

THE CRYSTALLIZATION TEMPERATURE OF AMORPHOUS TRANSITION-METAL ALLOYS

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Comparison of the formation enthalpy of the amorphous phase (ΔH^{am}) to the formation enthalpy of simple solid solutions (ΔH^{ss}) shows that diffusionless polymorphic crystallization occurs at low temperatures if $\Delta H^{am} > \Delta H^{ss}$. In the composition range where $\Delta H^{am} < \Delta H^{ss}$, crystallization occurs via diffusion and the crystallization temperature is roughly proportional to the formation enthalpy of holes the size of the larger constituent. This model is supported by data from literature of 74 binary alloys. Formation enthalpies are calculated using Miedema's macroscopic atom approach. To calculate ΔH^{am} the amorphous alloy should not be regarded as a random alloy, but a certain degree of chemical short-range order should be accounted for.

The unique properties of amorphous materials make them useful for a variety of applications. Because of their high wear and corrosion resistance amorphous alloys are used as protective coatings. Specific magnetic and optical properties are used in magnetic and optical recording. The absence of grain boundaries, which act as fast diffusion paths at moderate temperatures, makes amorphous alloys almost ideal diffusion barriers in IC technology. Also, new materials can be formed with amorphous phases as a starting point.

However, an amorphous phase is metastable. A key parameter characterizing the stability of amorphous alloys is the crystallization temperature (T_x). In the recent past the description of general trends in the behavior of T_x has received considerable interest. For binary alloys it has been shown by Buschow [1] that the heat of compound formation and T_x do not correlate, whereas the formation enthalpy of holes the size of the smaller constituent $\Delta H_{V_{small}}$ and T_x do correlate. The background of Buschow's model is that crystallization occurs when the smaller constituent of the alloy becomes mobile. This happens at a temperature T_x , which is proportional to the activation energy for the diffusion process, represented by $\Delta H_{V_{small}}$.

Barbour et al. [2] have pointed out that Buschow's model is in contradiction with observa-

tions of solid-state amorphization reactions, in which an amorphous phase forms by diffusion of the smaller constituent. Apparently, crystallization via a diffusion-controlled process requires mobility of both constituents. Therefore, Barbour et al. [2] modified Buschow's model and correlated T_x with the formation enthalpy of holes the size of the larger constituent ($\Delta H_{V_{large}}$).

Clearly, if crystallization occurs via a polymorphic transition long-range diffusion is not required and much lower values for T_x are found [3]. Using Miedema's macroscopic atom approach [4], Loeff et al. [5] calculated formation enthalpies of random amorphous alloys (ΔH^{ran}) and crystalline solid solutions (ΔH^{ss}). They showed a tendency towards high crystallization temperatures, according to Buschow's model [1], for the composition range in which the Gibbs free energy of the amorphous phase is lower than the Gibbs free energy of the solid solution, approximated by ΔH^{ran} and ΔH^{ss} , respectively. For the composition range in which $\Delta H^{ran} < \Delta H^{ss}$ a polymorphic transition from the amorphous phase into a simple crystalline solid solution is thermodynamically not possible and crystallization has to occur by either phase separation or by formation of equilibrium compounds, which usually have complicated crystal structures. These types of crystallization require long-range diffusion (i.e. diffusion over one or

more atomic distances) and relatively high values of T_x are expected. For the composition range in which $\Delta H^{ran} > \Delta H^{ss}$, polymorphic transitions are possible and T_x will be low. The same model was applied by van der Kolk et al. [6] to predict the glass-forming range for a number of systems.

In their calculations of ΔH^{ran} Loeff et al. [5] treated the amorphous alloy as a statistically disordered system, whereas Weeber [7] showed that a certain degree of chemical short-range order should be taken into account. The heat of formation of the amorphous phase (ΔH^{am}) calculated according to Weeber [7], in some cases differs substantially from ΔH^{ran} . Therefore, when predicting the glass-forming range based on the Miedema model, one should compare ΔH^{ss} to ΔH^{am} rather than to ΔH^{ran} . In the case $\Delta H^{am} < \Delta H^{ss}$, crystallization will occur through long-range diffusion and T_x is predicted by the Barbour approach [2]. In this paper we will first show how ΔH^{am} and ΔH^{ss} are calculated. Then T_x will be correlated to $\Delta H_{V_{large}}$ in the amorphous alloy, assuming the same degree of chemical short-range order as in the calculation of ΔH^{am} .

