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MASTER

FINAL REPORT

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to

LAWRENCE LIVERMORE LABORATORY

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Subject:

Subcontract No. 7210203

"DEVELOPMENT AND INITIAL CHARACTERIZATION
OF AMORPHOUS METALS RICH IN W AND/OR RE"

Program Period 10 - 1 - 77 to 9 - 30 - 78;

Authors

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FINAL REPORT

Subcontract No. 7210203 to Northeastern University from Lawrence Livermore Laboratory; Program Period 10-1-77 to 9-30-78.

Some of the work treated in this report is a continuation of work carried out in the previous report period, which is covered by Report UCRL 13787.

I. Areas of Study

In the contract period, studies were made in the following areas covered by this contract:

1. Preparation and characterization of high-density amorphous metals consisting of alloys of W and Re with metalloid element additions.
2. Preparation and characterization of high-density amorphous metals consisting of alloys of Nb and Ta (T_5) with Rh and Ir (T_9).
3. Participation in study of thermal properties of amorphous actinide metals based on U, Np, and Pu.

II. Experimental and Other Studies

Specifically, the following work was done:

1. In this period, studies of refractory metal alloys concentrated on two families of such alloys: ternary tungsten alloys and binary T_5 - T_9 alloys. The former were selected because of the possibility of finding desirable glasses consisting of low-cost components; the latter were chosen because they could be quenched into metallic glasses with high thermal stability and good toughness, as had been established by work in the previous period.
2. Alloys selected for study were prepared by arc-melting and were

subsequently rapidly quenched in an arc furnace quenching unit. The modifications of the arc furnace quenching process introduced in the last program and described in Ref. 1 were utilized for these experiments.

We continued to encounter considerable difficulties in preparing metal-metalloid alloys, such as W-B, as well as alloys combining high melting and low melting transition metals, such as W and Ni. The quenching experiments were repeated frequently as there are variations in the cooling rate obtained by this method. All samples were studied by X-ray diffraction; the patterns were examined especially to determine any partial crystallinity. Brittleness or ductility as revealed by a bend test was also noted. DSC measurements were made up to 1000 K and resistivity measurements (see below) up to 1300 K.

3. The probe for electrical resistivity measurements at high temperatures mentioned in the previous report has now been constructed and tested. It had been designed specifically for the short specimens of metallic glass (about 10 mm long) typically obtained by rapid liquid quenching using the hammer-and-anvil method; it can be operated in a vacuum of $\sim 20\mu$ Hg up to >1300 K.

Heating rates presently available with this unit decrease from about 20 K/min at 400 K to 1 K/min at 1250 K. The unit was used to determine the thermal stability of all refractory metal glasses which had crystallization temperatures (T_c) exceeding

the range of the DSC 2 calorimeter; T_c was obtained from the resistance drop taking place at that temperature. An approximate value for the resistivity and the temperature coefficient of the resistivity were also obtained in this measurement.

4. To determine the elastic (Young's) moduli of new metallic glasses prepared in this program, equipment utilizing the pulse-echo method has been set up. In its present form (and as used by other workers relying on this technique) the equipment permits the determination of E for long (melt-spun) ribbons; a modification to adapt this method for short, arc furnace quenched samples was therefore necessary for the present program. Such a technique, the "impulse-induced resonance" (IIR) method was subsequently developed under a different program. With the help of this method, the elastic moduli of several glass samples prepared under the present program have been measured, as reported below.
5. Interaction with a program on amorphous actinide metal alloys ongoing at Los Alamos Scientific Laboratory has been continued. As previously, diffraction patterns and DSC data obtained on metallic glasses prepared at LASL were analyzed at NU. Results are reported below.

III. Summary of Results

1. In the course of the comprehensive study² of the refractory binary alloy glasses with compositions lying in the four homologous T_5 - T_9 systems Nb-Rh, Ta-Rh, Nb-Ir, Ta-Ir, the composition range was determined in which glasses can be formed by the arc

furnace quenching method; it was generally found to range from ~40 at.% T_g to ~50 at.% T_g . The glass forming compositions are listed in Table I. Further, crystallization temperatures T_c and Vickers microhardness H_v values were determined for glasses from all four systems having the composition $(T_5)_{.55}(T_9)_{.45}$; the results were correlated with each other as well as with the melting points of the crystalline alloys, averaged component melting points and averaged Young's moduli of the components. Approximately linear relations between T_c and H_v as well as between T_c (or H_v) and the three parameters of the components listed above were found to exist.

These results are especially significant because the local atomic environments of all four glasses can be assumed to be identical; hence all property changes must be due to changes of the inter-atomic forces which, as the results show, can be related simply to approximate properties of the components.

2. A number of metallic glasses were prepared besides those discussed above; a listing is provided in Table II. In addition, some alloys were prepared but could not be retained as glasses despite multiple attempts; these are also listed in Table II. Other W-Ir-B alloys and several W-Fe-B alloys were prepared; it was not established whether these alloys form glasses. The Re-containing glasses listed in Table II are brittle; the T_5 - T_9 glasses listed are malleable and tough; other glasses lie in between. Glasses containing fractions of crystalline material tend to be brittle.
3. The electrical resistivities and their temperature coefficients

(TCR) were measured for a series of $(T_5)_{.55}(T_9)_{.45}$ glasses; the TCR values were found to be negative for all of these glassy alloys. Values are given in Table III. A publication containing these results is in progress³.

4. Measurement of the Young's moduli E for the homologous series of $(T_5)_{.55}(T_9)_{.45}$ glasses discussed above using the impulse-induced resonance technique for short samples described above have been completed. Results are given in Table II and will be published³.
5. The formation of glasses based on the actinide metals U, Np and Pu and containing Mn, Fe, Co, Ni, and other metals (T) had been reported in the previous period. In the present period, these results were extended to some other glass forming addition T elements and consolidated into a comprehensive publication⁴. These amorphous metals are listed in Table IV. The principal results of this work were: (a) the determination of the valences and sizes of the actinide metal elements in these glasses, and (b) the attribution of ready glass formation of actinide element alloys to the presence of f-electron bonding in these alloys which energetically favors low-symmetry crystal structures and the molten state, resulting in low melting temperatures relative to the vaporization energy. Further, a follow-up study⁵ was made on U glasses; several glasses with a range of compositions in systems of U with Cr, Mn, Fe, Co and Ni were studied. The crystallization temperatures T_c of these glasses were determined; the glasses and their properties

are listed in Table V. The crystallization behavior for many of these alloys was complex, proceeding in several steps; the T_c values for the initial crystallization could be correlated with the elastic moduli and atomic volume of the addition elements⁵.

IV. Publications

1. M. Fischer, D.E. Polk and B.C. Giessen: Refractory Metallic Glasses Prepared by an Arc Furnace Quenching Unit, in Rapid Solidification Processing, Principles, and Technology, R. Mehrabian, B.H. Kear and M. Cohen, Eds., Claitor's Publ. Div., Baton Rouge, La., p. 140 (1978).
2. S. Davis, M. Fischer, B.C. Giessen and D.E. Polk: Formation and Properties of Refractory Metal Glasses II: T_5 - T_9 Glasses (T_5 = Nb, Ta; T_9 = Rh, Ir), in Rapidly Quenched Metals III, Vol. 2, ed. B. Cantor, The Metals Society, London, p. 425 (1978).
3. B.C. Giessen, M. Fischer, D.E. Polk and S.H. Whang: Young's Moduli and Electrical Resistivities of T_5 - T_9 Glasses (T_5 = Nb, Ta; T_9 = Rh, Ir), to be published.
4. R.O. Elliott and B.C. Giessen: F-Electron Enhanced Glass-Forming Ability of Actinide Alloys: New Metallic Glasses Rich in U, Np, and Pu, *Acta Met.*, accepted.
5. B.C. Giessen and R.O. Elliott: Properties of Metallic Glasses Containing Actinide Metals: I. Thermal Properties of U-M Glasses (M = V, Cr, Mn, Fe, Co and Ni), Rapidly Quenched Metals III, Vol. 1, ed. B. Cantor, The Metals Society, London, p. 406 (1978).

V. Presentations

1. M. Fischer, D. E. Polk and B. C. Giessen: Refractory Metallic Glasses Prepared by an Arc Furnace Quenching Unit, Intl. Conf. on Rapid Solidification Processing, Reston, Va., November 1977.
2. B. C. Giessen, S. Davis, R. O. Elliott, M. Fischer, J. Hong, D. E. Polk and R. St. Armand: Formation and Stability of New Metallic Glasses, Conf. on Dense Random Packing, Liege, Belgium, October 1978.
3. S. Davis, M. Fischer, B. C. Giessen and D. E. Polk: Formation and Properties of Refractory Metal Glasses II: T₅-T_g Glasses (T₅ = Nb, Ta; T_g = Rh, Ir), 3rd Intl. Conf. on Rapidly Quenched Metals, Brighton, July 1978.
4. B. C. Giessen and R. O. Elliott: Properties of Metallic Glasses Containing Actinide Metals: I. Thermal Properties of U-M Glasses (M = V, Cr, Mn, Fe, Co, and Ni), 3rd Intl. Conf. on Rapidly Quenched Metals, Brighton, July 1978.

