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Inhibitors of the crystallisation of amorphous materials

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Abstract. The problems arising in the choice of additives that will improve the temporal and thermal stability of the non-crystalline state of materials are discussed. Transition metal oxides and amorphous metal alloys form suitable subjects for studying the effect of crystal-chemical and energy factors on the stabilisation of amorphous substances. Data on the stabilisation of the amorphous matrix by introducing alloying additives which form solid solutions with isovalent and heterovalent substitution in the cationic sublattice, chemical compounds, and alloys, are reviewed. Criteria for selecting inhibitors that will stabilise the amorphous state of a material are formulated. The bibliography comprises 63 references.

I. Introduction

In the technology of the production of many inorganic materials, e.g. oxides and metal alloys, use is often made of metastable and amorphous modifications of substances. The use of amorphous oxides in the preparation of complex coordination compounds makes it easier for solid state reactions to occur. Such oxides are used in energy-saving technologies that allow homogeneous materials to be produced under optimum conditions. Amorphous metal alloys possess special magnetic properties and resistance to corrosion; this makes them interesting topics for research. One of the problems in studying the amorphous state of a material is to find the factors affecting its time-dependent and thermal stability. This review is only concerned with an analysis of certain general structural and energy characteristics of the non-crystalline state of a solid which can be used to formulate criteria for searching for inhibitors that will hinder the transition of the amorphous to the crystalline state. As the non-crystalline state of matter is as widespread as the crystalline state, we may expect that general physicochemical principles will also be satisfied for amorphous materials.[1]

When analysing publications on the physicochemical properties of amorphous compounds we encounter the problem of comparing the properties of materials with the same or similar compositions but which have sometimes been produced under extremal conditions. For example, in the production of amorphous metal strips the rate of quenching reaches 10^8–10^{10} deg s^{-1}. This makes comparison (and recommendations) difficult because the thermodynamic functions of a substance are dependent on the method of preparation if the material is not in an equilibrium state. In a practical respect the temperatures of relaxation (T_{rel}) and crystallisation (T_{cr}) of amorphous materials, at which irreversible changes in the structure takes place, are very important, as is also, in a number of cases, the loss of valuable technological qualities. These temperatures sometimes vary by some tens of degrees for similar specimens produced in different laboratories. One must therefore concentrate on criteria for the correctness of the measurements of thermodynamic properties. Such measurements are valid if the internal state of the system remains unchanged during the measurement of the property. In this respect the certification of amorphous compounds produced by chemical methods is simpler and more reliable because such methods are milder and more easily reproduced and monitored.

Chemical methods for obtaining complex coordination compounds frequently involve the use of coprecipitation of metal hydroxides followed by dehydration which produces an intermediate state that is amorphous to X-rays. The crystallisation of such amorphous oxides sometimes has an 'explosive' character and is accompanied by a chemical reaction between the oxides giving a 100% yield of the substance being prepared. Oxides play an important role in chemical thermodynamics and can be used as models for the study of physicochemical aspects of the metastable state of matter.

Measurements of the heat capacity (C_p) and crystallisation temperature of amorphous compounds are fully valid if the time over which the property is measured is shorter than the relaxation time of the system. In most instances the thermodynamic properties of amorphous materials are measured with the use of differential thermal analysis (DTA) and/or differential scanning calorimetry (DSC) with a rate of heating less than 10 deg min^{-1}, which is much higher than the rate of relaxation of the system at temperatures a long way from the relaxation and crystallisation temperatures. This guarantees reproducibility of the properties of the specimens because the conditions under which heat is absorbed and evolved are reversible. The thermodynamic properties of metastable and amorphous modifications of solids can serve as characteristics of their stability and reactivity.

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Most transition metal oxides and metal alloys belong to the category of coordination compounds. Structural studies on amorphous materials of different provenance indicate that the metal atoms have coordination polyhedra (CP), the various modes of linking of which provide short-range order in these materials in the absence of translational symmetry. A knowledge of the distinctive features and types of CPs is essential for an understanding of the reaction mechanisms in crystalline and non-crystalline states of solids and the use of the CP as a structural fragment which is common to both states enables them to be discussed from a common standpoint.

Examples indicating the polyhedral structure of amorphous oxides are given below. In films of amorphous oxides (e.g. Fe_2O_3, Al_2O_3, Nb_2O_5, and WO_3) obtained by pyrolysis of organometallic compounds in an O_2 atmosphere the first coordination number (CN) of the metal is smaller than in known crystal structures. The parameters of the structure of amorphous phases are determined by analysing the radial distribution function (RDF).[2] For example, an analysis of the RDF of an amorphous Fe_2O_3 film showed that the Fe–O distance (1.95 Å) is smaller than the corresponding distance in crystalline α-Fe_2O_3 (2.01 Å). The iron atoms in amorphous Fe_2O_3 are located in both octahedral and tetrahedral holes in a disordered packing of oxygen atoms. The presence of such holes is characteristic of the metastable modification γ-Fe_2O_3. The short-range order in the amorphous α-Fe_2O_3 is similar to that in γ-Fe_2O_3. The first coordination peak in the RDF at an Fe–O distance of 1.95 Å and the fact that $5 < CN < 6$ indicates that amorphous Fe_2O_3 can be described with the use of the most likely structural elements (MLSE).[3] A similar approach was developed elsewhere.[4]

The quantitative relationships between the types of polyhedra may vary depending on the method by which the amorphous materials have been obtained. For example, the model for the structure of an amorphous film of Al_2O_3 is a linear group of three polyhedra, two of which are AlO_6 octahedra with a shared edge and the third is an AlO_4 tetrahedron which shares a corner with one of the octahedra. For a film obtained by pyrolysis of aluminium isopropoxide at 670 K with 50 vol.% O_2 in the gas phase on an NaCl base, the mean CN(Al) is 5.3. If the O_2 concentration is raised to 75 vol.% the MLSE is a group of three AlO_4 tetrahedra, two of which have a shared face and the third is linked to them by a corner.[5]

The model of MLSE for an amorphous film of Nb_2O_5 is a linear group of three polyhedra: two tetragonal pyramids and one tetrahedron linked by corners, with a mean CN(Nb) of 4.5. The model of MLSE for amorphous WO_3 is a group of tetragonal pyramids and octahedra with a mean CN(W) of 5.5. In crystalline WO_3 the octahedron is the main coordination polyhedron. Thus the models of the atomic groupings can be regarded as subcells of the structure of amorphous oxides which are joined together to form a chain without any long-range order and are space-filling. This enables models for amorphous oxides to be obtained.[6]

A similar situation is observed in studies of amorphous alloys. The amorphous state of metal alloys is characterised by atomic short-range order and it is thermodynamically metastable.[7] Fragments of the crystal structure of metal alloys are retained in the amorphous state and the chief 'amorphising' elements are boron, carbon, and phosphorus. The stability of amorphous alloys against diffusion decomposition is associated with the presence in the alloy of fragments with rigid metal–non-metal covalent bonds. These fragments may have a composition corresponding to a stable or metastable crystalline state and a similar nearest coordination sphere.[8] To describe the Fe–B system (alloys with the approximate composition $Fe_{0.8}B_{0.2}$ form the subject of experimental studies particularly frequently) a trigonal prism model with an Fe_3C type CP has been used.[9] The tendency to amorphisation is related to the variation in the type of linking of these prisms. Clearly, the more stable such fragments the more difficult it is for disintegration of the amorphous alloy to occur on its crystallisation.

The view that transition metal oxides can be regarded as inorganic polymers with M–O covalent bonds and that the structure of the polymers can be modelled by a three-dimensional chain composed of deformed oxygen polyhedra[10] is valid. Most transition metal oxides are semiconductors or insulators. According to Ioffe "all the main properties of a semiconductor, including its band structure, are determined by the short-range order — the chemical bonds within one unit cell of the crystal".[11]

These preliminary remarks are, of necessity, fragmentary in nature but they indicate that the structures of the first coordination spheres of amorphous and crystalline structures have similar features and it is only in the more distant coordination spheres that differences are observed. It may therefore be expected that when explaining the reasons responsible for the features of the crystallisation of amorphous compounds, irrespective of their nature, the energy and crystal-chemical properties of the coordination polyhedra will be of predominant importance.

