SUPERCONDUCTING PROPERTIES OF RAPIDLY QUENCHED AND HEAT TREATED Zr-V AND Hf-V FOILS

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ABSTRACT

The results of rapid quenching and subsequent heat treatments on the superconducting properties of the Zr-V and Hf-V binary systems are presented. Metallic glasses can be prepared in these systems which have very attractive properties for practical application. The existence of a flexible glassy phase raises the prospect of alternative methods for the construction of superconducting devices. As-quenched, partially crystalline material is characterized by small critical currents, yet relatively large upper critical fields and transition temperatures. Heat treatments considerably enhance the current carrying capability.

INTRODUCTION

Since the discovery of superconductivity in the Laves phase compound ZrV_2 by Matthias et al [1] and the illumination of the exceptional properties of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{V}_2$ by Inoue et al [2], the C-15 class of materials have been of great interest. From a practical standpoint, Inoue et al found for example that in the ternary system Hf-Zr-V, very large critical fields ($H_{c2} > 200$ kOe) and high critical currents ($J_c > 10^5 \text{ A/cm}^2$ at 4.2°K and $H_{\text{ext}} = 130$ kOe) could be obtained. It has also been demonstrated by Brown et al [3] that for HfV_2 unlike the A-15 compounds and Chevral phases the superconducting properties are not substantially degraded by exposure to fast neutrons [4]. These materials, therefore possess desirable characteristics for practical applications. As is the case for many materials which possess excellent superconducting properties, the Laves phase compounds are characteristically very brittle. The nature of the applications one imagines for these materials along with the A-15 compounds (Nb_3Sn , V_3Ga) requires that at some point in the fabrication process the materials display a considerable amount of mechanical flexibility.

Two methods for the construction of high field, high current superconducting devices presently being explored involve the use of composites [5-7] and metallic glasses. Composites are formed by incorporating the superconducting materials (Nb_3Sn or V_3Ga) in a matrix which has good mechanical properties, usually copper. This method has met with considerable success, for example recent experiments on $\text{Cu-V}_3\text{Ga}$ [5] composites have shown that for this material $H_{c2} (4.2^\circ\text{K}) = 224$ kOe, $T_c = 15.5^\circ\text{K}$, and $J_c (4.2^\circ\text{K}) = 2 \times 10^5 \text{ A/cm}^2$ at $H_{\text{ext}} = 40$ kOe. The metallic

glasses containing 4d and 5d transition metals [8-9] are somewhat unique high field superconducting materials in that they frequently exhibit excellent mechanical properties. Furthermore, recently there has been indications that they are highly resistant to damage by high energy neutrons [10].

In this investigation, I report the results of rapidly quenching Zr-V and Hf-V alloys. It is possible to prepare metallic glasses in these systems which possess very desirable mechanical properties. The nature of superconductivity and possible application and fabrication methods are discussed.

EXPERIMENTAL

Alloys were prepared by levitation melting in an Argon atmosphere of 99.99% pure Vanadium, 99.9% pure Zirconium (1.2% Hf) and 99.9% pure Hafnium (2% Zr). Of primary importance in the preparation of the alloys is the exclusion of Oxygen. This was especially true for the alloys with higher V content. The ingots were repeatedly broken open and remelted to insure homogeneity. Weight loss after the first melt was typically less than 1 mg in a 2 gram ingot, and the compositions reported are the nominal ones. The samples were rapidly quenched into circular foils approximately 1 cm in diameter and 30 μm thick by splat cooling [11] in a Helium atmosphere. Material quenched without paying strict attention to the exclusion of Oxygen resulted in brittle foils, frequently not amorphous. Similar behavior has also been observed in the Ti-Ni metallic glass system [12].

The nature of the as-quenched and heat treated foils was characterized

by conventional x-ray diffraction methods. The foils were classified amorphous when the x-ray intensity as a function of diffraction angle showed a smooth featureless band.