Table 1: Glass Formation Upon
Arc Furnace Quenching in T_5 - T_9 Alloy Systems

Alloy Composition	Equilibrium Structure at T_E	Extent of Central Structure after Minimum G.F. Range Two Phase Field at T_E and at 300 K (at.pct. T_9)	Rapid Quenching in T_5 - T_9 System (at.pct. T_9)
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Nb. ₆₅ Rh. ₃₅	σ		σ
Nb. ₆₀ Rh. ₄₀	$\sigma + \alpha_1$		A.M.
Nb. ₅₅ Rh. ₄₅	$\sigma + \alpha_1$	$\left\{ \begin{array}{c} 39 \text{ to } 46.5 \\ 39.5 \text{ to } 51.5 \end{array} \right\}$	A.M. $\left\{ \begin{array}{c} < 40 \\ \text{to} \\ > 51 \end{array} \right\}$
Nb. ₅₀ Rh. ₅₀	α_1		cryst. (α_1 ?)
Nb. ₄₈₅ Rh. ₅₁₅	α_1		A.M.
Ta. ₆₅ Rh. ₃₅	σ		σ
Ta. ₆₀ Rh. ₄₀	σ		A.M.+tr.cryst.
Ta. ₅₅ Rh. ₄₅	$\sigma + \alpha_3$	$\left\{ \begin{array}{c} 40 \text{ to } 49 \\ \sim 38 \text{ to } \sim 54 \end{array} \right\}$	A.M. $\left\{ \begin{array}{c} \sim 40 \\ \text{to} \\ \sim 50 \end{array} \right\}$
Ta. ₅₀ Rh. ₅₀	α_3		A.M.+tr.cryst.
Ta. ₄₆₅ Rh. ₅₃₅	α_3		cryst.
Ta. ₄₅ Rh. ₅₅	α_3		cryst.
Nb. ₆₀ Ir. ₄₀	σ		σ
Nb. ₅₇₅ Ir. ₄₂₅	$\sigma + \alpha_1$		A.M.+tr. cryst.
Nb. ₅₅ Ir. ₄₅	$\sigma + \alpha_1$	$\left\{ \begin{array}{c} 41.5 \text{ to } 52.0 \\ \sim 41 \text{ to } 52 \end{array} \right\}$	A.M. $\left\{ \begin{array}{c} \sim 43 \\ \text{to} \\ < 55 \end{array} \right\}$
Nb. ₅₀ Ir. ₅₀	$\sigma + \alpha_1$		A.M.
Nb. ₄₅ Ir. ₅₅	α_2		A.M.+cryst. (major)
Ta. ₆₅ Ir. ₃₅	σ		σ
Ta. ₆₂₅ Ir. ₃₇₅	σ		A.M.+tr.cryst.
Ta. ₆₀ Ir. ₄₀	σ	$\left\{ \begin{array}{c} 41 \text{ to } 50.4 \\ \sim 35 \text{ to } \sim 51.5 \end{array} \right\}$	A.M.+tr.cryst. $\left\{ \begin{array}{c} \sim 38 \\ \text{to} \\ \sim 52 \end{array} \right\}$
Ta. ₅₅ Ir. ₄₅	$\sigma + \alpha_1$		A.M.
Ta. ₅₀ Ir. ₅₀	α_1		A.M.
Ta. ₄₇₅ Ir. ₅₂₅	α_1		A.M.+tr.cryst.

TABLE II

Results of Rapid Quenching Experiments on Refractory Metal Alloys
(Excluding T₅ - T₉ Alloys)

A. Glass Forming Alloys

W. _{.62} Co. _{.15} B. _{.23}	amorphous with some bcc phase
W. _{.60} Rh. _{.20} B. _{.20}	amorphous with some bcc phase
W. _{.60} Ir. _{.20} B. _{.20}	amorphous
Ta. _{.30} Ir. _{.50} B. _{.20}	amorphous
Re. _{.60} B. _{.40}	amorphous with trace of crystalline phase
Re. _{.65} Si. _{.35}	amorphous

B. Non Glass Forming Alloys

W. _{.60} C. _{.40}
Re. _{.73} Si. _{.27}
Re. _{.70} Si. _{.30}

TABLE III

Electrical Resistivities and Young's Moduli of $T_5 - T_9$ Glasses

Alloy	ρ ($\mu\Omega\text{cm}$)	$\frac{1}{\rho} \frac{d\rho}{dT} \cdot 10^4$ (K^{-1})	E (10^{11} dyne cm^{-2})
Nb _{.55} Rh _{.45}	137	-0.74	12.26
Nb _{.55} Ir _{.45}	159	-0.8	15.06
Ta _{.55} Rh _{.45}	169	-1.1	14.85
Ta _{.55} Ir _{.45}	192	-1.9	16.91

Note: ρ values accurate to $\pm 10\%$.

Table IV

New Amorphous Actinide Metal Alloys $Ac_{1-x}M_x$ Prepared by Rapid Quenching from the Liquid

Alloy System	Quenching Method	Glass-Forming Composition (at.% M)	T_{ex} (°K)	Eutectic Temp. T_E (°K)	Eutectic Comp. x_E (at.% M)	Radius Ratio r_{Ac}/r_M	Comments
U-Mn	AQ ^a	30	~610	989	22	1.24 ^b	
U-Fe	AQ	33	~570	998	34	1.26	
U-Co	AQ	33	~555	1007	34	1.25	
U-Ni	AQ	33	~600	1013	33	1.24	
Np-Mn	SQ ^a	13.9	ND ^a	---	---	1.21; ^b 1.24 ^c	+ 30% unknown phase
Np-Fe	SQ	14.3	ND	---	---	1.23; 1.26	
Np-Co	SQ	14.3	ND	---	---	1.22; 1.25	
Np-Ni	SQ	14.3	ND	---	---	1.21; 1.24	Glass formation uncertain
Np-Cu	SQ	---	---	---	---	1.18; 1.24	No glass formation at 14.3 at.% Cu
Np-Ga	SQ	30 to 40	ND	---	---	1.06; 1.09	
Pu-Mn	SQ	~10 to >14	ND	798	10	1.27 ^b	
Pu-Fe	SQ	~15 to >20	ND	678	10	1.28	Glass formation not observed at 20% Co; assumed due to poor quench
Pu-Co	SQ	---	---	673	12	1.28	
Pu-Ni	SQ	~12 to >30	~425(20%)	738	12	1.27	
Pu-Cu	SQ	~14 to <20	ND	899	5	1.24	
Pu-Ru	AQ	20	ND	801	12	1.18	+ e-Pu solid solution
<u>Previously Reported Actinide Glasses</u>							
U-V	MS ^{a,d}	20 to 40 ^d	>773 ^d	1313	18	1.15 ^b	
U-Cr	MS ^{a,d}	20 to 40 ^d	>773 ^d	1132	19	1.20	

^aAQ = arc-furnace quenching; SQ = splat-quenching; MS = melt spinning; ND = not determined.^bFor Ac radii: $\gamma(U)$, Ref. 23; $\gamma(Np)$, Ref. 12; $e(Pu)$, Ref. 11. For transition-metal radii: values as appropriate for nonmagnetic phases containing these elements as minor components (see Ref. 22, pp. 156-158).^cRadius of Np corrected for "valence change," Refs. 12 and 13 (see text).^dRef. 8.

Table V

Results of Differential Scanning Calorimetry of Arc-Quenched U-M (M = V, Cr, Mn, Fe, Co, and Ni)
(Heating rate $\dot{T}$ = 40 K/min)

Composition (at.pct. M)	Structure after Arc-Quenching ^a	Equilibrium Structure	Exothermic Effects (K) and Est. ΔH (% of total $\Delta H_{\text{cryst.}}$)			Endothermic Effect (K) (Tentative)	T_E (K)	$T_E - T_{C1}$ (K)	T_{C1}/T_E
			1.	2.	3.				
27 V	γ -U s.s.+A.M. (minor) + α -U (?) (minor)	γ -U+V	658 (100);	-	-	-	1313	655	0.50
27 Cr	A.M.	γ -U+Cr	684 (100);	-	-	-	1132	448	0.60
20 Mn	A.M.+ α -U+U ₆ Mn (trace)	U ₆ Mn+UMn ₂	578 (24) ^b ;	642 (76) ^b ;	-	-	989	384	0.61
25.5 Mn	A.M.+U ₆ Mn (?) + U.P. (trace)	"	605 (46) ^b ;	695 (54) ^b ;	-	-	"		
30 Mn	A.M.+U.P. (trace)	"	605 (75) ^b ;	677 (25) ^b ;	-	-	"		
35.3 Mn	A.M.+U.P. (trace)	"	593 (50) ^b ;	745 (50) ^b ;	-	-	"		
20 Fe	A.M.+U ₆ Fe s.s. (minor)	U ₆ Fe+UFe ₂	553 (100);	-	-	541	998	438	0.56
27 Fe	A.M.+U ₆ Fe s.s. (minor)	"	560 (100);	-	-	527	"		
33 Fe	A.M.+U ₆ Fe s.s. (trace)	"	566 (100);	-	-	-	"		
40 Fe	A.M.+U.P. (trace)	"	560 (32);	584 (68);	-	-	"		
20 Co	U ₆ Co s.s.+A.M. (minor)	U ₆ Co+UCo	545 (85);	575 (5);	585 (10)	-	1007	453	0.55
27 Co	A.M.+U ₆ Co s.s. (trace)	"	554 (55);	563 (13);	578 (30)	527	"		
33 Co	A.M.+U.P.	"	554 (40);	573 (60);	-	533	"		
40 Co	A.M.+U.P.	"	555 (25);	588 (75);	-	530	"		
20 Ni	α -U+U.P. (trace)+ A.M. (trace)	U ₆ Ni+UNi _x	613 (21) ^{b,d} ;	645 (79) ^{b,d} ;	-	593	1013	436	0.57
27 Ni	A.M.+ α -U (minor)	"	577 (-) ^c ;	632 (-) ^c ;	693 (-) ^c	-	"		
33 Ni	A.M.+U.P. (trace)	"	599 (20);	641 (38);	677 (42)	-	"		
40 Ni	A.M.+U.P. (minor)	"	613 (15);	663 (73);	683 (12)	-	"		

Notes: a s.s. = solid solution; U.P. = unidentified crystalline phase; A.M. = amorphous metal.

b Averages of two measurements.

c ΔH_1 and hence ΔH_{Total} not obtained; $\Delta H_1/\Delta H_2 = 38/62$.

d Alloy largely crystalline; exotherms not plotted in Fig. 1.

Appendices

Copies of published and submitted papers (References 1, 2, 4 and 5).

REFRACTORY METALLIC GLASSES PREPARED BY AN ARC FURNACE QUENCHING UNIT

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Abstract

In the course of a development program for metallic glasses of high strength and thermal stability, alloys of transition metals with high elastic moduli, such as W, Re, Rh and Ir, and other elements, such as B, Si, Ta and Nb, were rapidly quenched using an arc-furnace quenching unit. The "hammer-and-anvil" arc-furnace quenching unit used is described; it utilizes a stationary copper hearth as "anvil" and a movable plunger as "hammer". Modifications of previously described, similar devices are discussed which are required to obtain optimally quenched thin foil specimens of refractory metals. Six new metallic glasses, $\text{Nb}_{.55}\text{Ir}_{.45}$, $\text{Ta}_{.55}\text{Rh}_{.45}$, $\text{Ta}_{.55}\text{Ir}_{.45}$, $\text{Re}_{.65}\text{Si}_{.35}$, $\text{Ta}_{.10}\text{Ir}_{.90}\text{B}_{.20}$ and $\text{W}_{.60}\text{Ir}_{.40}\text{B}_{.20}$, were prepared; limits for their crystallization temperatures and their Vickers microhardnesses were determined. A seventh amorphous solid, $\text{Nb}_{.60}\text{Rh}_{.40}$, had been prepared earlier but was then described as microcrystalline.

The relation of glass formation in binary systems to phase diagram features such as melting point depression and compositional vicinity to equilibrium phases with complex coordination such as β phase is examined; atomic size ratios are also considered. The effect of ternary metalloid element additions to inter-transition metal alloys on glass formation is discussed. Correlations between the crystallization temperatures and the microhardnesses of the glasses and the melting points of the alloys were observed; further, the microhardness values were found to be correlated to the averaged elastic moduli of the alloy constituents.