For most amorphous oxides and metal alloys, which are investigated by thermal methods, simultaneous structural studies are not carried out. The crystallisation of amorphous compounds may be accompanied by a change in the CN in the nearest neighbours. The enthalpies of the change in CN of some cations with oxygen nearest neighbours are known[12] and they are less than 5% of the enthalpies of atomisation of the oxides. Hence, to a first approximation, the effect of a change in the coordination of the metal cation when amorphous oxides and their solid solutions crystallise can be neglected (such data are not yet available for some cations). Furthermore, the ratio of the different polyhedra in the MLSE may vary depending on the method used to obtain the amorphous compound. Therefore it will henceforth be assumed that the coordination numbers of the cations are the same in the primary matrix and in the alloying constituent.

II. Crystallisation of oxides that are amorphous to X-rays

The general criteria for searching for inhibitors that will stabilise the amorphous state of a solid can be recognised by experimental studies of the crystallisation of simple amorphous (to X-rays) oxides, solid solutions, and chemical compounds with different polyhedral structures. The principal method for obtaining amorphous oxides is the careful decomposition of the hydroxide at low temperatures. Suitable model subjects are the oxides Fe_2O_3, Cr_2O_3, Al_2O_3, and ZrO_2, solid solutions based on them, and chemical compounds formed by them; these are widely used in electronic engineering. The phase transformations occurring on dehydration of the hydroxides and subsequent crystallisation of the amorphous oxides are normally studied by DTA, DSC, X-ray phase analysis, and Raman spectroscopy. By using these methods the sequence of chemical and physical changes can be reconstructed.

The preparation and crystallisation of amorphous Fe_2O_3, forming α-Fe_2O_3, had already been described by Mendeleev[13]

Table 1. *Temperatures of commencement of crystallisation and enthalpies of crystallisation of oxides from the amorphous state.*

Oxide	T_{cr} / K	$-\Delta H_{cr}$ / kJ mol^{-1}	$-\Delta H_{fus}$ / kJ mol^{-1}	$-\Delta H_{cr}/\Delta H_{fus}$	Ref.
Fe_2O_3	533	37.9±2.3	–	–	14
	533	134	–	–	17
Cr_2O_3	653	22.3±1.5	125	0.18	15
	663	50		0.40	17
Al_2O_3	443	58	111	0.52	17
ZrO_2	666	21.0±0.5	90	0.23	16
TiO_2	523	63	68	0.93	17

Table 2. Temperatures and enthalpies of crystallisation of amorphous oxides.

Oxide	$\frac{T_{cr}}{K}$	$\frac{-\Delta H_{cr}}{kJ\ mol^{-1}}$	$\frac{a_0}{Å} \pm 0.005$	$\frac{c_0}{Å} \pm 0.005$
$Sc_{0.04}Fe_{1.96}O_3$	535	32.7±1.0	5.046	13.754
$Sc_{0.1}Fe_{1.9}O_3$	579	24.8±0.4	5.054	13.764
$In_{0.1}Fe_{1.9}O_3$	524	34.2±2.1	5.057	13.782
$Ga_{0.2}Fe_{1.8}O_3$	519	41.2±4.5	5.036	13.748
$Al_{0.1}Fe_{1.9}O_3$	593	33.9±2.3	5.018	13.704
Fe_2O_3	533	37.9±2.3	5.036	13.748
$\langle Yb_{0.1}Fe_{1.9}O_3\rangle$[a]	603	–	–	–
$\langle Tm_{0.1}Fe_{1.9}O_3\rangle$[a]	646	–	–	–
$\langle La_{0.1}Fe_{1.9}O_3\rangle$	709	–	–	–

[a] According to initial mixture; the crystallisation products are α-Fe_2O_3 + $MFeO_3$.

who remarked on the spontaneous heating of dehydrated $Fe_2O_3 \cdot 1.5H_2O$.

Hydroxides of iron, chromium, and zirconium have been obtained by precipitation from solutions of the nitrates with ammonia solution[14-16] The DSC thermograms of hydroxides previously dried (100–120 °C) show endothermic effects due to the removal of water. After this the materials were oxides amorphous to X-rays. At higher temperatures exothermic effects due to crystallisation were observed, and these effects are sometimes 'explosive' in character.

The changes occurring in the hydroxides on heating have been assessed from X-ray phase analysis and Raman spectroscopic data. In the Raman spectra the bands due to M–O–H and H–O–H stretches disappear as the temperature is increased. The temperatures and enthalpies of crystallisation of the amorphous oxides are given in Table 1. T_{cr} and ΔH_{cr} from different publications show marked differences, i.e. undoubtedly the method of preparing the amorphous compounds affects their properties. As short-range order exists in the amorphous phase the value of ΔH_{cr} for the amorphous material cannot be larger in absolute magnitude than ΔH_{fus} for the crystalline material.

Publications on the determination of ΔH_{cr} for Fe_2O_3 have been analysed critically.[14] It was shown, in particular, that the value of ΔH_{cr} for Fe_2O_3 found by quantitative differential thermal analysis (−134 kJ mol^{-1} [17]) is obviously too high. This method is inaccurate and therefore the values of ΔH_{cr} for Fe_2O_3 and the other oxides (TiO_2, Al_2O_3, Cr_2O_3) must be regarded as estimates.

The enthalpies of fusion of crystalline M_2O_3 (M = Al, Cr, Ti, Sc) are 100–125 kJ mol^{-1} but the entropies of fusion are ~46 J mol^{-1} K^{-1}.[18] Since hematite α-Fe_2O_3 dissociates to magnetite and O_2 at 1 700 K (which is much lower than the melting points of the other M_2O_3, *viz.* 2 100–2 700 K), it is unlikely that the enthalpy of crystallisation of Fe_2O_3 would be of the same order of magnitude (100–125 kJ mol^{-1}) or even exceed the enthalpies of fusion of the thermodynamically stable oxides. The ratios $\alpha = \Delta H_{cr}/\Delta H_{fus}$, indicating the high energy capacity of the amorphous oxides, are also given in Table 1.

III. Crystallisation of solid solutions of oxides

The effect of adding 5–10 mol% of oxides on T_{cr} and ΔH_{cr} of amorphous Fe_2O_3 and ZrO_2 has been investigated.[15, 19-23] The main aim of this research was to find oxides which might stabilise the amorphous state of the primary matrix in the model specimens. Small amounts of additives can be introduced into a matrix of the main component and may form a solid solution, if this is permitted by the size factor, or form a chemical compound with the main component.

1. Formation of solid solutions with isovalent substitution

Studies of the effect of M_2O_3 additives (M = Al, Ga, Cr, Sc, In, La, Tm, Yb) on the variation in T_{cr} of amorphous Fe_2O_3 led to the following conclusions. In the same type of processes of solid-solution formation there is a correlation between increasing crystallisation temperature and an increase in the bond energy ε(M–O) as compared to ε(Fe–O). The higher ε(M–O) the higher the temperature of commencement of reorganisation of fragments of the structure of amorphous oxides that are formed by dehydration of coprecipitated hydroxides with subsequent crystallisation of the solid solutions based on hematite. Such solutions are formed by introducing the oxides of aluminium, chromium, gallium, indium, and scandium but the introduction of lanthanum, thulium, and ytterbium oxides, whose cations are larger, leads to crystallisation of a two-phase mixture of the orthoferrite-perovskites $MFeO_3$ with Fe_2O_3. T_{cr} and $-\Delta H_{cr}$, obtained by the DSC method, for the amorphous oxides $M_xFe_{2-x}O_3$ are given, together with their rhombohedral lattice parameters, in Table 2; crystal-chemical and energy characteristics of M^{3+} cations, and the bond energies ε(M–O) in the oxides, calculated by a method proposed previously,[24] are given in Table 3.

The increase in T_{cr} on the introduction of lanthanum, terbium [thulium? (Ed. of translation)], and ytterbium oxides is determined mainly by the high M–O bond energies. On crystallisation in an iron oxide matrix a chemical reaction takes place to form islets of a new phase: the orthoferrite $MFeO_3$. The new phase, which is distributed uniformly throughout the whole volume of the oxides crystallising, inhibits the formation of hematite and consequently the upper temperature boundary of the exothermic effect is not recorded and the large lanthanide ions do not enter into the hematite structure.

