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SUPERCONDUCTIVITY OF DUCTILE TITANIUM-NIOBIUM-BASED AMORPHOUS ALLOYS

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INTRODUCTION

Superconducting materials possessing good mechanical properties as well as a high transition temperature (T_c) are desirable for applications. Since amorphous alloys exhibit superconductivity /1/ and high strength as well as good ductility compared to the crystalline alloys /2/, it is expected that a superconducting material possessing a high T_c as well as good mechanical properties may be obtained in the amorphous state. Further, it was recently shown /3/ that amorphous superconductors also possess a high tolerance to irradiation in contrast to their crystalline counterparts. From these points of view, we have investigated the composition ranges for the formation of amorphous phases and their superconducting properties in splat-quenched refractory metal-based alloys /4-13/ and reported that Ti-, Nb-, Mo- and W-based amorphous alloys exhibit superconductivity above the liquid helium temperature (4.2 K). More recently, with a view to get superior superconducting properties in these metastable alloys, we have carried out systematic experiments on the effect of additional elements on Ti-Nb-based amorphous alloys. This paper deals with aspects involving the composition range for the formation of the amorphous single phase in the Ti-Nb-Si-M (M=Mo, Ru, Rh, Pd, Ir, B, C and Ge) systems and the mechanical and superconducting properties of the amorphous alloys. These alloying elements were chosen to increase the average outer electron concentration (e/a) of the metal component, since T_c in the amorphous state was found to be closely related to the e/a showing a broad maximum around $e/a=6.5$ for the 4d and 5d transition-metal series /14/.

EXPERIMENTAL

The alloys were prepared from pure components under a protective argon atmosphere in an arc furnace. The ingots were repeatedly turned over and remelted to insure homogeneity of composition. Continuous ribbon specimens of about 1-2 mm width and

0.02-0.04 mm thickness were prepared from these parent alloys under a protective argon atmosphere using a modified single roller quenching apparatus adapted to a levitation furnace described in Ref. /5/. Typically, the amount of alloy melted in one run was about 3 g and the rotation speed of the copper roller (20 cm in diameter) was about 4000 rpm. Identification of the as-quenched phases was made by conventional X-ray diffraction and transmission electron microscopy techniques.

The superconducting transition was monitored by measuring the resistivity using a conventional four-probe method. The specimen current used was 1 mA. The temperature was measured with an accuracy of ± 0.05 K using a calibrated Au-Fe + Chromel thermocouple. The critical current was defined as the current at which a measurable voltage (1 μ V) appeared across a 50 mm-length specimen in a liquid helium bath at zero field. Upper and lower critical magnetic field (H_{c2} and H_{c1}) measurements were performed using a superconducting solenoid for magnetic fields up to about 7.2×10^6 A/m applied transversely to the specimen in a liquid helium bath.

RESULTS AND DISCUSSION

1. Formation range and mechanical properties of the amorphous alloys

Figures 1 and 2 show the formation range of amorphous single phase for the Ti-Nb-Si ternary and $Ti_{55-x}Nb_{30}M_xSi_{15}$ (M=Mo, Ru, Rh, Pd and Ir) and $Ti_{55}Nb_{30}Si_{15-x}M_x$ (M=B, C and Ge) quaternary systems. The amorphous phase forms in the wide range of 0-43 at.% Nb and 13-21 at.% Si for Ti-Nb-Si system and in the ranges of 0-7 at.% Mo, 0-25 at.% Ru, Rh or Pd and 0-11 at.% Ir for $Ti_{55-x}Nb_{30}M_xSi_{15}$ systems. Additionally, the amorphous single phase of the $Ti_{55}Nb_{30}Si_{15}$ alloy was retained even by the replacement of Si with B or C up to 7 at.% and Ge up to 4 at.%.

Vickers hardness and tensile fracture strength of the Ti-Nb-Si and Ti-Nb-Si-B amorphous alloys are

Fig. 1 Composition range for the formation of amorphous single phase in the Ti-Nb-Si system and the change in transition temperature (T_c) (marked by numbers on the open circles) of the amorphous alloys.

