Conf-780726--1

LA-UR -78-1865

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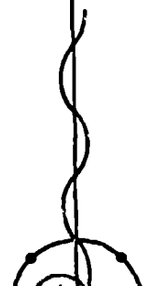
SUBMITTED TO: Proceedings of the 3rd Intl. Conf. on Rapid Quenching, July 3-7, 1978, Sussex, Brighton, England



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ENERGY RESEARCH AND
DEVELOPMENT ADMINISTRATION
CONTRACT W-7405-ENG. 36

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 formation[1] 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-V[3] 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 ascribed[4] to the low melting points T_m of these elements (compared to their boiling points);[5] the low T_m in turn are thought to be related to the f-electron bonding present in these metals.[6] It was also observed[4] 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 = Mn, 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_6M 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_x, 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 Kα 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 [illegible] point 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. Mn and Fe, respectively; for the U-Co and U-Ni systems the U-rich limit is between 20 and 27 at.pct. Co and Ni, respectively. (However, a small amount of amorphous material sufficient 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;[3] 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 U_6M phases (M = Fe, Co) were found, indicating metastable composition ranges of these phases of $\sim$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 seven 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 $U_{.73}V_{.27}$ and $U_{.73}Cr_{.27}$, there are single strong exotherms, which presumably correspond to the reaction: glass $\rightarrow$ α-U + M (M = V, Cr), in accordance with the absence of intermediate phases in these systems. As the quenched $U_{.73}V_{.27}$ 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 $U_{.67}Fe_{.33}$ and $U_{.73}Co_{.27}$, respectively. In the U-Co system there are, in addition, weak exotherms at 20 and 27 at.pct. Co

Beside the exotherms, endotherms were seen for the $U_{.73}Fe_{.27}$ and $U_{.67}Co_{.33}$ 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 lin 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 constants.

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,[8,12] 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 metals[13]) 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_c and low T_E of U-Mn combine to produce

interval T_E-T_c 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 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 = 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 M, 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.

Acknowledgement

One of us (B.C.G.) acknowledges support of this work by the Department of Energy under subcontract with the Lawrence Livermore Laboratory. We thank Dr. D.E. Polk for helpful discussions.

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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)