The change in the CN of the metal on insertion into the hematite structure (CN = 6, octahedron) also has an effect on the temperature range for crystallisation. The insertion of Ga^{3+} and Cr^{3+} ions, with radii similar to that of Fe^{3+}, leads to differing thermograms. The crystallisation range of the Ga–Fe solid solution is more extended than the Cr–Fe crystallisation range, reflecting the diffusion difficulties associated with the change in

Table 3. Crystal-chemical and energy characteristics of M^{3+} ions and bond energies ε(M–O) in the oxides M_2O_3.

Property	In^{3+}	Ga^{3+}	Fe^{3+}	Cr^{3+}	Sc^{3+}	Al^{3+}	Yb^{3+}	Tm^{3+}	La^{3+}
ε(M–O)[a]/kJ g^{-1} electron^{-1}	179	195	199	222	–	255	–	–	–
ε(M–O)[b]/kJ g^{-1} electron^{-1}	178.5	197	199	222	283	255	238	257	282
$r(M^{3+})$[a]/Å	0.80	0.62	0.65	0.62	0.75	0.53	0.87	0.88	1.03
ΔT_{cr}/K	−9	−7	–	40	46	60	70	112	176
$\Delta\varepsilon$/J g^{-1} electron^{-1}	−20	−2	–	23	84	56	39	58	83
Crystallisation products	Solid solution based on hematite α-Fe_2O_3 + $MFeO_3$								

Note. ΔT_{cr} is the change in the crystallisation temperature of Fe_2O_3 per 5 mol% of additive and $\Delta\varepsilon = \varepsilon(M-O) - \varepsilon(Fe-O)$; the scale of $\Delta\varepsilon$ shows the enthalpy of formation of the paired-electron bonds per 1 g-mol of electrons.

[a] CN = 6.

[b] In the individual oxide.

the CN of one of the gallium ions in the thermodynamically stable modification β-Ga_2O_3. This modification may be produced in the crystallisation of the coprecipitated hydroxides. In β-Ga_2O_3 one of the cations is tetrahedrally, and the other octahedrally, coordinated by O^{2-} ions. The structure of Cr_2O_3 is however similar to that of Fe_2O_3 and there is therefore no change in the CN of chromium on formation of a $Cr_2O_3-Fe_2O_3$ solid solution.

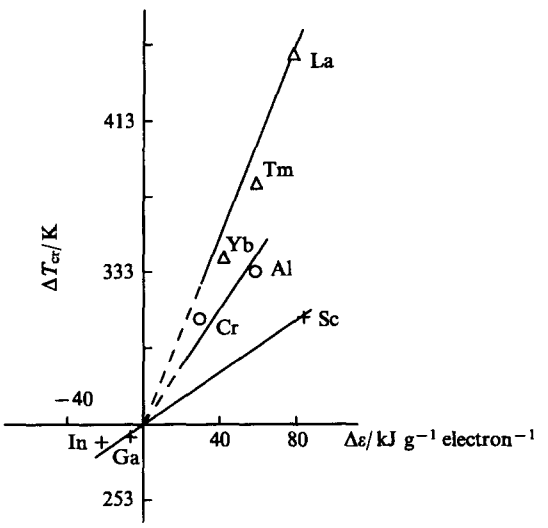


Figure 1. The change in the temperature of commencement of crystallisation of amorphous oxides $\Delta T_{cr} = T_{cr}[(M_xFe_{1-x})_2O_3] - T_{cr}(Fe_2O_3)$ plotted as a function of the bond energy difference Δε.

The function $\Delta T_{cr}(\Delta\varepsilon)$ is shown in Fig. 1 for three groups of additive cations: Al and Cr; In, Ga, and Sc; and La, Tm, and Yb. For the cations in the first group a CN of 6, which is characteristic of them in the pure oxides and in a thermodynamically stable state, is retained in the solid solution. The CN of the cations in the second group changes on formation of the solid solution. On insertion of the additive cations in the third group crystallisation of the two-phase mixture α-Fe_2O_3 + $MFeO_3$ takes place. For all three groups of additive cations the dominant factor affecting the stabilisation of the amorphous state of iron oxide is the metal–oxygen bond energy.

2. Formation of solid solutions with heterovalent substitution

The effect of heterovalent additives on the stability of the amorphous oxide has been investigated in the case of ZrO_2. Crystallisation of amorphous ZrO_2 on heating in a calorimeter leads to the formation of the metastable cubic modification, in contrast to the crystallisation of amorphous Fe_2O_3 in which the stable phase α-Fe_2O_3 is formed. The high-temperature cubic modification of ZrO_2, which is formed by crystallisation from the melt, is stabilised at low temperatures by the introduction of lanthanide oxide additives. The introduction of 5 mol% $MO_{1.5}$ leads to stabilisation of the cubic modification of ZrO_2 which persists down to 1 070 K and on subsequent cooling to 300 K. T_{cr} and ΔH_{cr} for the cubic solid solutions are shown in Table 4 and Fig. 2. ε(M–O) and the radius of the lanthanide ion (CN = 8) clearly have the main influence on T_{cr}. In Fig. 2 two coordinate fields, situated above and below the abscissa axis, can be distinguished. The ions occuring in the first field are those of yttrium, scandium, terbium, praseodymium, and neodymium, the insertion of which increases the temperature stability of the amorphous ZrO_2 matrix. The M–O bond energies in these oxides are greater than or almost the same as ε(Zr–O), which is equal to 268 kJ g^{-1} electron^{-1} in the cubic modification. In the second field the europium and ytterbium ions, which have ε(M–O) < ε(Zr–O), occur. The introduction of oxides with a lower chemical potential for oxygen favours an increase in the crystallisation temperature of the solid solution, i.e. these oxides are inhibitors of crystallisation of the amorphous state.

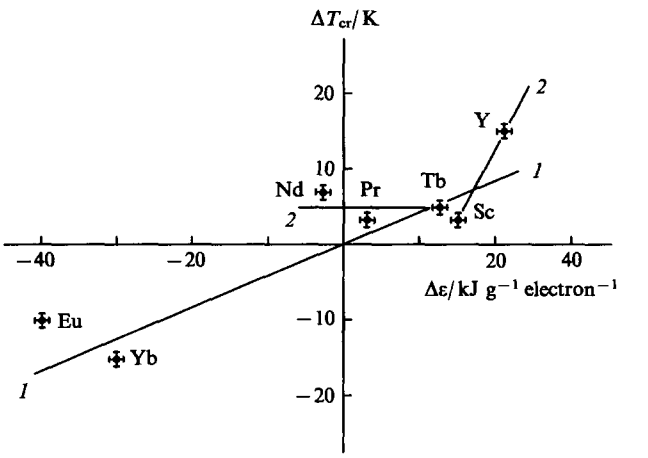


Figure 2. The change in the crystallisation temperature of solid solutions $\Delta T_{cr} = T_{cr}(Zr_{0.95}M_{0.05}O_{1.975}) - T_{cr}(ZrO_2)$ plotted as a function of the bond energy difference $\Delta\varepsilon = \varepsilon(M-O) - \varepsilon(Zr-O)$.

Table 4. Crystal-chemical and energy characteristics of the oxides $Zr_{1-x}M_xO_{2-x/2}$.