Alloy System (at.%)	Concentration of additional elements, X (at.%)			
	5	10	15	20
Ti _{55-x} Mo _x Nb ₃₀ Si ₁₅	Am.	Crystalline		
Ti _{55-x} Ru _x Nb ₃₀ Si ₁₅	Amorphous			
Ti _{55-x} Rh _x Nb ₃₀ Si ₁₅	Amorphous			
Ti _{55-x} Pd _x Nb ₃₀ Si ₁₅	Amorphous			
Ti _{55-x} Ir _x Nb ₃₀ Si ₁₅	Amorphous	Crystalline		
Ti ₅₅ Nb ₃₀ Si _{15-x} B _x	Am.	Crystalline		
Ti ₅₅ Nb ₃₀ Si _{15-x} C _x	Am.	Crystalline		
Ti ₅₅ Nb ₃₀ Si _{15-x} Ge _x	Am	Crystalline		

Fig. 2 Composition range for the formation of amorphous single phase in the Ti_{55-x}Nb₃₀M_xSi₁₅ (M=Mo, Ru, Rh, Pd and Ir) and Ti₅₅Nb₃₀Si_{15-x}M_x (M=B, C and Ge) systems.

about 570 DPN and 2040 MPa. Crystallization temperatures are in the range of 690–770 K. Further, all the amorphous alloys are so ductile that no crack is found at the tip of a specimen bent through 180°. These alloys continued to be ductile at least for 1 h at temperatures below 670 K.

2. Superconducting properties

2-1. Transition temperature (T_c)

As shown in Fig. 1, the Ti-Nb-Si alloys containing more than about 10 at.%Nb show a superconducting transition above liquid helium temperature (4.2 K). The T_c increases with increasing Nb content or decreasing Si content and reaches 5.1 K for the Ti₄₅Nb₄₀Si₁₅ alloy. Figure 3 shows the change in T_c of Ti_{55-x}Nb₃₀Mo_xSi₁₅ and Ti₅₅Nb₃₀Si_{15-x}M_x amorphous alloys with the concentration of additional elements. As seen in (a), the replacement of Ti by Mo results in a drastic decrease of T_c despite

Fig. 3 (a) change in transition temperature (T_c) of Ti_{55-x}Nb₃₀Mo_xSi₁₅ amorphous alloys by the replacement of Ti with Mo. (b) change in transition temperature (T_c) of Ti₅₅Nb₃₀Si_{15-x}M_x (M=B, C and Ge) amorphous alloys by the replacement of Si with M elements.

that the e/a of metal components in these amorphous alloys approaches the e/a corresponding to the expected maximum T_c . Superconducting transition could not be detected above 3.5 K when Ti is replaced by Ru, Rh, Pd or Ir. This result indicates that a plurality of alloy component is not an effective method for producing amorphous superconductors with a high T_c . On the other hand, as seen in (b), replacement of Si by B brings about a slight increase of T_c and the maximum value is 5.1 K for Ti₅₅Nb₃₀Si₁₀B₅ alloy. Further, one can notice that replacement of Si with C or Ge decreases T_c much less than in the case of the replacement of Ti by alloying elements. The above results indicate that an effective element for increasing T_c of Ti-Nb-Si amorphous alloys is only boron. Hence, our subsequent research was focused on the Ti-Nb-Si-B quaternary alloys.

The formation range of amorphous single phase and the T_c values for (Ti-Nb-Si)₉₇B₃ alloys are shown in Fig. 4, wherein the data of Vickers hardness are also presented. Similar to the (Ti-Nb)₈₅Si₁₅ alloys, the (Ti-Nb)₈₅Si₁₂B₃ amorphous alloys show a superconducting transition above 4.2 K in a

Fig. 4 Composition range for the formation of amorphous single phase in the Ti-Nb-Si-B system and the changes in transition temperature (T_c) and Vickers hardness (H_v) of the amorphous alloys.

limited composition range. The T_c value increases with increasing Nb content, attains 5.4 K for $Ti_{45}Nb_{40}Si_{12}B_3$ and decreases rapidly with further increasing Nb content. Such a Nb concentration dependence is similar to the tendency /15/ noted for crystalline Ti-Nb binary alloys, suggesting that the electron-phonon bare density of states at the Fermi level ($E_F=0$) $N(0)$, the electron-phonon coupling constant λ and the Debye temperature θ which play an important role in determining T_c /16/ change significantly in the range of 40-60 at.%Nb. The highest T_c value in this system is 5.5 K for the $Ti_{45}Nb_{40}Si_{10}B_5$ alloy.