* Communication No. 24 from the Institute of Chemical Analysis, Applications and Forensic Science

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Fig. 1 Arc furnace quenching apparatus used in this study (see text).

metals and does not require a ceramic crucible capable of containing the melt. The basic unit used was supplied by Centorr Assoc., Suncook, N.H.

The melting and quenching is done within a central glass cylinder which has been evacuated and filled with argon. An arc is struck between the upper electrode and the lower block, the "anvil", which is water cooled. This arc is then directed at the small sample of the alloy of interest so as to melt it. The "hammer" poised above the sample is then propelled downward as the arc is turned off so as to spread the molten droplet into a thin layer between the hammer and the anvil whereupon it solidifies as heat is conducted from it.

Experience with the arc furnace quenching unit has shown that its efficacy varies with several experimental parameters including sample size and hammer velocity. It was further noted that the quench rate which is obtained is not fully reproducible; while alloys which form a glass at a relatively low quench rate will always be amorphous upon quenching, those requiring rates near the maximum attainable may be amorphous, partly amorphous, or crystalline after quenching.

In the case of the refractory alloys, it was found best to use rather small sample sizes, typically $\sim 2 \text{ mm}^3$. This appears to be necessary in view of the high melting temperatures to obtain the small sample thicknesses required for high cooling rates.

It has been observed that the quenching effectiveness increases as the surfaces of the hammer and of the anvil are made smoother and flatter. Both pieces A & B in Fig. 1 can be removed for ready mechanical polishing. As importantly, the surfaces must be parallel when they flatten the sample droplet. Because of the entire bottom section being lowered in order to place the sample in the unit, the small tolerances resulting from the low foil thicknesses, and the small but still significant horizontal movement possible in the shaft holding the hammer, exact prealignment of the two surfaces is not

thought to be practical. Instead, part A is attached to the threaded shaft such that it is slightly flexible; prealignment is adequate to produce spreading of the liquid before hard contact occurs while the flexible attachment allows full alignment upon impact.

Further, the especially high melting points of the alloys present additional difficulties. Upon melting very small pieces of the alloy for quenching, it was observed that the droplet sometimes reacted with the substrate. Such reaction was found to increase as the time during which the sample was molten increased. Thus, it was attempted to use as short a melting time as possible for the quenching process. A further approach taken to avoid reactions of the liquid metal droplet with the Cu substrate consisted of using an iron substrate as the "anvil" plate. Due to the lower electrical and thermal conductivities of iron compared to those of copper the iron was locally melted by the arc and this approach was abandoned.

A discussion of design considerations for hammer-and-anvil quenching devices using horizontally propelled plates has been given by Cahn et al.⁽¹⁴⁾ and a theoretical study of operation parameters for such a system was made by Blötry.⁽¹⁵⁾ The actual cooling rate achieved by the present quenching procedure is not known. However, it is comparable to that obtained with a number of other rapid quenching devices capable of preparing amorphous metals.^(6,16,17) Thus, in an earlier investigation of glass formation in the Ti-Ni-Si system,⁽¹⁸⁾ it was deduced that arc-furnace quenching produced a higher quench rate than melt spinning since some alloy compositions which did not form a glass upon melt spinning⁽¹⁹⁾ (i.e. which were not quenched rapidly enough to form a glass) did form a glass upon arc-furnace quenching for similar sample thicknesses. The higher cooling rate of arc-furnace quenching may be due in part to the two-sided cooling and potentially higher surface heat transfer coefficient resulting from the more intimate specimen-substrate contact inherent in the hammer-and-anvil cooling.

Results and Discussion

New Amorphous Refractory Metal Alloys: The combination of the requirements that the alloy have high elastic constants and that its composition be relatively low melting so as to have a high probability of forming a glass severely restricts the number of alloy systems which are of primary interest. A consideration of the potential systems suggests that alloys containing W, Re, Ir and Rh in combinations with each other and/or combined with elements such as B, C, Si, Ta, and Nb may satisfy the criteria. For example, alloys based on the eutectics in the W-Ir, W-B, W-Re, W-Rh, and Ta-Ir systems are of special interest, especially when a third suitably selected element is added to further enhance the ease of glass formation.

A limited number of such alloys were subjected to arc-furnace quenching. Alloys which were found to form an amorphous phase upon quenching are listed in Table I. They are classified and discussed from an alloy chemical viewpoint in the following section. Amorphous Nb-Rh alloys had been prepared earlier,⁽²⁰⁾ although at that time they were characterized as being microcrystalline. The second column of Table I gives the melting points or melting intervals for the five binary alloys and the third column lists preliminary data on the thermal stability of the glasses obtained as discussed above. Accordingly, T_c values fall into three ranges $T_c < 820^\circ\text{C}$, $820^\circ\text{C} < T_c < 950^\circ\text{C}$, and $T_c > 950^\circ\text{C}$. The lower limit for T_c of the Re-Si glass was obtained from the limit of operation of a DSC2 calorimeter; the actual value of T_c can be expected to be substantially higher, based on the melting point and microhardness correlation given below.

TABLE I
COMPOSITIONS AND PROPERTIES OF REFRACTORY METAL BASED AMORPHOUS ALLOYS

Alloy Composition	Melting Temperature T_m (°C)*	Crystallization Temperature T_c (°C)**	Vickers Hardness H_v (kg/mm ²)***
Nb _{.60} Rh _{.40} ⁺	1500, 1580	$T_c < 820$	730 ± 40
Nb _{.55} Ir _{.45}	1840	$820 < T_c < 950$	910 ± 30
Ta _{.55} Rh _{.45}	1740	$820 < T_c < 950$	805 ± 40
Ta _{.555} Ir _{.445}	1950	$T_c < 950$	-
Re _{.65} Si _{.35}	~1900, ~1950	$T_c < 730$	1040 ± 60
Ta _{.30} Ir _{.50} B _{.20}	-	$820 < T_c < 950$	1340 ± 70
W _{.60} Ir _{.20} B _{.20}	-	Partially crystallized at 950°C	1290 ± 70

* two numbers indicate solidus and liquidus temperature, respectively.

** range of T_c determined by isothermal anneals for 5 min at given temperature, except for Re_{.65}Si_{.35} where value is upper limit of DSC measurement made at 80 K/min.

*** values represent lower limits, see text.

+ previously reported as microcrystalline phase by Johnson and Fuoss. (20)

Also shown in Table I are the hardnesses measured for these samples; these numbers are expected to be lower limits because the foils are rather thin. For example, the W_{.60}Ir_{.20}B_{.20} foil was 12-14 μ m thick, which is only about 5 times the depth of the indentation. Thus, true hardnesses may be significantly higher.

The ductility of amorphous metals is difficult to judge on the basis of samples made by air-furnace quenching since the ductility often varies with the details of the quenching process. However, the Nb-Rh, Nb-Ir, Ta-Rh and Ta-Ir alloys deformed in a ductile manner upon severe bending while the other three alloys would crack upon bending.

Discussion

Alloy Chemistry and Glass Formation in Refractory Systems: The refractory metal alloy systems selected for the present study fall into three, partly overlapping categories (see Table I). a) Binary Ts-Ts alloy systems, where Ts and Ts are transition metals belonging to the V and Cr groups, respectively of the second and third long periods; b) Re-Si alloys; c) Ternary alloys containing boron, such as Ta-Ir-B and W-Ir-B.

We briefly discuss the results in the context of the alloy chemistry of these systems.

(a) The phase diagrams of the four binary Ts-Ts systems (Nb,Ta)-(Rh-Ir) are known in detail.⁽²¹⁻²⁴⁾ The Ta-Ir phase diagram⁽²⁴⁾ is given here as that of a representative system (Fig. 1). Some alloy chemical characteristic common to these four systems are:⁽²¹⁾ First, Frank-Kasper phases (tetrahedra

Fig. 2 Constitution diagram of the Ta-Ir system.⁽²⁴⁾

close packed phases)^(25,26) of two types occur at Ta-rich compositions; specifically, NbRh and NbIr have Cr-Si-Al₃ type structures and all four Ta-Ta systems contain σ type phases. Second, the central composition ranges are relatively low melting, with eutectics at 55 at.pct. Ta. Third, clusters of twelve-coordinated close-packed phases of various stacking sequences are found at 50-75 at.pct. Ta.

The Ta-Ta element glasses are of interest in several respects: First, they form in a composition range lying near a Frank-Kasper phase, here σ . Such phases have complex atomic coordination with coordination numbers ranging from 12 to 16;⁽²⁵⁾ another representative, σ , has been found to be associated with inter-transition metal glass formation in the Nb-Ni system.⁽¹³⁾ Second, the glass forming composition range lies at an average group number (AGN) of about 7, which is also found to be associated with the center of the glass forming range in the Zr-Cu system.⁽⁹⁾ Third, it is noteworthy that glasses form fairly readily in the present four systems although the general size criterion for glass formation ($R_2/R_1 \geq 1.15$)⁽⁶⁾ may not be fulfilled ($R_{Ta}/R_{Ir} = 1.08$, using 12-coordinated elemental radii;⁽⁶⁾ however, in the absence of a complete radial distribution analysis the radius ratio should be computed from interatomic distances measured in an adjacent intermediate phase such as σ rather than from the elemental values.) Last, the reduced melting point depression $\Delta T_m = (T_m - T_g)/T_m$ is considered, yielding $\Delta T_m = 0.26$ and 0.27 for Nb₅₅Rh₄₅ and Ta₅₅Ir₄₅, respectively. These values are about 20% smaller than $\Delta T_m = 0.33$ for Ni-Ni or Zr-Cu glasses;⁽⁶⁾ this suggests that the glass forming ability of Ta-Ta alloys is comparable to but less than that of the readily glass forming Nb-Ni or Zr-Cu alloys,⁽⁶⁾ as observed here.

(b) The Re-Si system is characterized by three intermetallic phases which have typical transition metal silicide structures, viz., Re₃Si₂ (Cr₃Si₂ type), ReSi (FeSi type), and ReSi₂ (MoSi₂ type) melting at 1400, 1830, and 1680°C, respectively.⁽²⁷⁾ There is a eutectic between Re and Re₃Si₂ at 33 at.pct. Re melting at 1900°C. The diagram thus shows a moderately rapid initial decrease of the melting point from that of Re followed by approximately constant melting points in the central portion of the diagram.