Oxide	ε(M – O) / kJ g^{-1} electron^{-1}	$r_{M^{3+}}$ / Å	$\Delta r_{M^{3+}}$ / %	T_{cr} / K	$-\Delta H_{cr}$ / kJ mol^{-1}
ZrO_2	268	0.84	–	666–715	21.0±0.46
$Zr_{0.95}Y_{0.05}O_{1.975}$	290	1.02	21	680–715	18.0±0.86
$Zr_{0.95}Sc_{0.05}O_{1.975}$	283	0.87	3.6	669–771	17.5±0.53
$Zr_{0.95}Pr_{0.05}O_{1.975}$	271	1.13	34	669–775	15.0±0.78
$Zr_{0.95}Nb_{0.05}O_{1.975}$	266	1.11	27	672–775	14.5±1.6
$Zr_{0.95}Eu_{0.05}O_{1.975}$	229	1.07	23	655–754	17.5±1.0
$Zr_{0.95}Tb_{0.05}O_{1.975}$	281	1.04	24	671–781	18.0±0.6
$Zr_{0.95}Yb_{0.05}O_{1.975}$	238	0.99	18	651–741	17.5±0.6

The large praseodymium and neodymium ions produce a slight increase in T_{cr} of amorphous ZrO_2 although their ε(M–O) values are close to ε(Zr–O). Y_2O_3, which has a high ε(Y–O) bond energy and also a large Y^{3+} cation, is an effective stabiliser of the amorphous state. In this instance the crystal-chemical and energy factors act in the same sense. The introduction of the large europium and ytterbium ions, which form oxides with lower M–O bond energies, does not have a stabilising influence. The straight line *1* in Fig. 2, which is drawn through all the points including the coordinate origin, confirms the dominant influence of the energy factor on T_{cr} but allowance for the crystal-chemical size factor adds a correction to the prediction. The broken line *2* also objectively reflects the influence of the additive on T_{cr} of the solid solution. It has been found[20] that introducing an M_2O_3 additive into the solid solution displaces ΔH_{cr} in a positive direction from −21 to −18 to −15 kJ mol^{-1}. The less negative values of ΔH_{cr} are due to the positive enthalpy of mixing (ΔH_{mix}) when heterovalent solid solutions are formed. An analysis of ΔH_{cr} with the aim of eliminating ΔH_{mix} showed that small ΔH_{mix} values are not at variance with the formation of solid solutions in the $Y_2O_3-ZrO_2$ system.

Table 5. Temperatures and enthalpies of crystallisation of the solid solutions $Zr_{1-x}Fe_xO_{2-x/2}$ and $Zr_{1-x}Mg_xO_{2-x}$.

Solid solution	T_{cr}/K	$-\Delta H_{cr}$/kJ mol^{-1}
$Zr_{0.75}Fe_{0.25}O_{1.875}$	851–943	12.0±1.5
$Zr_{0.5}Fe_{0.5}O_{1.75}$	921–1007	7.7±1.5
$Zr_{0.95}Mg_{0.05}O_{1.95}$	717–777	16.5±1.1
$Zr_{0.5}Mg_{0.5}O_{1.5}$	835–886	9.1±0.3

An unexpected result was obtained[21] regarding the effect of introducing Fe_2O_3 into ZrO_2 on T_{cr} for the solid solution $Zr_{1-x}Fe_xO_{2-x/2}$ (x = 0.25 and 0.50) (Table 5). The formation of the solid solution leads to an increase in T_{cr} compared to T_{cr} for the two amorphous oxides although $\varepsilon(Fe-O) < \varepsilon(Zr-O)$. This result is attributed to the polyhedral structure of the solid solution. Results obtained by the method of hyperfine structure of the X-ray absorption spectrum show[25] that in the cubic solid solution with x = 0.3 the ZrO_8 polyhedra are linked by their edges, the FeO_4 tetrahedra are linked by their edges to the ZrO_8 polyhedra and by two corners to other FeO_4 tetrahedra. The increase in T_{cr} is due to the formation of FeO_4 tetrahedra which are energetically less stable than FeO_6 octahedra which might appear on formation of the hematite structure. In order to form FeO_4 polyhedra a potential barrier must be overcome because the $FeO_6 \rightarrow FeO_4$ transition is accompanied by the absorption of heat (22.2 kJ mol^{-1}).[12] The small positive values of ΔH_{mix} which have been calculated[21] are not at variance with the formation of solid solutions in the $Fe_2O_3-ZrO_2$ system.

The introduction of the additive MgO has a similar effect on the increase in T_{cr} for ZrO_2.[23] In this instance the crystallisation is 'explosive' in character and T_{cr} increases compared to the value for zirconium dioxide by 200 K for every 5 mol% of MgO. MgO_8 polyhedra are formed in the cubic solid solution, the enthalpy change in the process MgO_6(octahedron)$\rightarrow MgO_8$(cube) being 71 kJ mol^{-1}.[24] To overcome the potential barrier on formation of the cubic environment of O^{2-} ions around the magnesium ion the amorphous oxides must be heated to $T > T_{cr}$ for ZrO_2, i.e. the reason for the stabilisation of the amorphous ZrO_2 is the same as when Fe_2O_3 is introduced although $\varepsilon(Mg-O) < \varepsilon(Zr-O)$.

Thus when the enthalpy of the change in the CN of the additive cations on their insertion into the solid solution has high positive values, a considerable increase in T_{cr} of the primary matrix is possible.

In research on the preparation of the adsorbents $xAl_2O_3 \cdot yZrO_2$, $xAl_2O_3 \cdot yY_2O_3$, etc.[26–28] the crystallisation temperature of coprecipitated hydroxides was shown to increase on formation of solid solutions. This phenomenon was called a protective effect from crystallisation of the components. The introduction of Al_2O_3 into a ZrO_2 matrix by heating the coprecipitated hydroxides $Al(OH)_3/Zr(OH)_4$ increases T_{cr} for tetragonal ZrO_2 by 400 K compared with the value for amorphous ZrO_2 (445 °C).[29] The energetics nature of this effect was not considered in these papers[26–29] although its interpretation may, in our opinion, be similar to that discussed above for the introduction of Fe_2O_3 and MgO into ZrO_2. The formation of Al_2O_3/ZrO_2 substitutional solid solutions will be accompanied by a change in the CN of aluminium on its insertion into zirconium positions with high CNs (7 or 8). This type of coordination is not typical of aluminium and in order to form AlO_7 or AlO_8 fragments a high potential barrier must be overcome. Magnus's crystal-chemical rules, which determine the possible CNs of cations from the ratio of the cation and anion radii, lead to the same conclusion. The enthalpy of the change in the coordination in the transition $AlO_6 \rightarrow AlO_n$ (n = 7 or 8) is not known but it probably has a high positive value. This inhibits the crystallisation of the oxides. The final products of the coprecipitation of the hydroxides $Al(OH)_3/Zr(OH)_4$ may be mixtures of polymorphs of ZrO_2 depending on the ratio of the aluminium and zirconium concentrations, the conditions used to precipitate the hydroxides, and whether the solid solutions are heated or maintained isothermally at high temperatures.[28, 30]

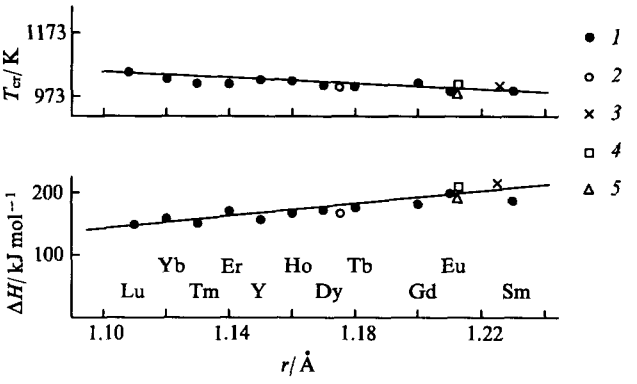


Figure 3. Variation of T_{cr} and ΔH_{cr} with the ionic radius of the lanthanide: *1*) lanthanide ions; *2*) $LuEu_2Fe_5O_{12}$, *3*) $Nd_{0.94}Gd_{2.06}Fe_5O_{12}$, *4*) $Lu_{0.48}Sm_{2.52}Fe_5O_{12}$, *5*) $La_{0.24}Gd_{2.76}Fe_5O_{12}$.

The effect of stabilisation of amorphous films based on ZrO_2 with Y_2O_3 introduced, which were obtained by electron-beam vaporisation, has been noted.[31] Crystalline films of ZrO_2 are obtained at as low a temperature as 420–470 K but the introduction of 10–20 mol% Y_2O_3 enables the amorphous state to be preserved up to 520–550 K. The crystallisation temperatures of the amorphous films are much lower than those of the amorphous compounds obtained from coprecipitated hydroxides but the introduction of Y_2O_3 into the film leads to stabilisation of the amorphous state.