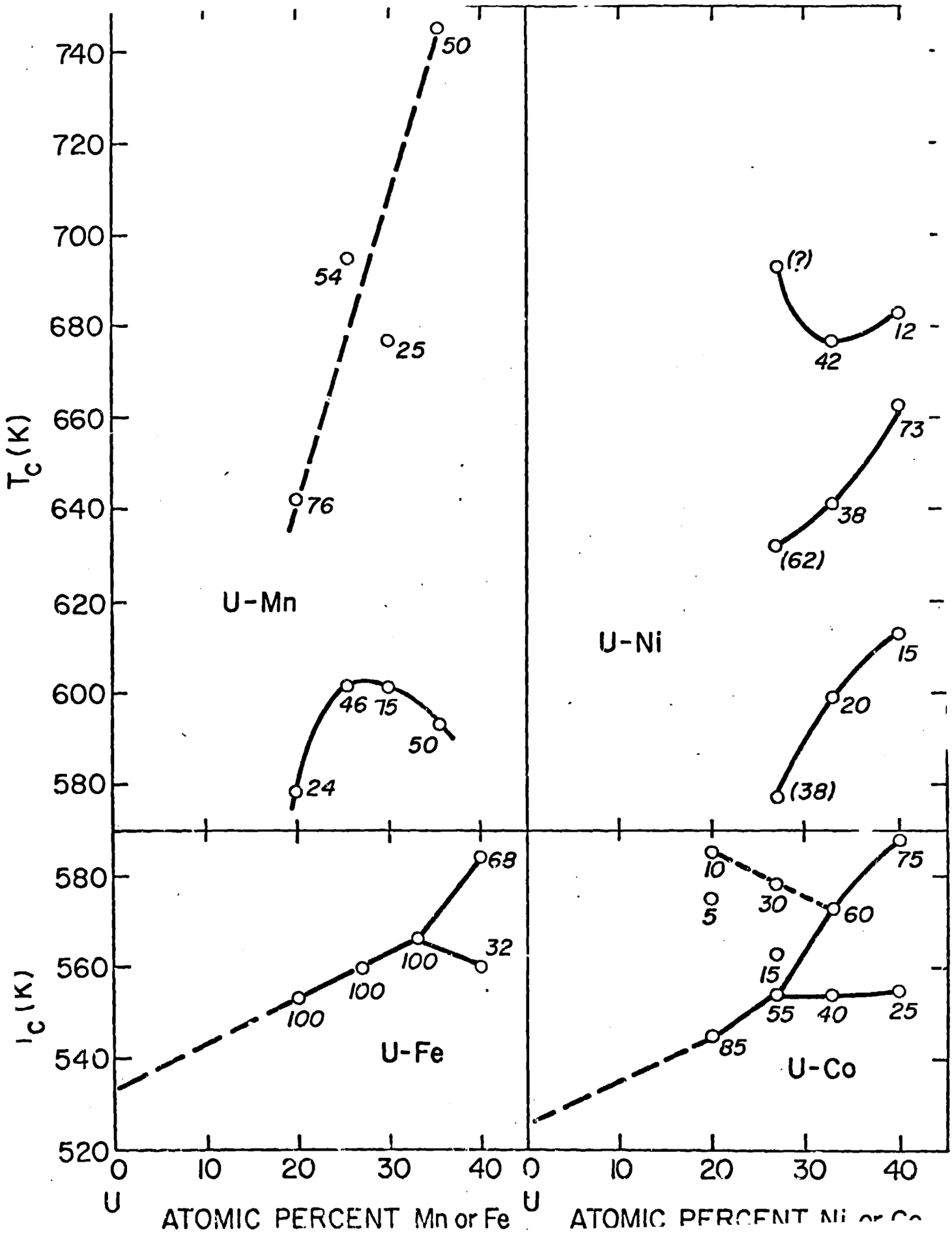
Composition (at.pct. M)		Structure after Arc-Quenching[a]	Equilibrium Structure	Exothermic Effects (K) and Est. ΔH (% of total $\Delta H_{cryst.}$) 1.	2.	3.	Endothermic Effect (K) (Tentative)	$T_E - T_c$ (K)	T_E (K)	T_{c1}/T_E
27	V	γ-U s.s.+A.M.(minor) + α-U (?)(minor)	γ-U+V	658 (100);	-	-	-	655	1313	0.50
27	Cr	A.M.	γ-U+Cr	684 (100);	-	-	-	448	1132	0.60
20	Mn	A.M.+α-U+U_6Mn(trace)	U_6Mn+UMn_2	578 (24)[b];	642 (76)[b];	-	-		989	
25.5	Mn	A.M.+U_6Mn(?)+U.P.(trace)	"	605 (46)[b];	695 (54)[b];	-	-	384	"	0.61
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_6Fe s.s.(minor)	U_6Fe+UFe_2	553 (100);	-	-	541		998	
27	Fe	A.M.+U_6Fe s.s.(minor)	"	560 (100);	-	-	527	438	"	0.56
33	Fe	A.M.+U_6Fe s.s.(trace)	"	566 (100);	-	-	-		"	
40	Fe	A.M.+U.P.(trace)	"	560 (32);	584 (68);	-	-		"	
20	Co	U_6Co s.s.+A.M.(minor)	U_6Co+UCo	545 (85);	575 (5) ;	585 (10)	-		1007	
27	Co	A.M.+U_6Co s.s.(trace)	"	554 (55);	563 (13);	578 (30)	527	453	"	0.55
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_6Ni+UNi_x	613 (21)[b,d];	645 (79)[b,d];	-	593		1013	
27	Ni	A.M.+α-U(minor)	"	577 (-)[c];	632 (-)[c];	693 (-)[c]	-	436	"	0.57
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
b Averages of two measurements.
c ΔH_3 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 Captions

Figure 1. Temperatures of exothermic effects for U-M glasses (M = Mn, Fe, Co, and Ni).