One may relate glass formation in the Re-Si system to that in other Ta-Si systems. Glass formation had been observed for a Ta₅₅Si₄₅ alloy⁽¹⁸⁾ which, like the glass forming Re₅₅Si₄₅ alloy consists in equilibrium of the terminal

transition element and an intermetallic phase T_3Si_3 ; T_1Si_3 has a Mn_3Si_3 type structure which is related to the Cr_3Si_3 type structure of Re_3Si_3 . The principal constitutional difference between the glass forming ranges of the two systems is that the much higher melting point of Re (3160°C) compared to that of Ti (1668°C) moves the eutectic composition closer to that of the T_3Si_3 compound and thus shifts the glass forming range to Si contents higher than the optimal one of ~20 at.pct. found also in the well-known Pd-Si system⁽⁶⁾

For $Re_{.63}Si_{.37}$, $\Delta T_{gr} = 0.21$, further reduced by ~20% from the value for $Ta_{.45}Ir_{.55}$; again, this agrees with the lower glass forming ability of the Re-Si alloy compared to that of the Ta-Ir alloy.

(c) The ternary boride alloys in the Ta-Ir-B and W-Ir-B systems cannot be discussed in terms of their equilibrium constitution as the latter is not known. However, the selection of these alloys was the result of several considerations. First, it was intended to combine the glass forming ability of the binary T-I systems, either observed (for Ta-Ir) or as yet unobserved (for W-Ir), with the well-known, glass formation promoting effect of B at a level of about 20 at.pct. B in T-B systems such as Fe-B.⁽²⁸⁾ (The W-Ir system is a potentially glass forming system because it is characterized by the occurrence of a c phase at 25 at.pct. Ir in a region of relatively fast melting point depression.) Further, the W-B system itself is potentially glass forming (considering melting point reduction and size criteria). Last, suitably selected ternary systems such as the present boride systems sometimes form glasses much more readily than the relevant binaries.⁽¹⁸⁾

Some Property Correlations for Amorphous Alloys Formed by Refractory Metals:

In the following, we give some preliminary, qualitative correlations between mechanical and thermal properties of the present glasses and properties of their elements, crystalline alloys, or phase diagrams.

For the four homologous T_3-T_3 alloy systems, the crystallization temperatures T_c (as given by the upper and lower limits, Table I) are correlated with the melting points T_m which increase by 100-200°C as Nb is replaced by Ta and 200-300°C as Rh is replaced by Ir.

The Vickers microhardness appears to increase with the crystallization temperature (and, by the relation mentioned in the preceding paragraph, the melting point as well) for those binary alloys for which these data are available. By contrast, for the ternary boride systems the measured microhardness values exceed those predicted in this way from their thermal stability limits.

The microhardness values for six of the seven new glasses correlate well with the weighted Young's moduli of the component elements. The exception is $W_{.60}Ir_{.20}B_{.20}$ for which H_v is about 10% lower than predicted by this relationship; however, as stated above, the present H_v values constitute lower limits of the true values.

The four T_3-T_3 alloys forming tough glasses also possess a certain degree of toughness in the crystalline equilibrium state.

Conclusions

The present work demonstrates the usefulness of the arc furnace quenching technique for the preparation of new metallic glasses, especially for refractory alloys such as those reported here which have melting points up to ~2000°C.

Thus, it was possible to produce amorphous metals from alloys having a high content of refractory metals with high modulus, as well as from such alloys containing effective strengthening additions such as boron. These

amorphous metals include those with the highest crystallization temperatures and Vickers microhardnesses yet reported, found to be $T_c > 1220$ K for Ta, $H_v > 1340$ kg/cm² for Ta, $H_v > 1340$ kg/cm² for Ta, respectively. Correlations between microhardness, crystallization temperature, alloy melting point and averaged elastic moduli of the components were noted.

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FORMATION AND PROPERTIES OF REFRACTORY

METAL GLASSES II: T_5 - T_9 GLASSES (T_5 =Nb, Ta; T_9 =Rh, Ir)

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Introduction

There is an increasing amount of evidence^{1,2} that the thermal and mechanical behavior of metallic glasses containing only transition metals (or rare earth metals and actinides) is closely related to the corresponding properties of the constituent elements. (This is in sharp contrast to glasses containing B-metals such as Al as a major alloying constituent or as a minor additive;² here the stabilizing and strengthening effect is frequently far in excess of the inherent stability of the additive.) Among inter-transition metal systems, then, high strength and thermal stability would be expected to be found in glasses formed by the combination of transition metals having high elastic moduli and/or high melting points.³

It is likely that the strongest and most stable metallic glasses will not be a binary metal-metal alloy but will contain one or more refractory metal(s) as well as metalloid additions. However, there is an interest in the systematic study of the properties of glasses formed by binary combinations of refractory metals; for instance, such alloys can give indications of the correlations existing between the thermal and mechanical parameters of the glass and its components. Such a study is reported here for the four possible combinations of the T_5 metals Nb and Ta on the one side and the T_9 metals Rh and Ir on the other.

The first amorphous T_5 - T_9 metal alloys to be prepared were Nb-Rh glasses, characterized as microcrystalline at the time of their initial preparation.⁴ Electronic properties of the Nb-Rh glasses, especially their superconductivity, were investigated.⁴ The preparation of all four of the possible T_5 - T_9 glasses (as well as some other refractory metal glasses) was recently reported;³ some approximate crystallization temperatures obtained by isothermal annealing and microhardnesses (lower limits) had also been given.³

In the present study, the glass forming (G.F.) composition ranges of all four systems have been determined; the crystallization temperatures T_c and microhardnesses H_V have been determined for four glasses with the composition (T_5)₅₅(T_9)₄₅. T_c values were determined from measurements of the electrical resistivity; the resistivities and their changes with temperature will be discussed in a different context elsewhere.⁵

The Ta-Rh constitution diagram⁶ is given schematically in Fig. 1; many features of it are typical of those of the other T_5 - T_9 systems.⁷ There is a central eutectic region in all four systems which contains the G.F. range; it is bounded on the left at ~40 a/o T_9 by a σ phase and on the right by phases with 12-coordinated close-packed structures at ~52 a/o T_9 . Both Rh systems

show high-temperature phases (α_2 for Ta-Rh) of unknown structures.

Experimental

The procedure used to prepare refractory metal glasses has been discussed in Ref. 3 together with design features of the arc furnace quenching unit which was used. Amorphous samples were selected from the quenched foils on the basis of the presence of the typical "amorphous" diffraction pattern.

Electrical resistivities were determined by a four-point ac technique using a Keithley 503 Milliohmmeter. The samples were heated in a fused silica tube held at high vacuum. The temperature was determined using a chromel-alumel thermocouple. Upon crystallization the electrical resistivity showed a decrease of 20 to 30% of the value for the amorphous sample; T_c was taken as the onset temperature (steepest tangent method) for this decrease. In the vicinity of T_c , heating took place at rates of $\dot{T} = 8$ K/min for $Nb_{.55}Rh_{.45}$, 3 K/min for $Nb_{.55}Ir_{.45}$, 3 K/min for $Ta_{.55}Rh_{.45}$, and 1 K/min for $Ta_{.55}Ir_{.45}$; i.e., the heating rates decreased with increasing T_c .

To obtain a cross-check on the resistometrically determined values, T_c was also determined by DSC in a Perkin-Elmer DSC 2 unit for a $Nb_{.55}Rh_{.45}$ sample at a heating rate $\dot{T} = 10$ K/min; this composition was the only one of the four alloys studied which crystallized below the temperature limit of 1000 K for this unit. The agreement of the two values (see-Table 2) was excellent.

The microhardness values were measured with a Kentron microhardness tester using a 100 g load.

Results and Discussion

Glass Formation: The structures of the quenched T_5 - T_9 alloys are listed in Table 1; G.F. ranges of about 12 a/o were found in all four systems. Among the crystalline phases that were found there were several that had not yet been reported as an equilibrium phase for their respective binary system;⁸ for the systems with Rh, these phases may be the high temperature phases. The extent of the G.F. ranges can be somewhat correlated with features of the constitution diagram: on the T_5 -rich side, G.F. is limited by the position of the σ phase field (i.e. crystallization to the σ phase occurs, preventing G.F.); on the T_9 -rich side, crystallization to the high-temperature phase(s) may be suppressed in favor of G.F. (e.g., for Nb-Rh) while, on the other hand, the low-temperature phases tend to form, preventing G.F., as the T_9 content increases.

Crystallization Temperatures: The crystallization temperatures T_c for the $(T_5)_{.55}(T_9)_{.45}$ glasses are listed in Table 2. In Fig. 2a the T_c values are plotted against the eutectic temperature T_E and the averaged melting temperatures $\bar{T}_M$ of the components. The straight line shown for T_c vs. T_E passes through the origin and is represented by $T_c/T_E = 0.550$. While the plot of T_c vs. T_E shows some scatter, all T_c/T_E values (Table 2) lie within 0.03 (~6%) of the straight-line value. This ratio agrees closely with those found for many other metal glasses^{2,9} and gives encouragement to attempts^{2,10} to link the crystallization temperatures of the glass and the eutectic melting temperatures of the solid, even though the latter is two phase at the G.F. composition. T_c also correlates well with $\bar{T}_M$; the straight line shown in Fig. 2 corresponds to $T_c = 0.61 \cdot (\bar{T}_M - 900)$; as is obvious, this relation cannot be generalized with these parameters to all metallic glasses.

Considerations of the atomic motions required for crystallization suggest that a relation exists between the elastic properties and thermal stability, measured only as T_c in the present systems, of a glass. In the absence of elas-

tic data for the glass itself, one can examine the correlation of T_c with $\bar{E}$, the averaged Young's modulus of the components, or $\overline{EV}/\bar{V}$, where $\bar{V}$ is the mean atomic volume and $\overline{EV}$ is the weighted average of $E \cdot V$. Both quantities correlate well with T_c (Fig. 2b), although again the resulting equations for the straight lines cannot be general for all metallic glasses.

Microhardness Data: The microhardness values H_V are given in Table 2 and are plotted vs. T_c and $\bar{E}$ in Fig. 3. The thermal and mechanical behavior of each glass are closely coupled; by the relations between T_c and T_E or $\bar{T}_M$ treated in the previous section, H_V is thus also related to T_E and $\bar{T}_M$. The solid line indicated in Fig. 3 for H_V as a function of T_c is given by $H_V = 1.04 \cdot (T_c - 200)$ kg mm⁻²K⁻¹; a dash-dotted line through the origin is also shown. For H_V vs. $\bar{E}$, the fit to a smooth curve is excellent. Since one might expect $H_V \rightarrow 0$ as $E \rightarrow 0$, a dashed straight line through the origin is again also shown; this one such line, $H_V/\bar{E} = 0.0320$, is correct for the stronger glasses (Table 2) but predicts lower values of H_V for the weaker ones than are observed. Like the thermal stability, the mechanical strengths of the glasses are again strongly correlated with the elastic moduli of the constituents.