IV. Crystallisation of chemical compounds from coprecipitated hydroxides that are amorphous to X-rays

The formation of chemical compounds with a more complex crystal structure than those of simple oxides or their solid solutions also increases the time-dependent and thermal stability of the amorphous state. Systematic studies have been carried out on the process of crystallisation of the ferrogarnets $E_3Fe_5O_{12}$, orthoferrites with the perovskite structure type $EFeO_3$ (E = a lanthanide ion), and compounds with the magnetoplumbite structure $MFe_{12}O_{19}$ (M = Pb, Sr, Ba).[32–37]

1. Formation of $E_3Fe_5O_{12}$

The distinctive features of the process of crystallisation of ferrogarnets from the amorphous (to X-rays) state of the oxides by DSC are associated with a change in the mechanism of the solid-state reaction. In the garnet structure there are three non-equivalent positions for the cations in an oxygen environment: $3E^{3+}$ are in EO_8 dodecahedra, $3Fe^{3+}$ in FeO_4 tetrahedra, and $2Fe^{3+}$ in FeO_6 octahedra. For the formation of the complex garnet crystal structure temperatures higher than T_{cr} for amorphous Fe_2O_3 are required (Fig. 3).

Lanthanide ferrites with the garnet structure are formed only for E = Sm ... Lu; larger lanthanide ions will not enter the garnet structure owing to steric hindrance. However, lanthanum, praseodymium, and neodymium ions can be inserted into the garnet structure if lanthanide ions with a smaller radius are introduced at the same time. The dependence of T_{cr} and ΔH_{cr} on the radius of the lanthanide is shown in Fig. 3. In general, ΔH_{cr} decreases and T_{cr} increases along the series Sm ... Lu. The formation of garnets with the large ions Sm ... Dy, and also the solid solutions $Lu_{0.48}Sm_{2.52}Fe_5O_{12}$, $La_{0.24}Gd_{2.76}Fe_5O_{12}$, $LuEu_2Fe_5O_{12}$, and $Nd_{0.94}Gd_{2.06}Fe_5O_{12}$ in which the mean radii of the lanthanide ions do not exceed the ionic radius of Sm^{3+}, is

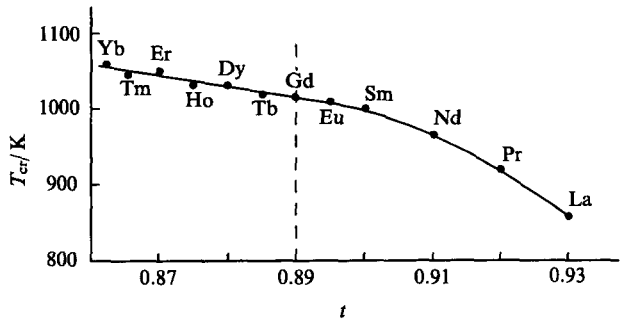


Figure 4. Dependence of T_{cr} for lanthanide orthoferrites on the stability factor t:

$$t = \frac{r_{Ln^{3+}} + r_{O^{2-}}}{\sqrt{2}(r_{Fe^{3+}} + r_{O^{2-}})}$$

accompanied by a single sharp exothermic effect within a narrow temperature range. The ferrogarnets of Ho ... Lu are formed by a more complex mechanism with an increasingly distinct separation into two crystallisation stages and a higher temperature range for the reaction. The decrease in ΔH_{cr} with increasing atomic number of the lanthanide is due to an increase in the degree of distortion of the EO_8 dodecahedra along the series Eu ... Lu. When the components are in a stoichiometric ratio crystallisation gives single-phase green garnets which have Raman spectra consistent with the published spectra. $Lu_3Fe_5O_{12}$ could not be prepared; all attempts gave a mixture of the garnet and the perovskite $LuFeO_3$ or the oxides.

The crystal-chemical factor is clearly dominant in the crystallisation of these coordination compounds which form three sublattices. On going from the state in the oxides ($6O^{2-} + 2\square$, where $\square$ represents a vacancy) there is a monotonic decrease in the enthalpy of the change in the CN of the lanthanide ions as the atomic number of the lanthanide increases, *viz.* $E(Gd^{3+}) = 33$, $E(Y^{3+}) = 71$, $E(La^{3+}) = -31$ kJ ($4O^{2-} + 3O^{2-} \rightarrow LaO_8$).[38] These individual values fit the straight line $E(E^{3+}) = f[r(E^{3+})]$, where r is the ionic radius of the lanthanide. The presence of the hydrates $E(OH)_3$ and $Y(OH)_3$ in the coprecipitated hydroxides increases T_{cr} for amorphous Fe_2O_3 from 260 to 720–770 °C, i.e. it promotes stabilisation of the amorphous state of the dehydrated oxides.

2. Formation of the orthoferrite-perovskites $EFeO_3$

Crystallisation of the coprecipitated hydroxides $E(OH)_3$/ $Fe(OH)_3$ to form lanthanide orthoferrites is observed in the range 850–1170 K. On formation of the orthoferrites of La ... Sm the DSC thermograms show a single exothermic peak due to crystallisation extending over a 70 K range. In the formation of $EuFeO_3$ the peak begins to split, the crystallisation of $GdFeO_3$ spans a range of 100 K, and at the end of the lanthanide series the crystallisation of thulium and ytterbium orthoferrites takes place in two stages extending over a range of 150 K. As for the ferrogarnets, the decrease in the ionic radius of the lanthanide at the end of the series is accompanied by a decrease in ΔH_{cr} of the orthoferrite and an increase in the thermal stability of the amorphous state. The dependence of T_{cr} on the stability factor is shown in Fig. 4. For perovskites with tervalent cations the lower limit of the t factor is 0.89. In the vicinity of $t = 0.89$ there is a change in the slope of the curve showing the dependence of T_{cr} (and ΔH_{cr}) on t and the peaks due to crystallisation start to split. The inhibiting effect of the E_2O_3 is shown by a 300–600 K increase in T_{cr}, or 6–13 K for each 1 mol% of the E_2O_3 additive if it is assumed that ΔT_{cr} is proportional to the amount of E_2O_3. These values of ΔT_{cr} are comparable with those observed when 5 mol% of ytterbium, thulium, or lutetium are introduced into Fe_2O_3 (15–30 K per mol% of the additive).

3. Formation of the hexaferrites $MFe_{12}O_{19}$

To prepare the hexaferrites $MFe_{12}O_{19}$ (M = Pb, Sr, Ba) with the magnetoplumbite structure the methods of obtaining coprecipitated hydroxides described previously[39–41] were used. The crystallisation of strontium and barium hexaferrites takes place in a single stage at 730 and 650 °C respectively. The complex coordination structure of the hexaferrites contains four types of CP in each formula unit: an MO_{12} cubo-octahedron, an FeO_5 trigonal bipyramid, two FeO_4 tetrahedra, and nine FeO_6 octahedra. This is a more complex structure than that of the perovskites or garnets. The formation of FeO_5 and FeO_4 polyhedra is energetically less favourable than the formation of FeO_6 octahedra and consequently the formation of the structure may be particularly inhibited when the crystal-chemical factor is added to the energy factor [$\varepsilon(Sr-O) > \varepsilon(Fe-O)$ and $\varepsilon(Ba-O) > \varepsilon(Fe-O)$].

A characteristic feature of the exothermic effect due to crystallisation of coprecipitated lead and iron hydroxides is that it is spread out over the range 390–670 °C on formation of $PbFe_{12}O_{19}$. Furthermore the products of the crystallisation reaction also contain α-Fe_2O_3; this is not inconsistent with the known metastability of $PbFe_{12}O_{19}$, whose enthalpy of formation from the oxides is estimated to be 37 kJ mol^{-1}.[42] In an attempt to synthesise $SrFe_{12}O_{19}$ a qualitatively similar thermogram was obtained by heating coprecipitated strontium and iron hydroxides; crystallisation of $SrFe_{12}O_{19}$ takes place at 567–777 °C. The higher temperature is due to the higher value of $\varepsilon(Sr-O)$. The formation of a mixture of the hexaferrite and hematite is also observed in this case.

