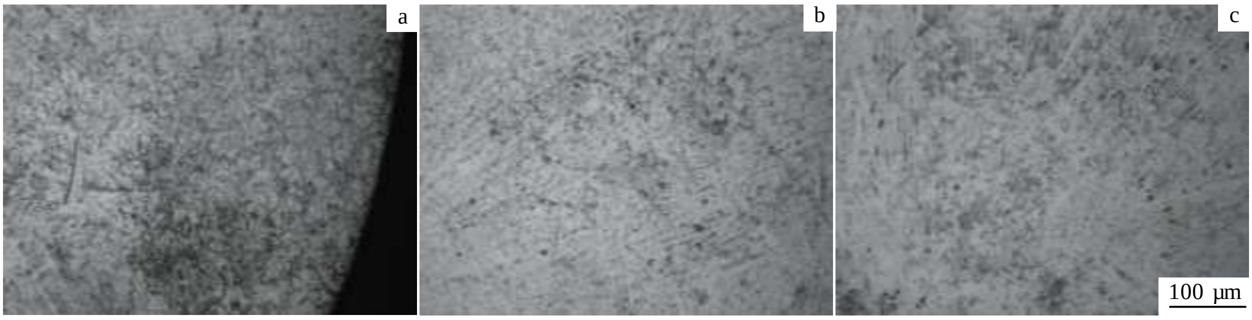

Fig.2 Metallographical structures of as-cast $Ti_{40}Ni_{40}Cu_{20}$ ternary alloy: (a) edge region, (b) transition region, and (c) center region

Table 1 Mechanical properties of $(Ti_{0.5}Ni_{0.5})_{100-x}Cu_x$ system

x	σ_s/MPa	σ_f/MPa	ε_p/%
0	1195	1893	13.54
10	2116	2226	10.23
15	1471	2440	17.15
20	1361	2235	18.31
25	660	2013	21.35
30	328	1018	14.26
35	610	806	7.69
40	1817	1817	-

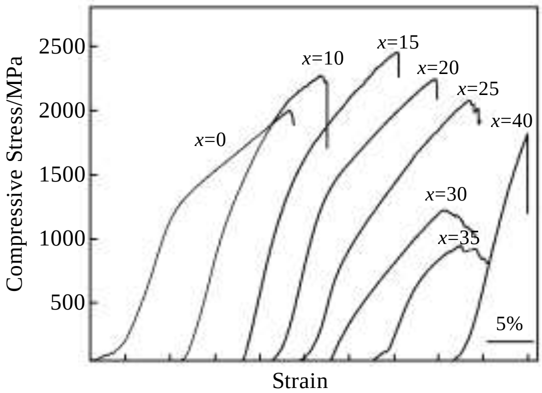

Fig.3 Compressive stress-strain curves of $(Ti_{0.5}Ni_{0.5})_{100-x}Cu_x$ system

strength increases along with an increase in the amorphous forming ability when the Cu content increases (x=0, 10, 15). Similarly, when x=20, 25, the strength decreases somewhat along with the decrease in the amorphous forming ability. As shown in Fig.1, when x=20, 25, the microstructure of composites consists of the amorphous matrix and shape-memory crystals; when x=25, amorphous formation ability decreases, while the shape memory crystals especially the austenite content increases. As a result, more austenites undergo a martensitic phase transition in the deformation process, that is, the transition induces plasticity effect. At x=30, 35, almost all of the crystal phases precipitate, providing a low strength, which is attributed to the existence of B19'-Ti(Ni, Cu) due to x=30, 35 while remaining some plasticity. There is a trend towards forming diffuse scattering peaks at x=40, and at the same time a new phase $CuNiTi_2$ precipitates, exhibiting the strength higher than those at x=30, 35, but little global plasticity of the sample as a whole. However, as can be seen from Table 1, in the range of x=20, amorphous composite materials possess both good plasticity and higher strength.