The superconducting transition temperatures were measured both inductively (T_C^{ind}) using an ac bridge circuit and resistively (T_C^R) using a standard four point probe. From these measurements, values for the onset of superconductivity as well as the midpoint of the transition were extracted. Values for several compositions of as-quenched foils are detailed in Table I. The upper critical magnetic field $H_{c2}(T)$ was measured by fixing the applied field normal to the direction of current flow in the sample and finding the temperature at which the resistivity reached half its normal value.

Samples for critical current (J_C) measurements were prepared by spot-welding pure gold pads to strips cut from the quenched foils. These samples were then sealed in evacuated quartz ampoules and heat treated at various temperatures for 24 hours as detailed in Table II. The samples were attached to the J_C probe by soldering the gold pads to two large copper bars. Both the sample and the copper bars were submerged in liquid helium (4.2°K). J_C was taken to be the current at which a measurable voltage (1 μ V) appeared across the sample. For several samples an external magnetic field from a 40 kOe Nb-Ti superconducting magnet was applied normal to the direction of current flow.

RESULTS AND DISCUSSION

An amorphous phase was found to be obtainable by splat cooling over a fairly broad range for both the Zr-V and Hf-V systems. Single phase

TABLE I. Superconducting transition temperature for as-quenched Zr-Hf-V foils.

SAMPLE	$T_C^{\text{ind}}(^{\circ}\text{K})$ ONSET	$T_C^{\text{ind}}(^{\circ}\text{K})$ $\frac{1}{2}$ point	$T_C^{\text{R}}(^{\circ}\text{K})$ $\frac{1}{2}$ point	PHASES PRESENT*
Zr ₇₀ V ₃₀	8.4	5.0	6.6	hcp, bcc, ZrV ₂
Zr ₆₄ V ₃₆	9.05	6.7	8.4	hcp, amorphous, bcc, ZrV ₂
Zr ₆₂ V ₃₈	9.0	4.4	5.2	amorphous, hcp, bcc, ZrV ₂
Zr ₆₀ V ₄₀		< 2.0	< 2.0	amorphous
Zr ₅₅ V ₄₅	7.5	4.9	5.6	amorphous, ZrV ₂ , bcc, hcp
ZrV ₂	9.3	8.2	8.2	ZrV ₂ , hcp, amorphous
Hf ₆₂ V ₃₈	9.2	6.9	7.2	amorphous, hcp, bcc, HfV ₂
Hf ₆₀ V ₄₀		< 2.0	< 2.0	amorphous

*The order of the phases is an indication of the relative amounts of each phase present. E.g. Zr₇₀V₃₀ is primarily hcp, some bcc, and a trace of ZrV₂.

amorphous material was obtained from 38% to 45% V. The x-ray patterns for these samples displayed a smooth broad band characteristic of metallic glasses. Below this region the as-quenched foils were found to consist of a combination of amorphous material, hcp $\text{Zr}(\text{Hf})$, bcc solid solution of $\text{Zr}(\text{Hf})$ and V, and the Laves phases $\text{Zr}(\text{Hf})\text{V}_2$. Above 45% V the foils consisted primarily of a mixture of $\text{Zr}(\text{Hf})\text{V}_2$ and an amorphous phase. The Bragg peaks associated with these phases were unusually broad indicating small crystal sizes. The foils were found to be at least partially amorphous from 34% to 66% V.

A considerable amount of work has been done on various Zr-based metallic glasses, primarily of the form Zr-LTM (LTM-late transition metals such as Pd, Rh, Cu, or Ni). The Zr-V and Hf-V glasses uncovered in the present study are in a sense quite unique in that both components are early transition metals. Preliminary results on their electrical and thermal properties indicate that they are very similar to the more conventional Zr-LTM glasses. An interesting fact discovered in this investigation is that the glass forming ability is strongly enhanced with small additions of Be and strongly degraded by small additions of Cu or Ni. This may suggest that the structure of the Zr-V and Hf-V glasses is closer to that of the Zr-Be glass than that of the Zr-Cu glass. A comprehensive study is now in progress on the properties and structure of the Zr-V and Hf-V glasses.