Let us start to point out how the different heats of formation are calculated in the Miedema model [4-6]. The formation enthalpy of the amorphous alloy is calculated by

$$\Delta H^{am} = \Delta H^{chem} + 0.0035 \bar{T}_m \text{ (kJ/mole)}, \quad (1)$$

in which \bar{T}_m is the averaged melting temperature of the solids (in Kelvin). The term comprising \bar{T}_m reflects the disordered nature of the amorphous phase and compares with the heat of fusion for liquids. The chemical contribution (ΔH^{chem}) for a binary alloy $A_x B_{1-x}$ is determined by

$$\Delta H^{chem} = x f_B^A \Delta H^{sol}(\text{A in B}), \quad (2)$$

in which x is the fraction of A atoms, f_B^A the degree to which A atoms are surrounded by B atoms, and $\Delta H^{sol}(\text{A in B})$ the solution enthalpy of A in B (tabulated in ref. [4]). In regular liquids or solid solutions f_B^A is given by

$$f_B^A = c_B^s, \quad (3)$$

where c_B^s represents the surface concentration of B atoms and is defined by

$$c_B^s = (1-x)V_B^{2/3} / [xV_A^{2/3} + (1-x)V_B^{2/3}], \quad (4)$$

where V_A and V_B are the molar volumes of pure A and B, respectively. Using eq. (3) for f_B^A , one obtains ΔH^{ran} . However, to calculate ΔH^{am} , one should not use f_B^A as given in eq. (3) but the following calculation of f_B^A recommended by Weeber [7]:

$$f_B^A = c_B^s [1 + 5(c_A^s c_B^s)^2]. \quad (5)$$

The formation enthalpy of the solid solution comprises three contributions and is given by

$$\Delta H^{ss} = \Delta H^{chem} + \Delta H^{elastic} + \Delta H^{structural}. \quad (6)$$

The first term (ΔH^{chem}) is given by eq. (2) in which (4) and (5) are substituted, assuming that the same degree of chemical short-range order is present as in the amorphous phase. The elastic contribution ($\Delta H^{elastic}$) arises from the size mismatch of the constituents, which occupy equivalent lattice sites in the solid solution. The structural contribution ($\Delta H^{structural}$) reflects the energy associated with the simple hcp, fcc, and bcc crystal structures and is determined as a function of the average number of valence electrons of the metal alloys. Both $\Delta H^{elastic}$ and $\Delta H^{structural}$ are described in detail elsewhere [4-6].

Hole formation enthalpies in the amorphous alloy can be calculated in the Miedema model [4] according to

$$\Delta H_{V_A}^{am} = (1 - f_B^A) \Delta H_{IV}^A + f_B^A (V_A/V_B)^{5/6} \Delta H_{IV}^B \quad (7)$$

for holes the size of A atoms. ΔH_{IV}^A and ΔH_{IV}^B are the monovacancy formation enthalpies for pure A and B, respectively. For f_B^A one should use eq. (5). To obtain formation enthalpies of holes the size of B atoms the indices A and B should be interchanged.

In the following we will evaluate the Re-W system as an example using the calculations described above. In the middle part of fig. 1 crystallization temperatures (T_x) are given measured as a function of composition. The data are from Collver and Hammond [8] (circles) and from Denier van der Gon et al. [3] (squares). Also indicated are the crystalline phases observed directly after crystallization [3]. A strong composition dependence is observed. The W-rich alloys crystallize by a polymorphic transition into a bcc solid solution of W(Re) at relatively low temperatures. The Re-rich alloys show similar behavior and the crystalline phase observed is a hexagonal Re(W) solid solution. The alloys with a composition around 60 at.% Re crystallize into the complicated σ phase