As mentioned before,³ the present glasses possess good bend ductility; some of the alloys even possess a certain degree of toughness in the crystalline state.

Conclusion

Probably due to the considerable similarity in the atomic size and periodic table position of their constituents, the thermal and mechanical properties of the present glasses possess a high degree of correlation (a) with each other, (b) jointly with features of the phase diagram, and, most interestingly, (c) jointly with pertinent properties of the constituents.

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Table 1: Glass Formation Upon
Arc Furnace Quenching in T_5 - T_9 Alloy Systems

Alloy Composition	Equilibrium Structure at T_E	Extent of Central Structure after Minimum G.F. Range Two Phase Field at T_E and at 300 K (at.pct. T_9)	Rapid Quenching in T_5 - T_9 System (at.pct. T_9)
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Nb. ₆₅ Rh. ₃₅	σ		σ
Nb. ₆₀ Rh. ₄₀	$\sigma + \alpha_1$		A.M.
Nb. ₅₅ Rh. ₄₅	$\sigma + \alpha_1$	$\left\{ \begin{array}{c} 39 \text{ to } 46.5 \\ 39.5 \text{ to } 51.5 \end{array} \right\}$	A.M. $\left\{ \begin{array}{c} < 40 \\ \text{to} \\ > 51 \end{array} \right\}$
Nb. ₅₀ Rh. ₅₀	α_1		cryst. (α_1 ?)
Nb. ₄₀ 5Rh. ₅₁₅	α_1		A.M.
Ta. ₆₅ Rh. ₃₅	σ		σ
Ta. ₆₀ Rh. ₄₀	σ		A.M.+tr.cryst.
Ta. ₅₅ Rh. ₄₅	$\sigma + \alpha_3$	$\left\{ \begin{array}{c} 40 \text{ to } 49 \\ \sim 38 \text{ to } \sim 54 \end{array} \right\}$	A.M. $\left\{ \begin{array}{c} \sim 40 \\ \text{to} \\ \sim 50 \end{array} \right\}$
Ta. ₅₀ Rh. ₅₀	α_3		A.M.+tr.cryst.
Ta. ₄₀ 5Rh. ₅₃₅	α_3		cryst.
Ta. ₄₅ Rh. ₅₅	α_3		cryst.
Nb. ₆₀ Ir. ₄₀	σ		σ
Nb. ₅₇₅ Ir. ₄₂₅	$\sigma + \alpha_1$		A.M.+tr. cryst.
Nb. ₅₅ Ir. ₄₅	$\sigma + \alpha_1$	$\left\{ \begin{array}{c} 41.5 \text{ to } 52.0 \\ \sim 41 \text{ to } 52 \end{array} \right\}$	A.M. $\left\{ \begin{array}{c} \sim 43 \\ \text{to} \\ < 55 \end{array} \right\}$
Nb. ₅₀ Ir. ₅₀	$\sigma + \alpha_1$		A.M.
Nb. ₄₅ Ir. ₅₅	α_2		A.M.+cryst. (major)
Ta. ₆₅ Ir. ₃₅	σ		σ
Ta. ₆₂₅ Ir. ₃₇₅	σ		A.M.+tr.cryst.
Ta. ₆₀ Ir. ₄₀	σ	$\left\{ \begin{array}{c} 41 \text{ to } 50.4 \\ \sim 35 \text{ to } \sim 51.5 \end{array} \right\}$	A.M.+tr.cryst. $\left\{ \begin{array}{c} \sim 38 \\ \text{to} \\ \sim 52 \end{array} \right\}$
Ta. ₅₅ Ir. ₄₅	$\sigma + \alpha_1$		A.M.
Ta. ₅₀ Ir. ₅₀	α_1		A.M.
Ta. ₄₇₅ Ir. ₅₂₅	α_1		A.M.+tr.cryst.

Table 2: Properties of $(T_5)_{.55}(T_9)_{.45}$
Transition Metal Glasses

Alloy	T_c (K)	$T_c/\bar{T}_m$	T_c/T_E	H_V (kg/mm ²) (Vickers)	$\bar{E} \cdot 10^6$ (kg/cm ²)	$H_V/\bar{E}$ $\cdot 10^2$
Nb _{.55} Rh _{.45}	973 $\pm$ 10 980 $\pm$ 2	0.387	0.549	780 $\pm$ 40	2.30	3.39
Ta _{.55} Rh _{.45}	1118 $\pm$ 10	0.399	0.529	890 $\pm$ 50	2.72	3.27
Nb _{.55} Ir _{.45}	1133 $\pm$ 10	0.415	0.563	970 $\pm$ 50	3.01	3.22
Ta _{.55} Ir _{.45}	1283 $\pm$ 10	0.425	0.577	1100 $\pm$ 70	3.44	3.20

(a) by DSC, at 10 K/min.

Figure 1. The Ta-Rh constitution diagram.⁶

Figure 2. (a) Crystallization temperature T_C of glass vs. eutectic temperature T_E ($\square$) and averaged melting point of the components T_M ($\circ$).

$\circ$ = Nb₅₅Rh₄₅; $\square$ = Nb₅₅Ir₄₅; $\circ$ = Ta₅₅Rh₄₅; $\square$ = Ta₅₅Ir₄₅

(b) T_C vs. the averaged elastic (Young's) modulus of the components $\bar{E}$ ($\circ$) and $\bar{E}/\bar{V}$ ($\square$) (see text).

Figure 3. Vickers micro-hardness H_V vs. T_C and $\bar{E}$ for (Ta₅₅, Ir₄₅) glasses.

F-ELECTRON ENHANCED GLASS-FORMING ABILITY OF ACTINIDE ALLOYS:
NEW METALLIC GLASSES RICH IN U, Np, AND Pu*

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ABSTRACT

New metallic glasses rich in the respective actinide (Ac) metals were prepared by arc-furnace quenching in the systems U-M, where M = Mn, Fe, Co, and Ni, and by splat cooling in the systems Np-M, where M = Mn, Fe, Co, and Ga, and Pu-M, where M = Mn, Fe, Ni, Cu, and Ru.

The Ac-Ac distances were determined from x-ray diffraction data; for Np, a size increase was observed which has been associated with increasing f-electron localization. Preliminary thermal stability data are reported. The easy glass-forming ability of Ac systems has been ascribed to the anomalously low melting points of U, Np, and Pu and is a consequence of the f-electron contribution to bonding in Ac metals which favors low-symmetry or random atomic arrangements.

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INTRODUCTION

The ability to form metallic glasses upon rapid quenching¹ has now been demonstrated for alloys whose major constituents represent most of the subdivisions of the periodic table.²⁻⁶ However, one group of metallic elements about which relatively little is known in this respect is the actinide metals Th, U, Np, and Pu. Of these, Th has been found to form amorphous phases with Fe and Cu.⁷ Amorphous U alloys containing V and Cr as glass-forming additions are the subject of a patent,⁸ but there is no published information as yet for other U alloy glasses or for glasses containing Np and Pu. In this note, we report the preparation and initial characterization of 13 (and possibly 14) new metallic glasses rich in U, Np, and Pu and discuss factors that contribute to the glass-forming ability of actinide metal alloys.

EXPERIMENTAL METHODS

Actinide alloys were prepared by arc-melting weighed amounts of the 99.9% pure components. They were then rapidly quenched from the liquid state with a Duwez-Willens type gun⁹ onto copper-sheet substrates (splat-quenching) or with a hammer-and-anvil, arc-furnace quenching unit.¹⁰ Both of these units were operated in gloveboxes because of the toxicity of Np and Pu. The "splat" deposits and arc-quenched foils were examined by x-ray diffraction (XRD) with CuK α radiation. Details of these procedures are given in a series of papers¹¹⁻¹³ and are reviewed in Ref. 14. Differential scanning calorimetric (DSC) studies were also carried out and the results will be reported in detail.¹⁵

RESULTS AND DISCUSSION

This work on glass formation of the actinides U, Np, and Pu (denoted by Ac) has concentrated on Ac systems with additives from Mn to Cu in the first long period and two others, Ga and Ru (all denoted by M). Phase diagrams of the relevant U and Pu systems¹⁶⁻¹⁸ are given in Fig. 1; those of the corresponding Np systems are not known, although some pertinent intermetallic phases of the Np₂M type have been studied.¹³ To date, only selected compositions in the 16 alloy systems involved have been studied. For each U and Np system (other than Np-Ga) only a single eutectic or near-eutectic composition was investigated (the constitution diagrams of the Np systems were assumed to be similar to those of the corresponding Pu systems). For Pu systems (other than Pu-Ru) a somewhat wider composition range has been investigated. The results are given in Tables I and II and the principal features are discussed below.

a. Metallic Glasses Prepared. Metallic glasses were retained in all three sets of Ac systems; however, the glass-forming tendency (GFT) varied and decreased from U systems, for which the relatively slow arc-quenching method sufficed ($\dot{T} \sim 10^5$ - 10^6 K/sec), to the Np and Pu systems, for which splat cooling was required ($\dot{T} \sim 10^7$ - 10^8 K/sec) [see Ref. 19 and Table I].

There were some anomalous results: first, Np-Ni glasses were obtained only with low yield although the corresponding U-Ni and Pu-Ni glasses were readily prepared and second, Pu-Co glasses were not obtained at all although the elements Fe and Ni, which bracket Co in the periodic table, readily formed

glasses with Pu. Given the alloy chemistry of the Np-Ni and Pu-Co systems, we assume that these negative results are spurious and due to accidentally low cooling rates and that the missing glasses will be obtained by further splat quenching experiments. The absence of a Np-Cu glass probably is due to a low GFT in this system, as Cu lies at the end of the row of elements promoting glass-formation in actinides. Factors possibly active in glass formation are discussed below.

b. XRD Patterns, Peak Positions, and Nearest-Neighbor Distances.

The U foil samples yielded XRD patterns with large, asymmetric, broad first peaks. In the absence of a study of the radial distribution function (RDF), these first peaks were tentatively separated into a principal first maximum at $K_1^{\text{Ac-Ac}}$ due to U-U distances and having a half-width $\Delta K \sim 15\%$ of $K_1^{\text{Ac-Ac}}$ and a weaker shoulder at $K_1^{\text{Ac-M}}$ due to the U-M distances and having a half-width $\Delta K \sim 10\text{-}13\%$ of $K_1^{\text{Ac-M}}$ (Table II).^{*} A typical x-ray diffraction pattern is shown in Fig. 2. For Np and Pu, where splat samples were used, less material was available for diffraction and the peaks were thus generally weaker. The peak shoulder could not be identified and only $K_1^{\text{Ac-Ac}}$ with a half-width $\Delta K \sim 10\%$ of $K_1^{\text{Ac-Ac}}$ was visible. These differences are probably explained primarily by the different composition ranges studied (see Table I). At low addition-element levels (as for the Np and most Pu glasses), there are fewer Ac-M nearest neighbors; this, along with the small sample quantity, probably accounts for the absence of the shoulder. The narrower

^{*} K is defined as $4\pi\sin\theta/\lambda$.

peak at low addition-element levels may indicate a smaller Ac-Ac distance spread than in glasses with higher addition-element contents.