The T_c values of Ti-Nb-Si and Ti-Nb-Si-B amorphous alloys are plotted as a function of the average e/a of the transition metal components in Fig. 5, wherein the data of the Nb- and Mo-based amorphous alloys obtained by the present authors /5, 6, 11/ are also included and compared with the variation of T_c for amorphous transition metals obtained by Collver and Hammond /14/ who employed the technique of thin film evaporation on a cryogenic substrate. From this figure, it is seen that the vari-

Fig. 5 Transition temperature (T_c) vs. electron per atom ratio for the Ti-Nb-Si and Ti-Nb-Si-B amorphous alloys. Also, the data of Nb-Si, Nb-Mo-Si, Nb-Zr-Si, Nb-Si-B and Mo-Si-B amorphous alloys are represented by solid circles.

ation of T_c with alloy composition for each alloy system is related apparently to the average e/a. Johnson et al. /17/ have shown for $(Mo-Ru)_{80}P_{20}$ amorphous alloys that such a change of T_c with e/a corresponds well to the change of the $N(0)$ with e/a. It is also to be noticed that the T_c values of the Nb- and Mo-based alloys lie below the Collver-Hammond curve. The observation that T_c values of melt-quenched alloys lie below the Collver-Hammond curve was also noted earlier for Mo- and Zr-based alloys /17-20/. This implies that when the transition metal components in the alloys are widely separated in e/a and/or the alloys contain metalloid elements, the T_c tends to fall below the Collver-Hammond curve for metals and alloys of neighboring metals. On the other hand, the T_c values of Ti-Nb-Si and Ti-Nb-Si-B alloys are above the Collver-Hammond curve. Although the reason for such a difference is uncertain at present, its origin may be found in one or both of the following two factors: (1) the mixing of the metal elements from different transition metal series, and (2) the oxygen content. Previous investigations /18/ and our present results (Fig. 3 a) show that mixing of two or more metal elements from different series results in a decrease of T_c of amorphous alloys. On the other hand, it has been reported /21/ that a small amount of oxygen can significantly raise T_c of crystalline Ti-Ta alloys. Thus, it is possible that the T_c higher than the value expected from Collver-Hammond curve may be due to a small amount of oxygen contained in the Ti-Nb-Si and Ti-Nb-Si-B amorphous alloys. It is hoped that systematic investigations, currently in progress, on the effect of oxygen or nitrogen on T_c will shed some light on this problem.

2-2. Critical magnetic field (H_c) and critical current density (J_c)

The lower and upper critical magnetic fields, H_{c1} and H_{c2} were measured at liquid helium temperature by a standard four-probe resistance method. The H_{c2} (onset) and H_{c1} (overall) values obtained are 4.9×10^6 A/m and 1.1×10^6 A/m for $Ti_{55}Nb_{30}Si_{12}B_3$ and 6.1×10^6 A/m and 8.8×10^5 A/m for $Ti_{45}Nb_{40}Si_{12}B_3$, following the general tendency /22/ that the higher the T_c , the higher is H_{c2} . Additionally, one can notice that the H_{c2} values are much higher compared with the H_{c1} values. This large difference has been considered to be due to the large Ginzburg-Landau parameter /23/. These results indicate that

the present amorphous alloys can be classified as type II superconductors.

The critical current density J_c was measured at external applied magnetic field (H) in a liquid helium bath. Figure 6 shows the critical current density J_c as a function of H for $\text{Ti}_{55}\text{Nb}_{30}\text{Si}_{12}\text{B}_3$ and $\text{Ti}_{45}\text{Nb}_{40}\text{Si}_{12}\text{B}_3$ amorphous alloys. For $H=0$, J_c is found to be about 450–480 A/cm². For $H>0$, J_c is observed to fall very rapidly with increasing H . For example, at $H=3.2 \times 10^6$ A/m (40 kOe), J_c is of the order 220 A/cm². Such small values of J_c indicate that flux pinning forces in these materials are comparatively weak.

Fig. 6 Critical current density (J_c) of $\text{Ti}_{55}\text{Nb}_{30}\text{Si}_{12}\text{B}_3$ and $\text{Ti}_{45}\text{Nb}_{40}\text{Si}_{12}\text{B}_3$ amorphous alloys as a function of magnetic field applied normal to the direction of current flow.

The superconducting properties (T_c and H_{c2}) of the amorphous alloys characterized in the present investigation are, within the authors' knowledge, the highest for ductile amorphous alloys showing complete bending, but are still insufficient for practical use. From the technological point of view, however, liquid-quenching makes the processing of superconducting materials much simpler. Especially, the existence of a readily obtainable amorphous phase in the Ti-Nb-Si and Ti-Nb-Si-B systems and the result /7/ that the superconducting properties of these amorphous alloys improve remarkably on crystallization offer alternative means of fabricating superconducting tapes or wires. In fact, Ti-Nb-Si-B alloys consisting of a duplex structure of amorphous and crystalline phases show superconducting properties much superior to those of completely amorphous alloys without a detectable loss of ductility /13/.

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