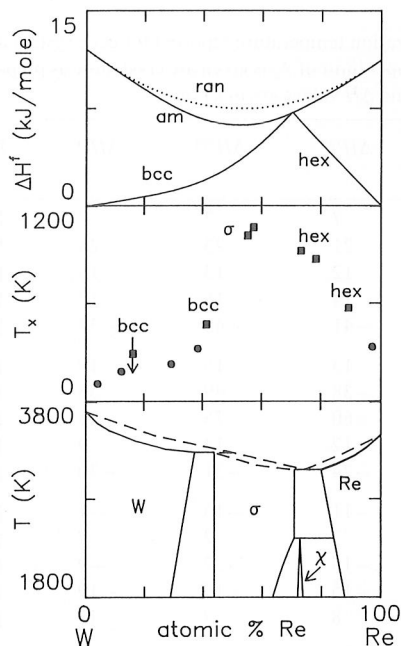


Fig. 1. Top: calculated formation enthalpies for the amorphous phase (ΔH^{am}), the random alloy (ΔH^{ran}), and the bcc and hexagonal solid solutions (ΔH^{ss}) in the Re-W system as described in the text. Middle: crystallization temperatures for various amorphous Re-W alloys. Data are taken from ref. [3] (squares) and ref. [8] (circles). Also indicated are the crystalline phases detected after crystallization. The arrow indicates that the $\text{Re}_{16}\text{W}_{84}$ alloy was crystalline at room temperature, which is taken as an upper limit of T_x . Bottom: phase diagram of the Re-W system (after ref. [9]).

and exhibit the highest values for T_x . Comparison with the phase diagram (bottom part of fig. 1, after ref. [9]) shows that also an equilibrium χ phase exists, which is not observed in the present experiments, even though one of the amorphous alloys has the exact stoichiometry. In all cases crystallization resulted in a single-phase material, irrespective of whether the composition was in a single- or a two-phase region of the phase diagram.

We now compare the formation enthalpy of the amorphous phase (ΔH^{am}) to the formation enthalpy of the solid solution (ΔH^{ss}). The values ΔH^{am} for the amorphous phase, and ΔH^{ss} for the bcc solid solution W(Re) and the hexagonal solid solution Re(W), were calculated as a function of composition using relationships (1), (5), and (6). The results are depicted in the top part of fig. 1. In the re-

gions where ΔH^{ss} is lower in energy than ΔH^{am} diffusionless crystallization is possible. Indeed, these are the regions where T_x is low and crystallization was observed into single-phase solid solutions. In the composition range where $\Delta H^{\text{am}} < \Delta H^{\text{ss}}$, crystallization has to occur either by phase separation, or into one of the equilibrium compounds. To make these types of crystallization possible, long-range diffusion is required and T_x should follow the predictions according to Barbour et al. [2]. Indeed, close to the abovementioned composition range crystallization was observed into the Re-W σ phase at 1070 K, whereas a value of 1030 K is predicted [2]. Although for the alloys which crystallized into the σ phase the calculated value for ΔH^{am} is slightly higher in energy than ΔH^{ss} , the energy difference (3 kJ/mole, see table 1) is within the error limits of the calculations (estimated ± 4 kJ/mole).

To illustrate the influence of chemical short-range order on the calculated heats of formation for ΔH^{am} and ΔH^{ran} , we also plotted the values of ΔH^{ran} in the top part of fig. 1 (dotted line). It is observed that ΔH^{ran} is higher in energy than ΔH^{ss} over the entire composition range. Introduction of chemical short-range order in the random alloy [7] yields ΔH^{am} , which is lower in energy than ΔH^{ss} in the composition range around 67 at.% Re. It will be clear that for several systems the use of ΔH^{am} instead of ΔH^{ran} will dramatically affect the predicted composition range in which Barbour's approach to T_x is valid.

The analysis of the Re-W system, as described above, will now be extended to a number of binary transition-metal alloys. In table 1 a compilation of data from literature is given for 74 systems. For each system the highest crystallization temperature reported and the associated composition are listed. Furthermore, formation enthalpies are presented, calculated as described above. Some alloys could not be prepared in the amorphous state and therefore the preparation temperature is given as an upper limit for T_x . We chose to use only the highest values reported for T_x , because these values should be indicative for diffusion-controlled crystallization if $\Delta H^{\text{am}} < \Delta H^{\text{ss}}$, where the model of Barbour et al. [2] is expected to apply.