Within each set of glasses, the positions of the first peak are approximately constant, suggesting that $K_1^{\text{Ac-Ac}}$ is independent of the nature of the individual M additive; it should be noted, however, that the late transition-metal additives are all very similar in size. The data for Pu-Ni glasses (Table II) show that K_1 varies insignificantly with composition, owing to the large weight of the approximately constant Ac-Ac distances. The systematic variation of $K_1^{\text{Ac-Ac}}$ for the sequence U-Np-Pu is discussed below.

Using the K_1 values, we derived approximate mean interatomic distances of the first nearest neighbor shell of atoms (d_1) by use of the Ehrenfest formula^{4,20,21} $d_1 \cdot K = \kappa$ where $\kappa = 7.90$ (Table II). This procedure has been shown to be applicable and useful as a first approximation in the absence of detailed study of the radial distribution function.⁴ The κ value is an average of Ehrenfest constants, derived for systems where d_1 has been determined by RDF analysis;⁴ this survey gave $\kappa = 7.90 \pm 0.1$ except for a few cases. The distances obtained by the procedure are generally compared with distances obtained from corresponding crystalline phases with twelve-fold coordination. Accordingly, $2 \cdot r_{\text{Ac}}$ and $r_{\text{Ac}} + r_{\text{M}}$ were taken for the Ac-Ac and Ac-M interatomic distances, respectively, where r_{Ac} and r_{M} are the actinide and transition metal atom radii corrected to a coordination number of 12.

A comparison (Table II) shows that the U-U and U-M distances calculated from K_1 as stated are about 2% smaller than those calculated from the metallic radii. The 2% difference may be due to the fact that there are fewer than 12 nearest neighbors. (In crystalline metals, the interatomic distances decrease by $\sim 0.7\%$ for each reduction by one in the number of nearest neighbors, e.g., $R(\text{CN} = 8) \sim 0.97 R(\text{CN} = 12)$ [Ref. 22].) The 2% difference also may be due in part to the inaccuracy of the κ value used or to a change in U-U distances on forming a binary metallic glass with ~ 30 at.% M additions.

For Pu, agreement between $d_i^{\text{Ac-Ac}}$ and $2r_{\text{Pu}}$ is excellent. The invariance of the Pu size effect upon glass formation can be interpreted in two ways. In simple valence language,²³ it suggests that the effective valence of Pu in the glass is approximately that in α -Pu or ϵ -Pu,¹¹ rather than the lower valence of δ -Pu.²³ In terms of the band structure, it suggests that the degree of f-electron delocalization²⁴ is equal to that in α -Pu or ϵ -Pu.

c. Electronic Structure of Np in Np Alloy Glasses. For Np glasses, the difference between $d_i^{\text{Ac-Ac}}$ and $2r_{\text{Np}}$ is opposite in sign to that for the U glasses, with $d_i^{\text{Np-Np}} \sim 1.03 \cdot (2r_{\text{Np}})$. This size increase of Np upon alloying is assumed to be electronic in nature and unrelated to packing changes as considered for U glasses. We assume the increase to be analogous to size increases of Np observed in two previous cases; metastable γ -Np(Ga) solid solutions¹² and Np_6M phases such as Np_6Fe (Ref. 13). In these two cases, the size increase has been ascribed

to increased f-electron localization and a concomitant decrease in the f-electron contribution to bonding²⁴⁻²⁶ or, in valence language,²³ a decreased effective Np valence. This electronic structure change was thought to be due to the increasing separation of Np atoms by alloying element atoms which, in turn, reduces the f-electron orbital overlap. When a numerical relationship between the size and valence of Np is used,^{12,23} the ~3% Np size increase in the Np glasses corresponds to an effective Np valence decrease to ~5.8 from 7. However an assignment of the change of f-electron charge density in the Wigner-Seitz cell of a reference Np atom in the glass would be a better measure of this effect than the "valence change."

d. Thermal Stability. Table I includes approximate temperatures for the major exothermic effect T_{ex} for the four new U glasses and for the Pu-Ni glass. The ratios T_{ex}/T_E , where T_E is the eutectic temperature, lie between 0.55 and 0.62, similar to ratios found for many other metallic glasses.⁴ For U-Co, a glass transition observed at 537°K confirms that the new noncrystalline alloys are glasses. A comprehensive study of the compositional and system-to-system variation of the thermal effects is in progress.¹⁵

e. Factors Active in Actinide Glass Formation. As mentioned, the U systems studied have a high GFT. Although the Np and Pu systems form glasses less readily than the U alloys, their ability to do so at addition-element levels as low as 10 at.% is remarkable. Let us review the alloy chemical criteria that have been associated with glass formation (see Table 2 of

Ref. 2). Alloy systems that form glasses upon rapid melt-quenching have characteristics in common that appear to be related to the GFT. Usually the liquid phase is stabilized in the region where glasses can be formed, and this has led to the formulation of the following empirical expressions.²

First, there is the reduced melting temperature (τ_m) which is a measure of the resistance in the alloy to atomic motions required for equilibration. It is defined by $\tau_m = kT_m/\Delta H_v$, where k is Boltzmann's constant, T_m is the melting temperature and ΔH_v is the heat of vaporization.²⁷ The GFT increases with decreasing τ_m . Second, there is the reduced melting-point depression (ΔT_{mr}) that is given by $\Delta T_{mr} = (\bar{T}_m - T_m)/\bar{T}_m$ is the weighted average of the melting points of the components.²

The GFT should increase with increasing ΔT_{mr} . Third, there is the reduced melting-point depression $\Delta T_{mr}^{id} = (T_m^{id} - T_m)/T_m^{id}$, which measures the depression of T_m from T_m^{id} , the liquidus temperature given by ideal solution theory.²⁸ The GFT and ΔT_{mr}^{id} should scale together.²

Applying the first of these criteria, one finds very low values of τ_m for the systems being studied. As examples, $\tau_m(U_{0.67}Fe_{0.33}) = 0.017$ and $\tau_m(Pu_{0.90}Fe_{0.10}) = 0.016$ compared to $\tau_m(Pd_{0.85}Si_{0.15}) = 0.022$. The Pd-Si alloy is known to form glasses readily upon quenching from the liquid. Even for the pure actinide elements (unalloyed) one finds $\tau_m(U) = 0.022$ and $\tau_m(Pu) = 0.022$ --values low compared to those of most metals, including those that are good glass formers with proper additives such as, $\tau_m(Ca) = 0.052$ (Ref. 29), $\tau_m(Fe) = 0.036$ and

$\tau_m(\text{Pd}) = 0.040$. These low values of τ_m are due essentially to the low melting points of the elemental actinides.^{24,25} The reduced melting point depressions for U-Fe and Pu-Fe alloys show $\Delta T_{mr}(\text{U}_{0.67}\text{Fe}_{0.33}) \cong 0.35$ and $\Delta T_{mr}(\text{Pu}_{0.90}\text{Fe}_{0.10}) \cong 0.32$, values that agree with those for broad-range glass-formers such as Zr-Cu and Nb-Ni (Ref. 2). On the other hand, the values of ΔT_{mr}^{id} are small and, in the case of $\text{U}_{0.67}\text{Fe}_{0.33}$, slightly negative (-0.032). The small values suggest near-ideal behavior of the melts in the actinide-rich range. Some T_m^{id} curves are shown in Fig. 3. These ΔT_m^{id} values are in striking contrast to those for metal-metalloid glasses²⁸ such as Pd-Si but agree with those calculated for Zr-Cu glasses.³⁰

Turning to atomic properties, the radius ratios are favorable, as appears to be a necessary condition; $r_{12}(\text{U})/r_{12}(\text{Fe}) = 1.22$ lies in the typical glass-forming range.² Other criteria,² such as component valence difference, average valence electron concentration, melt stoichiometry, or the presence of complex equilibrium phases in the glass-forming range, either do not apply or are of little relevance here.

Focusing then on the low melting points of the actinides, we suggest that the glass-forming ability of actinide alloys is associated with a factor not considered previously in this context: the contribution of f-electrons to bonding in actinide alloys. The melting points of U, Np, and Pu are anomalously low,³¹ as is shown in Fig. 4.^{32,33} Melting point deficits of 1300 K for U and 1700 K for Pu have been quoted.³¹ Kmetko and Hill^{24,26} have associated this effect with the partial

localization of f-electrons in these actinides and with the incompatibility of the symmetry of the f-electron wave functions in the highly symmetrical, bcc high-temperature forms of U, Np, and Pu. By contrast, low-temperature modifications with low symmetry occur only for the three actinides in question (Fig. 4). These modifications and the melt provide for better f-electron bonding.²⁶ Johansson²⁵ has estimated that ~21% of the cohesive energy of U, and 15% for Pu is due to f-electron bonding; Hill³⁴ estimated 30 and 50%, respectively. Because the structures of glasses generally are close to those of the corresponding liquids,⁴ a sizable f-electron bonding contribution can also be assumed to exist in the actinide glasses.

The stability of the liquid to low temperatures kinetically favors formation of the glass via the viscosity. The f-electron bonding contribution has been associated with the observed high viscosity of actinides, especially Pu (Ref. 24), which has the highest viscosity of any metal at the melting temperature.³⁵ High viscosity plays a major role in kinetic expressions for the critical cooling rate³⁶ and contributes strongly to the glass-forming ability of actinide alloys.

f. Features of U and Pu Phase Diagrams. Now, we turn to the difference between the GFTs of U and Pu (or Np) alloys. As Fig. 1 shows, the phase diagrams of the two sets of systems differ in the location of the low melting composition ranges which usually coincide with the largest GFT in any given system. The Pu systems have a higher melting point depression

(and hence a higher GFT) at lower additive contents ($x_M = 0.10-0.12$) then the U systems ($x_M \sim 0.22-0.34$). Even in systems that readily form glasses, the GFT decreases rapidly if the addition-element concentration decreases to < 10 at.%; thus, even at the composition of its highest value, the GFT for Pu systems will be lower than the maximum GFT for U systems, as observed. This difference in eutectic location (for instance, in the U-Fe and Pu-Fe systems) can be explained qualitatively by two factors,

$T_{\text{Fusion}}(\text{Pu}) < T_{\text{Fusion}}(\text{U})$ and $\Delta H_{\text{Fusion}}(\text{Pu}) \sim 1/3 \Delta H_{\text{Fusion}}(\text{U})$ (Ref. 33). Both factors combine to make the primary Pu liquidus curve lower and steeper than the corresponding curve in the U-Fe system. Because both AcFe_2 compounds melt at about the same temperature and assuming they have similar liquidus curves, the eutectics are shifted to considerably lower x_M for Pu-Fe (and Np-Fe) than for U-Fe.