The thermogram of coprecipitated barium and iron hydroxides shows a pronounced effect due to the 'explosive' formation of single-phase $BaFe_{12}O_{19}$ within the narrower temperature range 723–818 °C. The bond energies $\varepsilon(Sr-O) = 249$ and $\varepsilon(Ba-O) = 244$ kJ g^{-1} electron^{-1} agree with experimental error (± 10 kJ mol^{-1}) and overall the inhibiting effect of the large cations on the temperature of formation of the hexaferrites increases in the order Pb–Sr–Ba as $\varepsilon(M-O)$ increases. The increase in T_{cr} over the value for iron oxide is 130–460 K when 7.7 mol% of additive is introduced into the cationic sublattice, i.e. 16–60 K per mol% of the additive. This is the same order of magnitude as the increase in T_{cr} for the solid solutions based on hematite and containing 5–10 mol% of additive cations (see above). The increases in the crystallisation temperature (in K) occurring on formation of solid solutions of the oxides and chemical compounds with alloying additives introduced (calculated per 1 mol% of additive in the cationic sublattice) are given below:

Solid solution	$E_3Fe_5O_{12}$	$EFeO_3$	$MFe_{12}O_{19}$
14–30	17–20	6–13	14–60

We may conclude that the crystal-chemical (size) factor is predominant in inhibiting the crystallisation of the amorphous phase. However a definite answer to this problem is not possible in all instances. The bond energies must also be taken into account, especially if the effects of the bond energy and the size factor compensate each other to some extent.

V. Crystallisation of amorphous metal alloys

The chief 'amorphising' elements in transition metal (TM) alloys are boron, carbon, and phosphorus. One of the major problems in studying alloys (AAs) is to find the factors governing their thermal stability. We shall consider two factors which affect the stability of AAs: the nature of the metal and of the amorphising element. Both factors are, as a rule, connected with aspects of the metal–non-metal interaction and with thermodynamic stimuli of crystallisation of the AA.

Table 6. Bond energies $\varepsilon(M-X)$ and ΔH_f for compounds used to estimate the increase in thermal stability of AAs.

Compound	ε/ kJ g^{-1} electron^{-1}	$-\Delta H_f$/ kJ mol^{-1}
	Borides	
ScB_2	239.7	307.8
TiB_2	194.1	323.4
ZrB_2	210.5	328.0
HfB_2	213.4	329.3
VB_2	173.6	215.0
$TaB_{2.03}$	205.9	190.0
$NbB_{1.82}$	197.1	185.8
CrB_2	189.5	119.4
LaB_6	265.3	400.4
W_2B	194.0	68.2
WB	182.0	66.5
W_2B_5	181.6	199.6
Mn_2B	163.2	95.1
MnB	164.8	71.6
MnB_2	165.7	63.3
$AlB_{2.215}$	161.3	77.4
Fe_2B	186.1	67.9
FeB	174.3	64.6
Co_2B	188.3	58.1
CoB	176.6	69.5
Ni_2B	190.0	67.7
NiB	171.5	40.2
	Phosphides	
Fe_3P	162.1	164.1
Fe_2P	161.7	121.6
FeP	169.1	137.2
FeP_2	158.5	217.6
Co_2P	170.4	196.6
CoP	174.2	146.4
CoP_3	170.9	280.3
Ni_3P	174.0	219.7
Ni_2P	168.4	184.0
NiP_2	152.1	167.0
NiP_3	157.7	200.8
	Carbides	
Fe_3C	168.2	−25.2
Fe_2C	168.8	−20.6
Co_3C	168.7	−44.4
Co_2C	172.1	−16.8
Ni_3C	164.9	−75.3

An irreversible transition of an AA to the crystalline state is often of a diffusion character. As in the case of oxides, stability against diffusion decomposition can be attributed to the presence in the alloy of fragments with rigid metal–non-metal covalent bonds.[43] These fragments may have a composition corresponding to a stable or metastable composition of the crystalline compound or alloy and a similar nearest coordination sphere to that in the crystal. The tendency to amorphisation is dependent on the variation in the type of linking of the coordination polyhedra in the alloy. Clearly, the higher the chemical bond energy in such fragments the more difficult it is for diffusion decomposition of the AA to occur on its crystallisation.

The question of a correlation of the structure of AAs and the bond energies $\varepsilon(M-X)$ (X = B, C, P) with the thermodynamic stability of the alloys has been raised in a general form repeatedly. However, there has rarely been any estimation of $\varepsilon(M-X)$ in a quantitative form suitable for solving practical problems, particularly those associated with estimating the enthalpies of formation (ΔH_f) of the alloys. This is because, until recently, there were no reliable thermochemical data on ΔH_f for many borides, carbides, and phosphides. The regeneration of interest in fundamental investigations of the structural and thermodynamic properties of these compounds has promoted a substantial development of a simple model for calculating the bond energies $\varepsilon(M-X)$ and hence ΔH_f.

The calculation of $\varepsilon(M-X)$ was carried out using a simplified model which takes into account the structural, thermochemical, and electrophysical properties of the compounds. The basis of the calculation has been published[44–48] for the compounds MB_n, MC_n, MN_n, MC_nO_m, and MN_nO_m, where M is a transition metal.

In these calculations the enthalpy of atomisation (ΔH_a) of the compounds to the monoatomic gas state is represented by the sum of the bond dissociation energies. In the general case for metal-like compounds of the MX type we can write

$$\Delta H_a = E_{free} + E(M-X) + E(M-M) + E(X-X)$$

$$= \Delta H_aM + \Delta H_aX - \Delta H_fMX.$$

The terms in this equation allow for the partial contributions of the free electrons of the conduction band (E_{free}), the band of covalent metal–non-metal bonds [$E(M-X)$] and metal–metal bonds [$E(M-M)$], and also non-metal–non-metal bonds [$E(X-X)$] if they are formed, e.g. as in the higher borides. For some compounds the individual contributions cannot be taken into account (for example in lower borides of the MB type where the boron atoms can be regarded as isolated). Calculations of the bond energies $\varepsilon(M-X)$ and the enthalpies of formation of transition metal borides, carbides, and phosphides (Table 6) have been carried out.[48, 49] The method of calculation is fairly simple and does not involve quantum-chemical calculations.

The data in Table 6 show that in general within the Groups of the Periodic Table the bond energies $\varepsilon(M-B)$ increase as the atomic number of the metal increases. The same trend applies to other binary compounds (oxides, halides, nitrides, etc.). Within the Periods $\varepsilon(M-X)$ decreases as the atomic number of the element increases and is approximately constant for the elements in the iron triad. $\varepsilon(M-X)$ is approximately constant for the compounds within one system; this makes it possible to estimate ΔH_f for compounds recorded on the M–X equilibrium diagrams that are unstable or have not been studied, or to estimate the compositions of alloys from the mean values of $\varepsilon(M-X)$. The approximate constancy of $\varepsilon(M-X)$ is consistent with the known principle of transferability of the characteristics of a chemical bond in compounds.

The absolute deviations of the mean values of $\varepsilon(M-X)$ from the bond energies in the individual compounds do not exceed ± 10 kJ g^{-1} electron^{-1}, which is within the error of the thermodynamic quantities.

Alloying of the binary alloys with a third component (a transition metal or X) has an appreciable effect on the time-dependent and thermal stability of an AA. It is questionable whether the bond energies calculated using thermodynamic data for the crystalline state are adequate for the bond energies in an AA. A statistical analysis of ΔH_{cr} for 40 amorphous alloys with different chemical compositions showed that the mean value of ΔH_{fus} for substances forming AAs is 16.3 kJ g-atom^{-1} but ΔH_{cr} for the amorphous alloys is −7.5 kJ g-atom^{-1}. Thus for the transition liquid→amorphous material there is a margin of internal excess enthalpy per 1 g-atom of the AA of −8.8 kJ g-atom^{-1}.[50] The value 7.5 kJ g-atom^{-1} is close to the values of the enthalpies of phase transitions and represents the difference in the enthalpies of the amorphous and crystalline materials. This value is close to a theoretical estimate based on the assumption of a non-equilibrium electronic state for the interacting atoms.[51] Such estimates agree with the conclusion[1] that the main condition for obtaining a non-crystalline state of a solid is an excess binding enthalpy equal to $0.5\Delta H_{fus}$.