Superconductivity in the rapidly quenched materials, like the corresponding equilibrium alloys is highly dependent on the presence of the Laves phase compounds ZrV_2 and HfV_2 . Amorphous $\text{Zr}_{60}\text{V}_{40}$ and $\text{Hf}_{60}\text{V}_{40}$ were not found to be superconducting down to 2°K. Previous work [13] on hcp Zr-V and Hf-V as well as the corresponding bcc solid solution

has shown that they are not superconducting down to 4.2°K. It is difficult here to fix a value for T_C of the hcp or bcc phases since for all partially crystalline alloys quenched, some $Zr(Hf)V_2$ was formed, complicating the analysis of the T_C data. The small value for $J_C(H=0)$ at 4.2°K (Table II), yet relatively high T_C^R for a $Zr_{70}V_{30}$ foil which consisted of hcp, bcc, and a trace of ZrV_2 strongly suggest that the only supercurrent carrying phase present at 4.2°K is ZrV_2 .

The T_C values measured for the as-quenched materials have the same basic features. The onset values measured inductively are all close to the T_C of the Laves phase compound $Zr(Hf)V_2$. A slight depression of T_C occurs in those samples in which a sizable fraction of the sample is not superconducting. This is most noticeable for $Zr_{70}V_{30}$ (primarily hcp) and $Zr_{55}V_{45}$ (primarily amorphous). The widths of the transitions are all quite broad, reflecting the inhomogeneous nature of the samples. Superconductivity in the as-quenched foils can be understood as being due to the formation of the Laves phase compounds $Zr(Hf)V_2$. Those samples in which little $Zr(Hf)V_2$ was formed showed depressed T_C values and especially broad transitions. This is to be expected as being the result of the proximity effect [14] for a microstructure in which the superconducting particles are separated by substantially more than a coherence length. T_C^R is further depressed by the necessity of percolating a supercurrent path through the sample.

The data obtained from measuring H_{c2} of two as-quenched and two heat treated $Zr(Hf)$ -V foils is reproduced in Figure 1. The heat treated, fully crystallized foils of Hf_3V_2 and Zr_3V_2 displayed H_{c2} vs T curves in excellent agreement with previous work [15] on the HfV_2 and ZrV_2 compounds. As mentioned before, the pure amorphous foils were not found to

Fig. 1. Upper critical magnetic field as a function of temperature for several Zr-Hf-V foils. Open circles refer to fully crystallized foils and filled circles to as-quenched foils. The magnetic field is applied normal to the direction of current flow.

be superconducting. Samples in which there was a small amount of crystalline ZrV_2 are also shown in Figure 1. At high fields ($> 20 \text{ kOe}$) the as-quenched Zr_3V_2 and $\text{Zr}_{70}\text{V}_{30}$ samples have H_{c2} vs T curves which are linear, having roughly the same slope as the fully crystallized Zr_3V_2 foil and as-cast ZrV_2 . This behavior was found for all compositions studied which exhibited superconductivity. Together with the T_c data, this implies that ZrV_2 and HfV_2 formed as a result of rapid quenching retain the same superconducting characteristics they exhibit in as-cast alloys. The slight deviation from linearity near $T_c(H=0)$ and the depression of T_c for the as-quenched samples again represents the difficulty in percolating a supercurrent through these materials.

Critical current measurements on as-quenched and annealed samples demonstrate the need for having a substantial amount of the Laves phases present in order to obtain large J_c values. The results of the J_c measurements at 4.2°K and zero applied magnetic field are listed in Table II. The measurements on $\text{Zr}_{60}\text{V}_{40}$ as a function of heat treatment show that good current carrying capacity can be obtained after a 500°C , 24 hours treatment. The heat treatment parameters have not been extensively studied yet and some enhancement of J_c can be expected by a better heat treatment sequence.