The phase diagrams of Th-M systems^{16,17} differ substantially from those of the U-M and Pu-M systems. They resemble more those of other fourth period transition metals, such as Ti or Zr, with late transition metals. Therefore, glass formation in Th alloys⁷ is comparable to that in Zr-Ni and Zr-Cu alloys, for instance, and does not involve the f-electron effect discussed here.

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Table 2

New Amorphous Actinide Metal Alloys $Ac_{1-x}M_x$ Prepared by Rapid Quenching from the Liquid

Alloy System	Quenching Method	Glass-Forming Composition (at.% M)	T_{ex} (°K)	Eutectic Temp. T_E (°K)	Eutectic Comp. x_E (at.% M)	Radius Ratio r_{Ac}/r_M	Comments
U-Mn	AQ ^a	30	~610	989	22	1.24 ^b	
U-Fe	AQ	33	~570	998	34	1.26	
U-Co	AQ	33	~555	1007	34	1.25	
U-Ni	AQ	33	~600	1013	33	1.24	
Np-Mn	SQ ^a	13.9	ND ^a	---	---	1.21; 1.24 ^c	+ 30% unknown phase
Np-Fe	SQ	14.3	ND	---	---	1.23; 1.26	
Np-Co	SQ	14.3	ND	---	---	1.22; 1.25	
Np-Ni	SQ	14.3	ND	---	---	1.21; 1.24	Glass formation uncertain
Np-Cu	SQ	---	---	---	---	1.18; 1.24	No glass formation at 14.3 at.% Cu
Np-Ga	SQ	30 to 40	ND	---	---	1.06; 1.09	
Pu-Mn	SQ	~10 to >14	ND	798	10	1.27 ^b	
Pu-Fe	SQ	~15 to >20	ND	678	10	1.28	Glass formation not observed at 20% Co; assumed due to poor quench
Pu-Co	SQ	---	---	673	12	1.28	
Pu-Ni	SQ	~12 to >30	~425(20X)	738	12	1.27	
Pu-Cu	SQ	~14 to <20	ND	899	5	1.24	
Pu-Ru	AQ	20	ND	801	12	1.18	+ ϵ -Pu solid solution
<u>Previously Reported Actinide Glasses</u>							
U-V	MS ^{a,d}	20 to 40 ^d	>773 ^d	1313	18	1.15 ^b	
U-Cr	MS ^{a,d}	20 to 40 ^d	>773 ^d	1132	19	1.20	

^aAQ = arc-furnace quenching; SQ = splat-quenching; MS = melt spinning; ND = not determined.^bFor Ac radii: γ (U), Ref. 23; γ (Np), Ref. 12; ϵ (Pu), Ref. 11. For transition-metal radii: values as appropriate for nonmagnetic phases containing these elements as minor components (see Ref. 22, pp. 156-158).^cRadius of Np corrected for "valence change," Refs. 12 and 13 (see text).^dRef. 8.

Table II

X-Ray Diffraction and Atomic Size Data for New Amorphous Actinide Metal Alloys $Ac_{1-x}M_x$

Alloy Composition	First Set of XRD Maxima K_1 ($\text{\AA}^{-1}$)		Peak Width ΔK_1 ($\text{\AA}^{-1}$)		d_1 ($\text{\AA}$)		$2r_{Ac}$ ($\text{\AA}$) ^{b,d}	$r_{Ac} + r_M$ ($\text{\AA}$)
	K_1^{Ac-Ac}	K_1^{Ac-M}	ΔK_1^{Ac-Ac}	ΔK_1^{Ac-M}	d_1^{Ac-Ac}	d_1^{Ac-M}		
U _{0.70} Mn _{0.30}	2.59	2.89	0.35	0.30	3.05 ^a	2.73 ^a	3.09 ^b	2.79 ^{b,c}
U _{0.67} Fe _{0.33}	2.62	2.95	0.38	0.42	3.02	2.68	3.09	2.78
U _{0.67} Co _{0.33}	2.61	2.87	0.32	0.26	3.03	2.75	3.09	2.78
U _{0.67} Ni _{0.33}	2.61	2.89	0.37	ND ^e	3.03	2.74	3.09	2.80
Np _{0.861} Mn _{0.139}	2.57		0.27		3.07		3.01 ^b	3.09 ^d
Np _{0.857} Fe _{0.143}	2.55		0.29		3.10		3.01	3.09
Np _{0.857} Co _{0.143}	2.55		0.26		3.10		3.01	3.09
Np _{0.857} Ni _{0.143} ^f	~2.61		0.13 ^f		~3.03		3.01	3.09
Np _{0.70} Ca _{0.30}	2.54		0.28		3.11		3.01	3.09
Pu _{0.857} Mn _{0.43}	2.49		0.22		3.17		3.16 ^b	
Pu _{0.80} Fe _{0.20}	2.50		0.24		3.16		3.16	
Pu _{0.88} Ni _{0.22}	2.46 ₄		0.23 ₅		3.206		3.16	
Pu _{0.70} Ni _{0.30}	2.47 ₄		0.26 ₅		3.193			
	2.50		0.21		3.16		3.16	
Pu _{0.80} Ru _{0.20}	2.45		ND		3.22		3.16	

^aUsing Ehrenfest equation (see text).^bFor CN12 radii: $r(U)$, Ref. 23; $r(Np)$, Ref. 12; $r(Pu)$, Ref. 11.^cTransition-metal radii as appropriate for nonmagnetic phases containing these elements as minor components (see Ref. 22, pp. 156-158).^dRadius of Np corrected for "valence change," Refs. 12 and 13; see text.^eNot determined.^fGlass formation uncertain.

LIST OF FIGURE CAPTIONS

- Fig. 1. Constitutional diagrams of some of the actinide systems studied.
- Fig. 2. Diffraction pattern of amorphous solid $U_{0.67}Fe_{0.33}$. Tentative separation of K_1 into K_1^{U-U} and K_1^{U-Fe} is indicated.
- Fig. 3. Experimental U-Fe and Pu-Fe phase diagrams (superimposed) and hypothetical U-Fe and Pu-Fe liquidus curves given by ideal solution theory.
- Fig. 4. Crystal structures, transition temperatures, and melting points of the actinide elements radium to californium. Data from Ref. 33.

Fig. 1.
Constitutional diagrams of some of the actinide systems studied.

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Diffraction pattern of amorphous solid $U_{0.67}Fe_{0.33}$. Tentative separation of K_1 into

Fig. 3.
Experimental U-Fe and Pu-Fe phase diagrams (superimposed) and
hypothetical U-Fe and Pu-Fe liquidus curves given by ideal solution
theory.

Fig. 4. Crystals structures, transition temperatures, and melting points of the actinide elements from radium to californium.

PROPERTIES OF METALLIC GLASSES CONTAINING ACTINIDE METALS:

I. THERMAL PROPERTIES OF U-M GLASSES (M = V, Cr, Mn, Fe, Co, and Ni)

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Introduction

On the basis of alloy chemical factors found to be active in metallic glass formation¹ there was reason to expect that binary alloys consisting of one or more of the actinide metals Th, U, Np and Pu on the one side and suitable addition elements such as transition metals (M) from the V, Cr, Mn, Fe, Co, and Ni groups on the other would form glasses upon rapid quenching from the melt at moderately high cooling rates.¹ The previously reported metallic glasses containing Th, such as Th-Fe,² and glasses rich in U, such as U-Cr and U-V³ provided examples for this family of amorphous metals. More recently metallic glasses have been prepared in thirteen additional actinide alloy systems, among them the first ones to be reported that contain Np or Pu.⁴ In that report, nearest neighbor distances deduced from XRD patterns were given and factors active in actinide glass formation were discussed. Glass formation in alloys of U, Np and Pu was ascribed⁴ to the low melting points T_m of these elements (compared to their boiling points);⁵ the low T_m values in turn are thought to be related to the f-electron bonding present in these metals.⁶ It was also observed⁴ that metallic glasses containing U form more readily than the corresponding Pu glasses; this difference was ascribed to the lower concentrations of M at the eutectic compositions in the Pu-M alloy systems.⁷

In the present paper the results of a preparative and calorimetric study forming part of a continuing investigation of the new actinide glasses are reported. Specifically, lower bounds for the composition limits of glass formation (G.F.) at moderate cooling rates have been obtained for the U-M (M = Th, Fe, Co, Ni) systems and the thermal stabilities of glasses in these four systems as well as for a U-V glass and a U-Cr glass have been surveyed.

The four U-M phase diagrams for M = Mn, Fe, Co, and Ni are quite similar to each other; all contain peritectically melting U_2M phases on the U-rich side and relatively more stable, congruently melting Laves phases UM_2 on the M-rich side; in addition, the U-Co and U-Ni systems contain additional phases such as UCo and UNi_3 , respectively, in the central composition range which is of interest here.^{4,7} The U-V and U-Cr systems are simpler; their constitution diagrams show eutectics formed by γ -U and V or Cr, respectively.⁷

Experimental Methods

The preparative techniques used have been discussed in Ref. 4; they included arc-melting and arc furnace quenching in glove box systems, followed by XRD examination (Cu K α radiation) and DSC studies in a Perkin-Elmer DSC-2 calorimeter, carried out at 40 K/min. Some glass transitions were tentatively identi-

fied; their temperatures were obtained by the onset method rather than the midpoint method.⁸

XRD studies of the alloys after various stages of heat treating in the DSC unit have been delayed by the need for precautions required in the handling of samples prepared and treated in radioactively "hot" equipment; however, such studies are in progress.

Results

Table 1 lists the structures of the rapidly quenched alloys and the thermal effects observed; the latter are plotted for the four systems U-M with M = Mn, Fe, Co, and Ni in Fig. 1.