In fig. 2 we plotted T_x versus $\Delta H_{\text{Vlarge}}^{\text{am}}$ for the amorphous alloys listed in table 1. The filled symbols represent systems for which $\Delta H^{\text{am}} < \Delta H^{\text{ss}}$. The open

Table 1

Alphabetical list of several binary transition-metal alloys and the highest crystallization temperature reported for each system as well as heats of formation calculated as described in the text. The systems for which an upper limit of T_x is given are crystalline as prepared. For details the reader is referred to the text and the references quoted. T is in Kelvin and ΔH values are in kJ/mole

System	T_x	$\Delta H_{V_{large}}^{ran}$	$\Delta H_{V_{large}}^{am}$	Large element	ΔH^{ran}	ΔH^{am}	ΔH^{ss}	Ref.
Ag ₅₀ Cu ₅₀	360	110	116	Ag	7	7	7	[12]
Ag ₅₀ Ni ₅₀	< 300	128	139	Ag	21	25	25	[10]
Au ₂₅ Co ₇₅	470	164	179	Au	12	13	16	[10]
Au ₄₀ Fe ₆₀	813	150	165	Au	14	16	18	[12]
Au ₂₂ La ₇₈	453	130	131	La	-41	-45	-34	[1]
Au ₅₀ Ni ₅₀	< 300	137	148	Au	13	15	19	[10]
Au ₃₅ Ti ₆₅	670	140	150	Au	-38	-49	-55	[13]
Au ₃₅ Zr ₆₅	820	156	154	Zr	-60	-75	-75	[14]
Co ₅₀ Cu ₅₀	< 300	118	123	Cu	12	14	9	[10]
Co ₄₀ Hf ₆₀	823	196	199	Hf	-24	-31	-20	[12]
Co ₅₀ La ₅₀	473	189	205	La	-11	-15	-1	[12]
Co ₅₀ Mo ₅₀	1170	190	186	Mo	3	2	7	[13,15]
Co ₅₀ Ta ₅₀	1120	212	209	Ta	-15	-22	-9	[15]
Co ₇₈ Ti ₂₂	873	176	181	Ti	-15	-19	-19	[1]
Co ₅₅ W ₄₅	1070	215	205	W	8	7	13	[16]
Co ₄₀ Y ₆₀	642	172	180	Y	-13	-16	7	[12]
Co ₉₀ Zr ₁₀	833	221	225	Zr	-11	-13	-12	[12]
Cr ₅₀ Cu ₅₀	< 350	108	111	Cu	19	23	18	[17]
Cr ₄₃ Ni ₅₇	< 300	129	132	Cr	0	-2	-11	[18]
Cr ₅₀ Pd ₅₀	< 350	140	142	Pd	-8	-12	-20	[19]
Cr ₅₀ Ti ₅₀	920	154	156	Ti	0	-3	-3	[20]
Cu ₅₆ Hf ₄₄	831	173	171	Hf	-11	-16	0	[12]
Cu ₅₀ Mo ₅₀	280	167	157	Mo	26	32	32	[21]
Cu ₂₀ Ta ₈₀	1070	212	210	Ta	11	11	7	[11]
Cu ₆₅ Ti ₃₅	700	141	139	Ti	-3	-5	-4	[22]
Cu ₄₄ V ₅₆	280	138	132	V	11	13	9	[21]
Cu ₅₀ W ₅₀	450	196	179	W	31	38	37	[11,12]
Cu ₉₀ Zr ₁₀	877	168	168	Zr	-5	-5	-1	[23]
Fe ₄₀ Hf ₆₀	866	196	199	Hf	-11	-16	-10	[12]
Fe ₇₀ Mo ₃₀	870	183	179	Mo	6	5	6	[24]
Fe ₅₀ Pt ₅₀	< 300	168	170	Pt	-6	-10	-18	[25]
Fe ₆₃ Ti ₃₇	930	170	177	Ti	-10	-15	-10	[26]
Fe ₅₀ W ₅₀	1150	218	208	W	10	9	15	[12]
Fe ₅₀ Y ₅₀	741	186	201	Y	5	5	25	[12]
Fe ₈₇ Zr ₁₃	882	218	224	Zr	-6	-8	-3	[23,27]
Hf ₃₆ Ni ₆₄	923	201	208	Hf	-34	-46	-33	[12,28]
Hf ₄₇ V ₅₃	808	200	206	Hf	6	5	13	[1]
Ir ₅₅ Nb ₄₅	1133	202	208	Nb	-43	-60	-60	[12]
Ir ₄₅ Ta ₅₅	1283	224	223	Ta	-41	-56	-49	[29]
Ir ₂₅ W ₇₅	< 350	240	238	W	0	-2	4	[30]
La ₆₉ Ni ₃₁	443	157	160	La	-14	-16	-8	[1]
Mo ₉ Nb ₉₁	75	189	189	Nb	8	8	-3	[8]
Mo ₅₀ Ni ₅₀	900	187	183	Mo	1	-2	-2	[13]
Mo ₃₀ Re ₇₀	1020	224	230	Mo	6	4	4	[8]
Mo ₈₂ Rh ₁₈	155	197	197	Mo	1	0	0	[12]