Figure 2. Temperatures of first exotherm, T_{c1}, for $U_{.73}M_{.27}$ glasses (Table 1) and $\bar{E} \cdot V_M$ (see text) for M = V, Cr, Mn, Fe, Co, and Ni.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720
700
680
660
640
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600
580
560
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T_c (K)
T_c (K)
50
54
25
76
U-Mn
46
75
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24
(?)
12
42
73
38
(62)
U-Ni
15
20
(38)
68
100
100
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5
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ATOMIC PERCENT Mn or Fe
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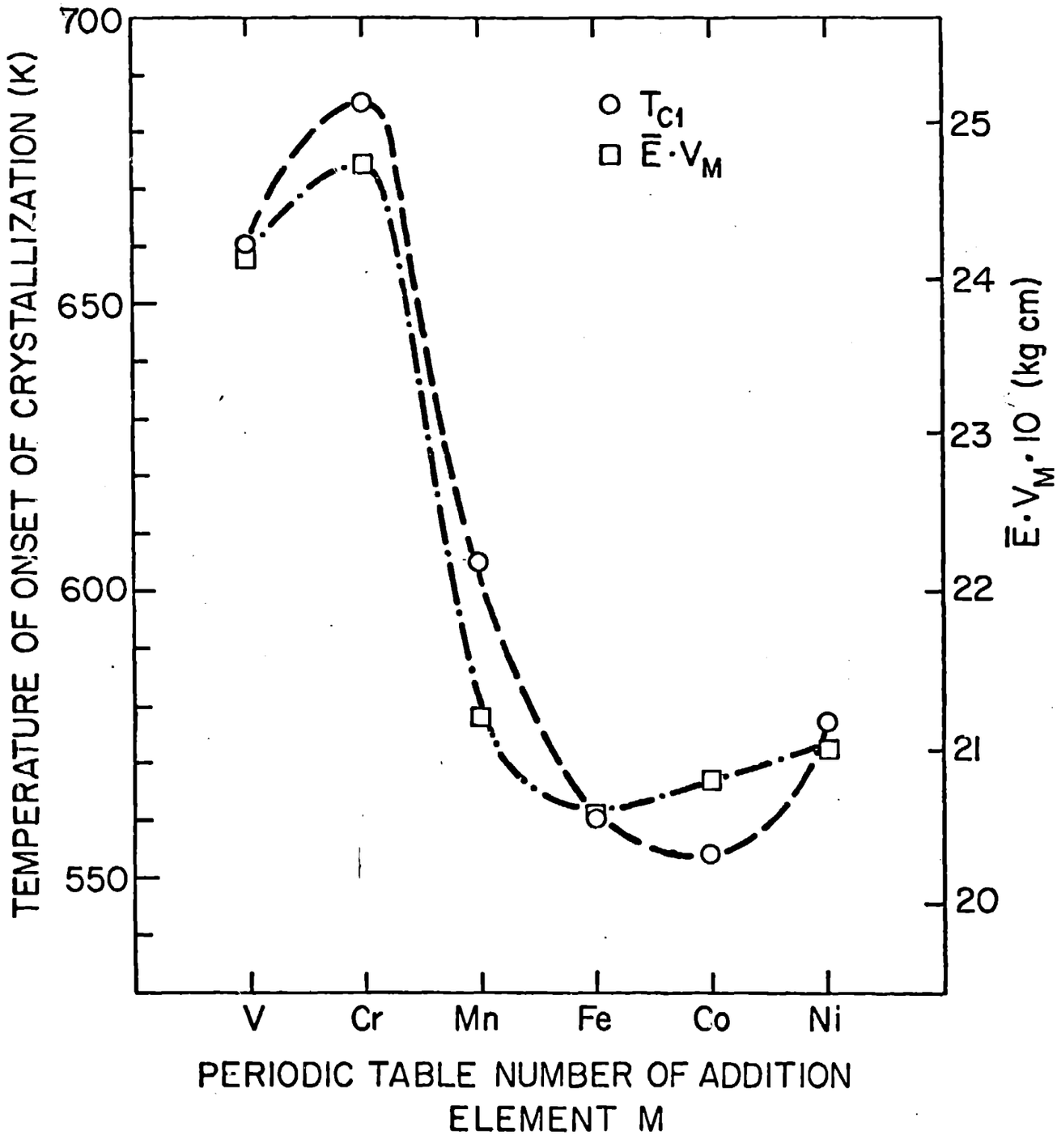
700
650
600
550
TEMPERATURE OF ONSET OF CRYSTALLIZATION (K)
T_{C1}
$\bar{E} \cdot V_M$
25
24
23
22
21
20
$\bar{E} \cdot V_M \cdot 10^{-1}$ (kg cm)
V
Cr
Mn
Fe
Co
Ni
PERIODIC TABLE NUMBER OF ADDITION ELEMENT M