Glass Forming Ranges

Table 1 shows that the U-rich limit of the region of easy G.F. for the U-Mn and U-Fe systems is at < 20 at.pct. for either Mn or Fe; for the U-Co and U-Ni systems the U-rich limit lies between 20 and 27 at.pct. for either Co or Ni. (However, a small amount of amorphous material sufficient in quantity to obtain thermal data was also retained at 20 at.pct. Co or Ni.) The upper limits of the region of easy G.F. lie above 35.3 at.pct. Mn and 40 at.pct. Fe, Co, and Ni, respectively. For the remaining two systems, U-V and U-Cr, glass formation had been reported to occur between 20 and 40 at.pct. V and Cr; however, in the present study the alloy at 27 at.pct. V was found to contain only small amounts of glass. The alloy at 27 at.pct. Cr was amorphous, as reported. In several of the alloys which were not completely amorphous (Table I), crystalline phases were found that were not among the known equilibrium phases; it would be of interest to identify these along with any transition phases forming in the course of the crystallization of the glasses. In the U-Fe and U-Co systems, metastable extensions of the intermediate U₆M phases (M = Fe, Co) were found, indicating metastable composition ranges of these phases of ≥ 6 at.pct. M, up to >20 at.pct. M.

Thermal Data Given by System

The most important results of the present work concern the thermal stabilities of the glasses in the six binary U alloy systems studied. In the number of exothermic effects and the composition dependence of the T_c values, the U-Fe and U-Co glasses show very similar behavior; The U-Mn and U-Ni systems, however, have thermal characteristics different from those of the other two. For the systems U-V and U-Cr in which only one composition has been studied to date, the thermal characteristics are again similar. We briefly discuss these systems, following their order in the periodic table.

For U₇₃V₂₇ and U₇₃Cr₂₇, there are single strong exotherms, which presumably correspond to the reaction: glass + α -U + M (M = V, Cr), in accordance with the absence of intermediate phases in these systems. As the quenched U₇₃V₂₇ alloy also contains a large amount of metastable γ -U(V) solid solution, transformation of γ may be involved in this reaction.

The U-Mn alloys show two major exotherms: the first one, T_{c1} , occurs between 578 and 605 K with no clear composition dependence; the second, T_{c2} , occurs at temperatures which increase rapidly with increasing Mn content.

Both the U-Fe and U-Co systems show single exotherms for the more U-rich glasses and double exotherms for the glasses less rich in U; as observed frequently in such cases,^{9,10} there are continuous transitions between both regimes, occurring approximately at U₆₇Fe₃₃ and U₇₃Co₂₇, respectively. In the U-Co system there are, in addition, weak exotherms at 20 and 27 at.pct. Co.

Resides the exotherms, endotherms were seen for the $U_{.73}Fe_{.27}$ and $U_{.47}Co_{.53}$ glasses; however, additional study will be required to distinguish whether these endotherms correspond to glass transitions or whether they are artifacts related to possible exothermic relaxation effects occurring at lower temperatures.

The U-Ni glasses were characterized by double and, at lower U contents, triple crystallization effects. As the alloy $U_{.80}Ni_{.20}$ was largely crystalline, the data collected for this alloy (Table 1) are not included in Fig. 1.

Discussion

Composition Dependence of Thermal Stability

In three of the four systems where comparisons of different compositions were possible (U-Fe, U-Co, and U-Ni), the thermal stabilities increase with increasing contents of the alloying elements M; only for U-Mn the present data are inconclusive in this regard. The results for the three systems are in line with observations on many binary metal-metal^{10,11} and metal-metalloid glasses,^{9,11} where the thermal stability generally increases with increasing contents of the component having the smaller size and higher elastic constant.

Further, the U-Fe and U-Co systems permit an extrapolation of the crystallization temperature to unalloyed uranium, obtained as $T_c(U) \sim 530 \pm 20$ K. This value, however, would apply only for a hypothetical U glass with a structure comparable to those of the binary U-M glasses.

Dependence of Thermal Stability on Alloying Element M

Perhaps the most interesting result contained in the present data concerns the change of T_{c1} with M. The T_{c1} for $U_{.73}M_{.27}$ glasses are presented in Fig. 2. The curve shows a stability maximum for glasses with $M = Cr$ and a minimum for glasses with $M = Fe$ and Co .

It is of interest to try to find correlations of the thermal stability (a) with other properties of the glass itself, (b) the phase diagram, and (c) properties of the alloying elements M, the latter especially with a view toward finding relations having a predictive quality. However, the existence of such correlations is uncertain for crystallization temperatures, as the crystallization products change discontinuously from system to system. [As pointed out,^{3,12} such correlations are more likely to exist for glass transition temperatures; however, it is not clear whether T_g data can be collected for actinide glasses, (see above).]

We review the correlations of types (a) - (c) which were obtained for the present data on U glasses. As to (a), other property measurements, e.g. elastic moduli, are not yet available for the U glasses. Regarding (b), phase diagram features, the best-fitting correlation seen in analogous families of glass forming systems (such as those containing Ca^{10} or refractory metals¹³) is that between T_{c1} and T_E , the lowest eutectic temperature in the glass forming region; a straight line relation with a ratio $T_{c1}/T_E \sim 0.56$ has been observed in such systems. While the crystallization temperatures for $M = Fe, Co$, and Ni lie close to this line (see the values for T_{c1}/T_E given in Table 1), for the $U_{.73}Cr_{.27}$ glass and the $U_{.73}Mn_{.27}$ glass (by interpolation) T_c lies above the straight line and for the $U_{.73}V_{.27}$ glass T_c lies below it.

The positive departure of T_c for the U-Cr glass from the straight line is probably related to the low T_E of U-Cr alloys relative to the melting point of Cr; the low T_E is primarily due to the absence of the intermetallic phases common to the other U-M systems with $M = Mn, Fe, Co$ and Ni . [We comment parenthetically that the high T_{c1} and low T_E of U-Mn combine to produce a small supercooling

interval $T_E - T_{C1}$ for alloys near the eutectic composition, thus providing a rationale for the observed, rather good G.F. ability of U-Mn glasses.) The negative departure of T_C for the U-V glass from the straight line, on the other hand, may be due to a too large value for the T_E which is due to the extensive solid solubility of V in γ -U, as compared to the other U systems. This solid solubility is made possible by the relatively small size difference between U and V.

As to (c), correlations of T_{C1} with elemental properties, a correlation of T_{C1} with elastic constants of the constituents and the atomic volume of M was tentatively identified. Figure 2 shows a plot of $\bar{E} \cdot V_M$, where $\bar{E}$ is the weighted average of the Young's moduli of the constituents and V_M is the atomic volume of M. [The V_M used here are those appropriate for the transition elements $M = \text{Mn, Fe, Co, and Ni}$ in dilute solutions or in intermetallic phases with a low content of these M metals; these V_M differ from the elemental values which contain magnetic contributions.¹⁴]

Both sets of points plotted in Fig. 2 are similar in their overall change with N, suggesting a relationship between T_{C1} and $\bar{E} \cdot V_M$. However, while there is reason to expect some such relationship to exist,¹⁵ the origin of the expression $\bar{E} \cdot V_M$ found to be usable here is not clear; this relation may not be confirmed if further data are considered and can therefore not be generalized at this time.

Conclusions

The ease of glass formation in actinide alloy systems suggests that comparative studies extending that reported here and including mechanical properties will be fruitful in leading to an understanding of the factors active in this particular category of metallic glasses.

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Table 1

Results of Differential Scanning Calorimetry of Arc-Quenched U-M (M = V, Cr, Mn, Fe, Co, and Ni)
(Heating rate $\dot{T} = 40$ K/min)

Composition (at. pct. M)	Structure after Arc-Quenching ^a	Equilibrium Structure	Exothermic Effects (K) and Est. ΔH (% of total $\Delta H_{\text{cryst.}}$)			Endothermic Effect (K) (Tentative)	T_E (K)	$T_E - T_{ci}$ (K)	T_{ci}/T_E
			1.	2.	3.				
27 V	γ -U s.s.+A.M. (minor) + α -U (?) (minor)	γ -U+V	658 (100);	-	-	-	1313	655	0.50
27 Cr	A.M.	γ -U+Cr	684 (100);	-	-	-	1132	448	0.60
20 Mn	A.M.+ α -U+U ₆ Mn (trace)	U ₆ Mn+UMn ₂	578 (24) ^b ;	642 (76) ^b ;	-	-	989	384	0.61
25.5 Mn	A.M.+U ₆ Mn(?) + U.P. (trace)	"	605 (46) ^b ;	695 (54) ^b ;	-	-	"		
30 Mn	A.M.+U.P. (trace)	"	605 (75) ^b ;	677 (25) ^b ;	-	-	"		
35.3 Mn	A.M.+U.P. (trace)	"	593 (50) ^b ;	745 (50) ^b ;	-	-	"		
20 Fe	A.M.+U ₆ Fe s.s. (minor)	U ₆ Fe+UFe ₂	553 (100);	-	-	541	998	438	0.56
27 Fe	A.M.+U ₆ Fe s.s. (minor)	"	560 (100);	-	-	527	"		
33 Fe	A.M.+U ₆ Fe s.s. (trace)	"	566 (100);	-	-	-	"		
40 Fe	A.M.+U.P. (trace)	"	560 (32);	584 (68);	-	-	"		
20 Co	U ₆ Co s.s.+A.M. (minor)	U ₆ Co+UCo	545 (85);	575 (5);	585 (10)	-	1007	453	0.55
27 Co	A.M.+U ₆ Co s.s. (trace)	"	554 (55);	563 (13);	578 (30)	527	"		
33 Co	A.M.+U.P.	"	554 (40);	573 (60);	-	533	"		
40 Co	A.M.+U.P.	"	555 (25);	588 (75);	-	530	"		
20 Ni	α -U+U.P. (trace)+ A.M. (trace)	U ₆ Ni+UNi _x	613 (21) ^{b,d} ;	645 (79) ^{b,d} ;	-	593	1013	436	0.57
27 Ni	A.M.+ α -U (minor)	"	577 (-) ^c ;	632 (-) ^c ;	693 (-) ^c	-	"		
33 Ni	A.M.+U.P. (trace)	"	599 (20);	641 (38);	677 (42)	-	"		
40 Ni	A.M.+U.P. (minor)	"	613 (15);	663 (73);	683 (12)	-	"		

- Notes: a s.s. = solid solution; U.P. = unidentified crystalline phase; A.M. = amorphous metal.
 b Averages of two measurements.
 c ΔH_1 and hence ΔH_{Total} not obtained; $\Delta H_1/\Delta H_2 = 38/62$.
 d Alloy largely crystalline; exotherms not plotted in Fig. 1.

Figure 1. Temperatures of major exothermic effects as a function of composition for U-M glasses, where M=Mn, Fe, Co, and Ni (Numbers near each data point show estimated percentages of ΔH_{cryst}).

Figure 2. Onset temperatures of first exotherm, T_{c1} , for $U_{.73}M_{.27}$ glasses (from Table 1; left scale) and $\bar{E} \cdot V_M$ (see text; right scale) shown plotted against the transition metal additive M arranged in order of increasing atomic number.