Figure 2 shows the results of the application of an external field to $J_c(4.2^\circ\text{K})$ for a fully crystallized $\text{Zr}_{55}\text{V}_{45}$ sample. The dependence with field for J_c measured here is very similar to the result of Inoue et al [2] on $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{V}_2$. The somewhat smaller absolute values for J_c measured here ($\sim 5 \times 10^4$) compared to Inoue et al ($\sim 5 \times 10^5$) is most probably a manifestation of the higher V content as well as an indication that the annealing parameters are not yet optimal. A

TABLE II. Critical current of as-quenched and heat treated Zr-V foils.

SAMPLE	HEAT TREATMENT	J_c (H=0) at 4.2°K (Amps/cm ²)
Zr ₇₀ V ₃₀	as-quenched	1.8 x 10
Zr ₆₀ V ₄₀	as-quenched	0
Zr ₆₀ V ₄₀	200°C, 24 hours	0
Zr ₆₀ V ₄₀	300°C, 24 hours	7.3 x 10
Zr ₆₀ V ₄₀	400°C, 24 hours	8.7 x 10 ³
Zr ₆₀ V ₄₀	500°C, 24 hours	2.3 x 10 ⁴
Zr ₆₀ V ₄₀	600°C, 24 hours	2.0 x 10 ⁴
Zr ₅₅ V ₄₅	500°C, 24 hours	5.6 x 10 ⁴

Fig. 2. Critical current at 4.2°K as a function of magnetic field applied normal to the direction of current flow. The sample is a fully crystallized foil of $\text{Zr}_{55}\text{V}_{45}$.

detailed study of the formation and size of grains upon crystallization using an Electron Microscope as well as investigations into other flux pinning mechanisms is needed. It seems likely that with proper treatments these materials will have critical currents equal to or exceeding that reported by Inoue et al [2] for $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{V}_2$.

X-ray analysis of heat treated Zr-V foils indicates that heat treating at temperatures greater than 300°C eventually leads to the formation of ZrV_2 and hcp Zr. This is to be expected since these are the equilibrium phases for this system [16]. Similar to the as-quenched foils, the only supercurrent carrying phase in the heat treated foils is ZrV_2 . In terms of superconducting properties, the microstructures of the as-quenched and heat treated foils are similar. Both consist of a good superconducting compound (ZrV_2) dispersed in an essentially nonsuperconducting matrix. The rise in J_c for heat treated $\text{Zr}_{60}\text{V}_{40}$ foils as the heat treating temperature is increased (Table II) is accompanied by an increase in the fraction of ZrV_2 in the sample. The enhancement of J_c for heat treated foils observed is simply a consequence of having a larger fraction of ZrV_2 in the samples.

The results reported in this paper show promise for practical application. The existence of a readily obtainable amorphous phase in these systems offers alternative means of fabricating superconducting lines, transformers, and magnets. As-quenched material from ~ 38 to 45% V was frequently found to be very flexible. The low melting points for the Zr-V and Hf-V alloys makes them amenable to the now well developed techniques of melt spinning and amorphous powder and filament production. Melt spun ribbons could be plated with copper, placed into the proper application (e.g. magnet winding) and then heat treated to produce the

desired superconducting properties.

Amorphous powders and filaments of Zr(Hf)-V might be valuable starting materials for the construction of composites. The amorphous powder or filaments could be mixed with Cu powder and extruded into a wire. The ductile nature of the glassy metals would likely lead to the formation of very fine filaments upon deformation. Upon crystallization, the material goes from the nonequilibrium glassy phase to the equilibrium phases hcp Zr(Hf) and Zr(Hf)V_2 . With a proper choice of heat treating parameters it may be possible to produce a very fine grain structure. From the work on A-15 composites fine filaments and small grain sizes are of crucial importance in obtaining high critical currents [5-7]. Starting with amorphous powders or filaments it may thus be possible to produce microstructures not obtainable by standard metallurgical techniques.

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