Table 1. Continued

System	T_x	$\Delta H_{V_{large}}^{ran}$	$\Delta H_{V_{large}}^{am}$	Large element	ΔH^{ran}	ΔH^{am}	ΔH^{ss}	Ref.
Mo ₅₅ Ru ₄₅	800	201	201	Mo	-5	-9	-8	[8,13]
Mo ₁₅ Zr ₈₅	910	183	183	Zr	5	5	6	[8]
Nb ₄₅ Ni ₅₅	920	187	187	Nb	-22	-32	-27	[12,13]
Nb ₅₀ Pd ₅₀	850	169	164	Nb	-45	-61	-69	[31]
Nb ₄₀ Rh ₆₀	1093	190	192	Nb	-36	-49	-49	[12]
Nb ₅₀ Zr ₅₀	750	195	203	Zr	12	14	12	[8]
Ni ₄₃ Ta ₅₇	1020	213	210	Ta	-19	-26	-15	[15,18]
Ni ₅₈ Ti ₄₂	822	166	171	Ti	-28	-39	-38	[32]
Ni ₃₆ W ₆₄	920	228	223	W	8	7	12	[33]
Ni ₃₁ Y ₆₉	591	158	161	Y	-17	-19	1	[34]
Ni ₆₅ Zr ₃₅	886	200	209	Zr	-41	-55	-42	[22]
Os ₄₅ Ta ₅₅	1220	234	237	Ta	-26	-37	-36	[30]
Os ₃₀ W ₇₀	1220	244	243	W	4	3	8	[30]
Pd ₄₀ Ta ₆₀	1050	198	191	Ta	-40	-54	-54	[31]
Pd ₅₀ Ti ₅₀	750	149	148	Ti	-58	-78	-85	[35]
Pd ₅₀ V ₅₀	570	152	158	Pd	-28	-39	-49	[31]
Pt ₅₀ Ti ₅₀	720	159	162	Ti	-68	-91	-98	[36]
Pt ₁₈ W ₈₂	1070	236	234	Pt	0	-1	3	a)
Pt ₂₂ Zr ₇₈	768	180	181	Zr	-59	-66	-75	[1]
Re ₇₂ Ta ₂₈	1220	247	252	Ta	-8	-12	-18	[30]
Re ₅₃ W ₄₇	1070	245	244	W	8	7	4	[3]
Rh ₄₅ Ta ₅₅	1118	214	211	Ta	-34	-47	-41	[12]
Rh ₃₀ Zr ₇₀	758	188	191	Zr	-50	-59	-59	[1]
Ru ₅₀ Ti ₅₀	450	181	190	Ti	-35	-49	-57	[37]
Ru ₃₅ W ₆₅	1070	236	233	W	3	0	7	[3]
Ru ₂₅ Zr ₇₅	670	191	194	Zr	-33	-38	-26	[37]
Ta ₃₇ W ₆₃	210	251	259	Ta	5	3	-12	[8]
V ₅₀ Zr ₅₀	870	196	204	Zr	4	3	11	[38] ^{b)}
W ₄₀ Zr ₆₀	1170	226	240	Zr	1	-1	0	[33]

^{a)} 350 Å thick amorphous Pt–W alloys were coevaporated in the composition range between 75 at.% W and 82 at.% W. T_x was determined by transmission electron microscopy after isochronal annealing for 15 min in a vacuum better than 1×10^{-7} mbar. T_x was 800°C for alloys with a composition between 77 at.% W and 82 at.% W. Amorphous Pt₂₄W₇₆ crystallized at 775°C. For all alloys crystallization occurred into a mixture of fcc W and an unidentified bcc phase with lattice parameter $a = 6.85(15)$ Å.