2.4 Fracture morphology of $(Ti_{0.5}Ni_{0.5})_{100-x}Cu_x$ alloy system

From Fig.4 we can see that when x=0, a typical veined structure can be clearly observed from the fracture surface so that there appears a small amount of small spheres similar to droplets in the middle of the veins, which are mainly generated by stress concentration. Highly localized shear bands induce a strain in the process of the compression, while the stress concentration has been accumulated in such shear bands. This is a morphology specific to amorphous structures. An inhomogeneous flow occurs in the microstructure of samples with x=10, 15, 20 and 25, resulting in shearing steps across the sample surface. There appear localized thin “vein lines” and multiple shear bands, but many flat and/or smooth surfaces. The experiments prove the samples to possess certain ductility. In other words, the sample has good plasticity which coincides with the plastic circle (following the elastic deformation stage) in the stress-strain curve, remaining consistent with the compression curve. In the x=30, 35 specimens, which are rough and uneven in their fracture surfaces, there is no obvious “vein line” but with the dimple-like characteristics feature. This is in conformity with the results from XRD test and the stress-strain curve. As compared with the amorphous fracture, it exhibits lower hardness and good plasticity, thus fitting with the compression curve. There is also a vein pattern in the microstructure of samples which is similar to amorphous

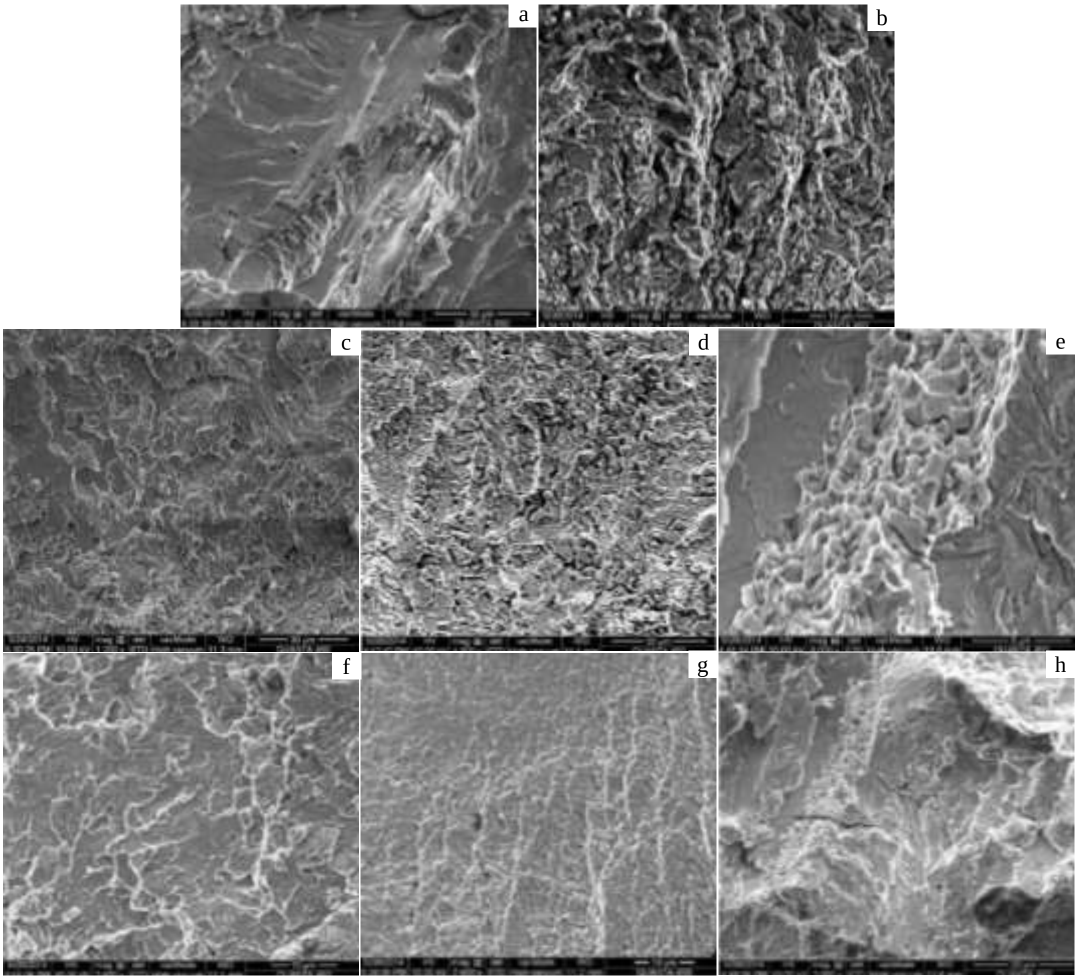

Fig.4 Fracture morphologies of $(Ti_{0.5}Ni_{0.5})_{100-x}Cu_x$ alloys: (a) x=0, (b) x=10, (c) x=15, (d) x=20, (e) x=25, (f) x=30, (g) x=35, and (h) x=40