The short-range order in the AA corresponds to the arrangement of the atoms in the crystal structures of some actual

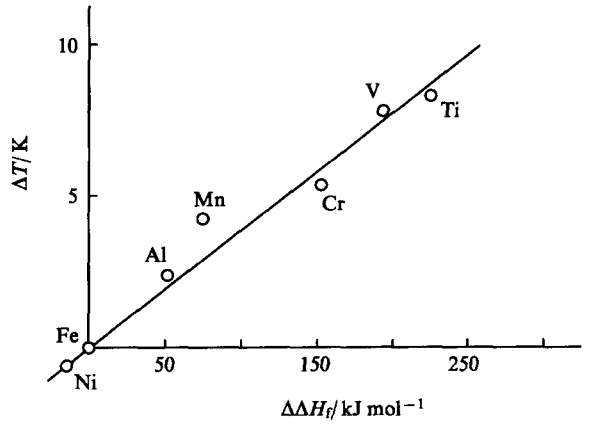


Figure 5. The change in the crystallisation temperature of the amorphous alloys $Fe_{80}M_5B_{15}$ for alloying with 1 atom % M plotted against the difference $\Delta\Delta H_f = \Delta H_f(M_3B) - \Delta H_f(Fe_3B)$ (3 atom % alloying in the case of Al).[52]

compounds that are present in the equilibrium diagrams (e.g. Co_3B or Ni_3B, where each boron atom is coordinated by nine metal atoms). The preservation in the AA of the coordination polyhedra that occur in the crystalline state makes it unnecessary to use the concept of variable valency to account for the energetics of the crystallisation of the AA.[51] The transition from the amorphous to the crystalline state can be treated as a form of polymorphic transformation. The amount 7.5 kJ g-atom^{-1} is only 1%–2% of the values of the enthalpies of atomisation of crystalline borides, carbides, and other compounds and the use of M–X bond energies calculated for compounds in the crystalline state for the amorphous alloys as well is therefore justified. It has been shown[50] that the ratio (α) of the experimental values of ΔH_{cr} for an AA and $\Sigma x_i \Delta H_i$ for the components of the alloy, where x_i is the mole fraction and ΔH_i the enthalpy of fusion of the ith component, is 0.3–0.5. This range of values corresponds to the excess enthalpy remaining in AAs obtained by various methods (spinning, condensation from the gas phase, cathode sputtering, etc.). It is easily seen that α for AAs is similar to α for oxides (see Table 1);† this indicates that the excess enthalpy in non-crystalline materials is approximately constant, irrespective of their chemical nature and method of preparation.

Let us consider two extreme cases in the variation of α. When $\alpha \rightarrow 1$ crystallisation of the amorphous material is accompanied by evolution of heat. The heat effect is similar in absolute magnitude to ΔH_{fus} of the crystal. The amorphous material retains the structure of the melt near to the equilibrium melting point. When $\alpha \rightarrow 0$ the quenched melt or other non-crystalline materials are similar in structure to the equilibrium crystal and there is no appreciable thermal effect on the thermogram. Such a material will have a similar diffraction pattern to the equilibrium crystal. In certain instances crystallisation of the AA gives strips containing a microcrystalline phase together with the amorphous phase.

For the methods used to obtain non-crystalline materials the degree of crystallinity could be described by the quantity $\beta = 1-\alpha$, so that $0.5 < \beta < 0.7$.

The introduction of 3*d* transition metals into an AA of the Fe_3B type increases the T_{cr} of the alloy if the 3*d* metal is in a Period to the left of iron. For $Fe_{80}M_5B_{15}$ (M = Ti ... Ni) T_{cr} increases, per 1 mol% M alloying content, in the order Mn–Cr–V–Ti but the introduction of nickel reduces T_{cr}.[52] Elsewhere[53] similar behaviour was observed for the series Ni–Co–Fe–Cr–V although different T_{cr} values are obtained by different authors owing to the use of different conditions for obtaining the AA and different rates of heating in the calorimeter. There is a linear relationship between the change in the crystallisation temperature of amorphous $Fe_{80}M_5B_{15}$ alloys when they are alloyed with metals and the difference in the enthalpies of formation of the alloys $\Delta\Delta H_f = \Delta H_f(M_3B) - \Delta H_f(Fe_3B)$ (Fig. 5).[48] $\Delta H_f(M_3B)$ was calculated on the basis of the bond energies ε(M–B) (see Table 6). There is obviously a connection between the decrease in the activity of boron on formation of borides with high ΔH_f values and the increase in the thermal stability of the AA. The thermal stability is associated with the formation of boron positions in the AA that have a lower energy and so inhibit crystallisation.[52] It can therefore be predicted that the T_{cr} of alloys of this type can be increased considerably by alloying with lanthanide, Sc, and Y borides.

It is clear from Table 6 that $\varepsilon(M-P) \simeq \varepsilon(M-C)$ and $\varepsilon(M-B)$ is ~10% higher. The similarity of the M–X bond energies in these compounds and the compatibility of the fragments facilitates alloying of amorphous alloys based on the Fe–B system with boron, carbon, and phosphorus. The formation of the more exothermic iron phosphides, for example, as compared to the borides, leads to a reduction in the thermodynamic activity of iron in the alloy. Analysis of experimental data on T_{cr} for AAs in M–X (M = Fe, Co, Ni) systems showed that T_{cr} is 610–680 K for the phosphides, 600–700 K for borides, and only 450 K for Fe_3C.[54] These values accurately reflect the main trends: Fe_3C, which is endothermic, has the lowest value of T_{cr} while the exothermic phosphides and borides have high thermal stability. Therefore the reason for the variation in T_{cr} of an amorphous material irrespective of its nature is the formation of more stable fragments of compounds that strengthen the matrix of the amorphous compound.

The validity of the conceptual approach based on a quantitative consideration of the energy non-equivalence of coexisting bonds is confirmed by recently published data on the effect of alloying the primary matrix with transition metal additives on the relaxation temperature. An analysis has been carried out[55] of publications[56–58] in which the effect of replacing iron in alloys with compositions close to Fe_4B or Fe_5B was determined. To a first approximation the compositions of the alloyed materials can be described as 95 mol% Fe_4B + 5 mol% M_4B (M = Co, V). The enthalpies of formation of the alloys were calculated[55] from the equation

$$\Delta H_f = 0.95\Delta H_f(Fe_4B) + 0.05\Delta H_f(M_4B),$$

on the assumption that the enthalpy of mixing is zero. The reduction in the relaxation temperature when cobalt is introduced into the alloy $Fe_{0.81}B_{0.19}$ and the increase when vanadium is introduced are due to the fact that $\Delta H_f(Co_4B) < \Delta H_f(Fe_4B)$ but $\Delta H_f(V_4B) > \Delta H_f(Fe_4B)$. The enthalpies of formation of Co_4B, Fe_4B, and V_4B are −21, −25, and −213 kJ (mol M_4B)$^{-1}$ respectively. The introduction of vanadium, which forms a boride whose ΔH_f is more negative than $\Delta H_f(Fe_4B)$, favours a reduction in the activity of boron in the Fe–B system, hinders the diffusion mobility of fragments of the amorphous structure, and

Table 7. Transition temperatures of amorphous alloys and the calculated enthalpies of formation of the alloys.

Alloy	T_{rel}/K, T_{cr}/K	ΔT_{rel}/K, ΔT_{cr}/K	$-\Delta H_f(M_xB)$ / kJ mol^{-1}
$Fe_{0.81}B_{0.19}$($Fe_{4.26}B$)	603	–	25
$Fe_{0.76}Co_{0.04}B_{0.20}$($M_4B$)	595	−8	24.8
$Fe_{0.75}V_{0.04}B_{0.21}$($M_{3.76}B$)	663	60	34.4
$Fe_{0.74}Co_{0.10}B_{0.16}$	688	–	24.7
$Fe_{0.74}Co_{0.05}Cr_{0.05}B_{0.16}$	733	45	34.2
$Fe_{0.74}Cr_{0.10}B_{0.16}$	763	75	43.5

Note. The values given for the first three alloys are T_{rel} from the data of Barricco et al.[56] (x = 4); those for the other alloys are T_{cr} from other data[57, 58] (x = 5). The possible error in ΔT_{rel} for the second alloy is ±50% owing the small scale of the figure in the paper.[56]

† We recall that the values of α from the data of Natarajan et al.[17] are estimated

Table 8. Changes in T_{cr} for the alloys $Fe_{79-x}B_{16}Si_5M_x$ (x = 4).