^{b)} As a). Amorphous V₅₀Zr₅₀ crystallized at 600°C into an unidentified phase.

symbols represent systems for which $\Delta H^{am} > \Delta H^{ss}$. The arrows indicate alloys which were crystalline as prepared. For the alloys which are believed to crystallize via diffusion, i.e. the alloys for which $\Delta H^{am} < \Delta H^{ss}$ (filled symbols), the relationship found between T_x and $\Delta H_{V_{large}}^{am}$ is

$$T_x = 4.7 \Delta H_{V_{large}}^{am} \quad (8)$$

in which T_x is given in Kelvin and $\Delta H_{V_{large}}^{am}$ in kJ/mole. This relationship is indicated by the solid line in fig. 2. A few exceptions seem to be encountered when $\Delta H^{am} < \Delta H^{ss}$ is used as the criterion to select

alloys for which T_x can be predicted using relationship (8). However, for most of these systems the differences $\Delta H^{am} - \Delta H^{ss}$ do not exceed the error limit of 4 kJ/mole. This is illustrated, e.g., by amorphous Au₂₅Co₇₅, which crystallized into a single-phase solid solution [10], and a Au₅₀Ni₅₀ alloy, prepared at LN₂ temperature, which appeared to be a solid solution instead of an amorphous phase [10]. Apparently, for these alloys $\Delta H^{am} - \Delta H^{ss} > 0$, whereas a negative value was calculated (see table 1). In fig. 2 a few open symbols, which belong to systems with $\Delta H^{am} > \Delta H^{ss}$, still show high T_x . Also, for these systems the dif-

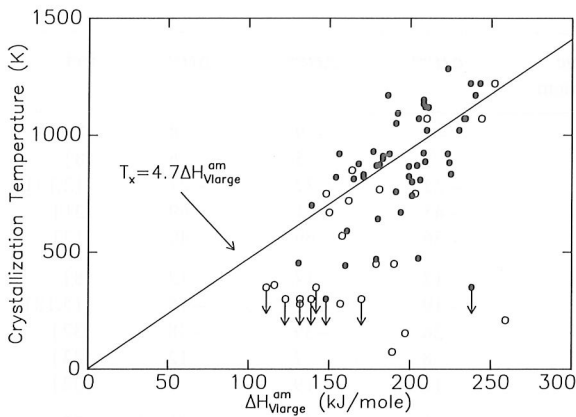


Fig. 2. Crystallization temperatures (T_x) versus formation enthalpy of holes the size of the larger constituent ($\Delta H_{V_{large}}^{am}$) for the amorphous alloys compiled in table 1. Closed symbols represent systems for which $\Delta H^{am} - \Delta H^{ss} \leq 0$ kJ/mole. Open symbols represent systems for which $\Delta H^{am} - \Delta H^{ss} \geq 0$ kJ/mole. Systems indicated with arrows were crystalline as prepared and the preparation temperature is given as an upper limit for T_x . The line $T_x = 4.7\Delta H_{V_{large}}^{am}$ gives a rough estimate of T_x for the systems represented by almost all closed symbols, i.e. for systems which are expected to crystallize via diffusion.

ferences $\Delta H^{am} - \Delta H^{ss}$ are less than the error limit. For instance, the Re-W system, as discussed above, or amorphous $Cu_{20}Ta_{80}$, which crystallizes into Cu and β -Ta at 1070 K by phase separation [11]. This requires diffusion and relationship (8) applies.

The proportionality constant 4.7 in relationship (8) appears slightly larger than the value of 4.2 determined by Barbour et al. [2]. The difference between the proportionality constants does not arise from the fact that in Barbour's model $\Delta H_{V_{large}}^{ran}$ was used instead of $\Delta H_{V_{large}}^{am}$, because the difference between $\Delta H_{V_{large}}^{ran}$ and $\Delta H_{V_{large}}^{am}$ is relatively small, as can be seen in table 1. The major difference is that in our least-squares determination of the proportionality constant each system is only included once, whereas in Barbour's case systems exhibiting positive heats of formation were excluded and, moreover, several systems were included many times for various compositions.

From the deviations between the measured values of T_x and the values predicted by relationship (8) it is clear that only an indication of T_x can be given this way. Yet, this may still be useful in order to predict

the thermal stability of amorphous alloys in the range of compositions not yet measured.

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