alloys when x=40. Its fracture is brittle with rough/sparse vein patterns. The size of the plastic deformation in bulk amorphous alloy can be predicted on the number of shear bands, that is, the more the number of shear bands, the smaller the veins and the better the plasticity. From this we may certainly refer that the Cu content in the alloy specimen will influence both plasticity and strength of such a specimen. Therefore, it is concluded that the resultant plasticity with respect to $x\approx 25$ is the best and that both resultant plasticity and strength of the composite material are optimal in terms of $x\approx 25$. This is consistent with the results from the XRD test and stress-strain curves.

3 Conclusions

1) As a result of the increase in x value, the $(Ti_{0.5}Ni_{0.5})_{100-x}Cu_x$ alloys exhibit a waveform change to amorphous forming ability from increasing to decreasing and then to increasing, but totally decreasing.

2) The plasticity of Ti-Ni-based amorphous materials can be improved by adding a proper amount of Cu element ($x\approx$ 25) to the Ti-Ni matrix amorphous composites. However, adding more amounts (x>30) neither can improve the amorphous forming ability of the alloy nor can improve its strength. Consequently, within x=15, the alloy has the highest breaking strength of 2440 MPa, higher yield strength value of 1471 MPa, and 17.15% plastic strain. The data are very high compared with those of other amorphous systems or other alloy systems with memory of their shapes. While x=25, the alloy shows increasing plastic strain to some extent and the plastic deformation reaches 21.35%.

References

1 Wang W H. *Progress in Physics*[J], 2013, 33(5): 177 (in Chinese)

2 Makino A, Inoue A, Masumoto T. *Mater Trans JIM*[J], 1995, 36(7): 924

3 Zhang B, Zhao D Q, Pan M X *et al. Phys Rev Lett*[J], 2005, 94(20): 205 502

4 Wang M L, Hui X D, Feng Q *et al. Rare Metal Materials and Engineering*[J], 2013, 42(11): 2217
5 Suo Z Y, Song Y L, Qiu K Q. *Rare Metal Materials and Engineering*[J], 2014, 43(9): 2289 (in Chinese)
6 Inoue A, Takeuchi A. *Mater Trans*[J], 2002, 43(8): 1892
7 Busch R, Schroers J, Wang W H. *MRS Bull*[J], 2007, 32(8): 620
8 Pauly S, Gorantla S, Wang G *et al. Nature Materials*[J], 2010, 9(6): 473
9 Zhao Y C, Kou S Z, Li C Y *et al. Journal of Functional Materials*[J], 2013, 44(1): 88 (in Chinese)
10 Wu Y, Xiao Y H, Chen G L *et al. Adv Mater*[J], 2010, 22(25): 2770
11 Chen G, Bei H, Cao Y *et al. Appl Phys Lett*[J], 2009, 95(8): 081 908

Cu 含量对钛镍基非晶复合材料的组织和力学性能的影响

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摘　要：采用铜模吸铸法成功制备Cu含量不同但直径相同的TiNi基非晶复合材料试样 $(Ti_{0.5}Ni_{0.5})_{100-x}Cu_x$，研究Cu含量（$x$=0，10，15，20，25，30，35，40）对TiNi基非晶复合材料组织和力学性能的影响。试验结果表明，在铜的含量x=20时，合金断裂强度和塑性应变都很高，此时合金具有最优良的综合性能。随着x值的增大，$(Ti_{0.5}Ni_{0.5})_{100-x}Cu_x$合金的非晶形成能力呈现一个从上升、降低再到上升的波形变化，但总体呈现降低趋势。Cu元素在TiNi基复合材料中的适量添加（x≈25）可以提高TiNi基非晶材料的塑性，但添加量较多（x>30）时，既不能提高合金的非晶形成能力又不能提高合金的强度。在x=15时，合金有最高的断裂强度2440 MPa，达到了较高的屈服强度1471 MPa，且其产生了17.15%的塑性应变，在x=25时，合金塑性应变有所提高，塑性变形达到了21.35%。

关键词：非晶复合材料；Cu 含量；显微组织；力学性能

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