Element	T_{cr}/K	ΔT/K	ΔT/K per 1 mol%
V	806	30	7.5
Cr	790	14	3.5
Nb	816	40	10
Mo	814	38	9.5
Ni	773	−3	−0.8
Fe	776	–	–

increases the potential barrier to relaxation. The introduction of cobalt, on the other hand, reduces the relaxation temperature of the alloy (Table 7).

In the case of alloys with compositions close to M_5B studies have been made of the effect of T_{cr} of replacing the cobalt in $Fe_{0.74}Co_{0.10}B_{0.16}$ by chromium.[57, 58] Replacing 50%–100% of the cobalt by chromium leads to an increase in T_{cr} by 45–75 K. The introduction of chromium, vanadium, molybdenum, niobium, and nickel into the AA with the more complex composition $Fe_{79-x}B_{16}Si_5M_x$, which contains two amorphising elements (boron and silicon), gives similar results (Table 8).[59]

Barrue et al.[59] arranged the alloying elements in order of decreasing atomic radius: Nb > Mo > V > Cr, noting that there is a correlation between the size of the substituent atom and T_{cr} of the alloy. However, the size of the atom is larger for 4*d* elements than for their 3*d* analogues. Comparison of the pairs V–Cr and Nb–Mo indicates a semi-quantitative correlation: the increase in T_{cr} on introducing vanadium and niobium is more marked than on introducing chromium and molybdenum; this is consistent with the greater thermodynamic stability of borides of Group V elements compared with those of Group VI elements.

The change in T_{rel} and T_{cr} for AAs with the still more complex compositions $Fe_{39}Ni_{36}Cr_5P_{14}B_6$, $Fe_{76}Co_4B_{20}$, and $Fe_{75}V_4B_{21}$, as compared with the typical matrix $Fe_{81}B_{19}$ (Fe_4B), has been studied by DSC.[56] The introduction of chromium, phosphorus, and vanadium into $Fe_{81}B_{19}$ leads to the formation of chromium and vanadium borides and phosphides that are thermodynamically more stable than Fe_4B. An important feature of the method used[56] was an X-ray diffraction examination of both sides of the amorphous strip from the quenched melt; this confirmed the absence of crystallisation throughout the whole thickness. A study has been made of the effect of high-melting metals on the thermal stability of amorphous bands of Ni–M–B alloys (M = Zr, Nb, Mo; 13–14 mol% B, 5–14 mol% M).[60] The alloys containing zirconium retain an amorphous state at higher temperatures than those containing niobium and molybdenum and the crystallisation temperatures of the AAs increase linearly with increasing zirconium and molybdenum concentrations. This effect is consistent with the greater stability of zirconium borides as compared with molybdenum and niobium borides.

A comprehensive study of the dependence of T_{cr} on features of the electronic structure of the AAs $Fe_{75}B_{20}M_5$, where M = Ni, Co, Cr, V, Mo, W, and Nb, has been carried out.[53] Calorimetric studies showed that T_{cr} increases for this set of metals: 415, 467, 502, 566, 597, 611, and 613 °C, and this is consistent with the increase in the thermodynamic stability of M_4B fragments in sets of 3*d* and 4*d* metals. The similarity of T_{cr} for the niobium and vanadium [tungsten? Ed.] alloys is also consistent with the known diagonal similarity between elements in the Periodic Table.[61] The increase in T_{cr} for the alloys formed by metals in the same Group, e.g. the Group VI metals Cr–Mo–W, is consistent with the general tendency for the borides to have increasing ΔH_f values and hence for there to be increasing stability of the structural fragments. K_α emission spectra have been studied for the series under discussion (with the use of an electron microbeam as the excitation source). The shift of the K_α band of the compound, as compared with the K_α band of boron, from 1 to 1.35 eV as we pass along the series Ni ... Nb is due to an increase in the degree of overlap of the *d* electrons of the transition metal atoms with the 2*p* electrons of boron. This implies an increase in the M–B bond strength along this series, as is confirmed by thermodynamic calculations.

The introduction of 5 mol% of such elements as chromium, vanadium, molybdenum, niobium, tungsten, and tantalum into the alloy $Fe_{80}B_{20}$ increases T_{cr};[62] however the interpretation of the observed linear relationship $T_{cr} = f(Z/U)$, where Z is the atomic number of the element and U is the $M \rightarrow M^+$ ionisation potential, raises doubts as to the appropriateness of using such an argument for the function because there is no evidence that the M atoms are singly ionised in the borides.

There are wide discrepancies in the published values of the crystallisation temperatures for the replacement of the iron in FeB_n alloys by other transition metals. This is due to differences in the conditions of preparation of the AAs; the preparation is carried out under extremal conditions and is evidently not sufficiently reliably monitored (rate of quenching, thickness of the AA strip, possible deviations from the prescribed composition of the mixture due to evaporation of the components with different vapour pressures, methods of measuring T_{cr}, etc.). The use of high-sensitivity DSC enables observations to be made up to the crystallisation temperature of the alloy on changes in the solid state due to relaxation of the quenched alloy, the Curie temperature of the α-Fe phase which separates out, the crystallisation temperature of α-Fe, and, only after this, on T_{cr} for the alloy.[63] Consequently in working on this review we did not undertake the task of covering all the published literature in this field but have selected for investigation only the most representative topics which had been dealt with properly and contain reliable primary information. The increasing number of publications on the experimental thermodynamics of AAs means that it is necessary to look for criteria for choosing model AAs which might serve as key compounds in the chemical thermodynamics of non-crystalline materials. The use of such 'benchmarks' in research will contribute to a more reasoned comparison of the properties of the alloys.

VI. Conclusion

This review deals with the results of experimental studies of the conditions of crystallisation of amorphous materials in the presence of alloying additives that reduce the diffusion mobility or increase the thermodynamic stability of fragments of the amorphous matrix. Additives that are effective stabilisers of the amorphous state of coordination compounds (oxides) are oxides in which the metal–oxygen bonds are stronger than those in the primary matrix and the cations are larger than those in the primary matrix. A change in the CN of the additive cation on insertion into the amorphous matrix has an inhibiting effect when the enthalpy of the change in coordination during crystallisation of the amorphous phase has a high positive value. An increase in the crystallisation temperature of the solid solution is due to a potential barrier being overcome on formation of the less stable coordination polyhedron of the additive cation which is 'finely adjusted' to the polyhedron of the cation in the matrix. As a simplification it is assumed that the enthalpies of the change in the coordination of the cations in the primary matrix and in the additive are identical in the amorphous and crystalline states.

The crystal-chemical factor is dominant for the introduction of additives capable of forming compounds with a complex polyhedral structure and with the same crystal structure. The variation in the bond energies ε(M–O) in a series of lanthanide oxides is not monotonic owing to the 'bivalence' of europium and ytterbium in the metallic state and the necessity, in contrast to the other lanthanides, to promote a third electron when the oxide E_2O_3 is formed. However, the crystallisation temperatures of the amorphous phases do increase monotonically with increasing atomic number of the lanthanide. The insertion of a new phase of compounds with a complex structure inhibits crystallisation and amorphous compounds must be heated to a higher

temperature even in those instances where the concentration of the additive is small but its insertion into the matrix of the primary material is impossible for crystal-chemical reasons.

The effects of introducing a third component into amorphous binary metal alloys on the thermal stabilisation are interpreted from the same conceptual standpoints. The main thermodynamic reason for an increase in the crystallisation temperature of the amorphous material irrespective of its chemical nature is the formation of fragments of more stable compounds which strengthen the amorphous matrix and inhibit diffusion processes.

The energy content of amorphous materials is 20% – 50% of the enthalpy of fusion of crystalline phases. The increase in the crystallisation temperature on the introduction of alloying components into amorphous oxides and metal alloys is 5 – 60 K per mol% of the component.

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