ON THE METASTABLE STATES OF AMORPHOUS Fe—B ALLOYS**

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Abstract

Stability studies on Fe—B alloys have been conducted for establishing the interdependence of the thermal properties of crystallization and the changes in the electronic structure. For thermal analysis DTA, for electronic structure analysis SXS method was used.

A correlation of the electronic structure and the heat of crystallization was observed. Based on the above information, the role of the electronic structure in determining the stability is established for $Fe_{1-x}B_x$ $(0.1 \leq x \leq 0.2)$ binary alloys and some ternary alloys with transition elements (TM). General remarks are made concerning the stability based on the trends of measured data.

Introduction

The problem of stability of alloys and their highly metastable states, — such as the amorphous-phases, — is in the centre of many scientific investigations. The problem of stability is much more fundamental than a particular question of amorphous alloys only, because it appears that metastability is the main idea underlying numerous exciting discoveries on superconductivity, on mechanical, electrical, etc. properties of alloys and ceramic media. Originating from Hume—Rothery's pioneering synthesizing works (W. Hume—Rothery (1946), W. Hume—Rothery et al. (1954)) we could enumerate the relevant factors affecting the stability. There are a lot of factors affecting the crystalline structure of alloys (W. B. Pearson (1972)).

1. the chemical and electrochemical factors (electronegativity differences (W. Gordy et al. (1956)), compound-forming abilities (L. Pauling (1960), etc.);
2. the geometrical factors (size factor (W. Hume—Rothery et al. (1934)), spacefilling factor (F. Laves (1956)), etc.);
3. electronic factor (number of electrons per atom (W. Hume—Rothery (1983)), Fermi surface-Jones zone interaction (N. F. Mott et al. (1958)),

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** Dedicated to Prof. J. Giber on the occasion of his 60th birthday.

Engel's (N. Engel (1964)) and Brewer's (L. Brewer (1963)) modifications, etc.)

In our present paper different Fe—B based amorphous alloys have been studied as model systems. Differential Thermal Analysis (DTA) was used to study thermodynamic changes and Soft X-ray Emission and Fluorescent Spectroscopies (SXES and SXFS respectively) for determining the electronic band structure. Our aim has been to clear the details of the stability and the special correlation between the local stability and changes in the electronic (band) structure.

Experimental

The SXES measurements were carried out by a home-adapted RSM-500 (Burevestnik) system, under 10^{-5} Pa vacuum, with turbo-pumps. Our resolution on B K_α, Fe L_{23} lines are 0.1 eV and 0.3 eV, respectively. The SXFS measurements were made by a SARF-1 (Burevestnik) equipment. The corresponding resolutions are 0.1 eV and 0.3 eV for the B K_α and Fe L_{23}, respectively.

DTA was performed in a home-made high-sensitivity system. The sensitivity in the 150—500°C region is about 0.005 K. The heating rate was always 10 K/min, all other parameters were kept constant. For checking the state of the samples standard X-ray diffraction was used.

The samples under investigation are collected in Table I. During isothermal anneals the temperature was kept constant within $\Delta T < 1$ K.

Table 1

The alloys under investigation

Alloy N°	$Fe_{1-x-y}TM_xB_y$						
	x (%)						y (%)
	Ti	Cr	Mo	Ta	W	Au	
1	—	—	—	—	—	—	13.5
2	—	—	—	—	—	—	16
3	5	—	—	—	—	—	13.5
4	—	5	—	—	—	—	13.5
5	—	—	3	—	—	—	13.5
6	—	—	—	3	—	—	13.5
7	—	—	—	—	1	—	16
8	—	—	—	—	2	—	16
9	—	—	—	—	3	—	16
10	—	—	—	—	5	—	16
11	—	—	—	—	—	1	13.5
12	—	—	—	—	—	3	13.5

Results

The SXES and SXFS curves agree well with literature curves both for boron and iron components (M. Tanaka (1982)) of binary Fe—B alloys.

The series of measurements for samples with transition elements (TM) added is collected in Figs 1 and 2. As it was expected from the very similar

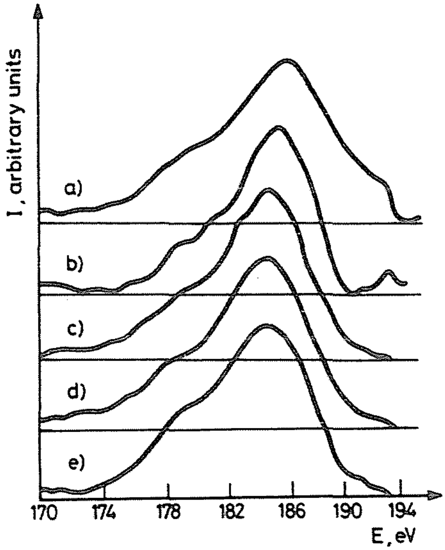

Fig. 1. The B K_α spectra of some $Fe_{0.865-x}TM_x^{3d}B_{0.135}$. ($TM^{3d}$ — transition metal from 3d-period, $0.01 \leq x \leq 0.05$) amorphous alloys.

a) $FeAu_1B_{13.5}$; b) $FeMo_3B_{13.5}$; c) $FeCr_5B_{13.5}$; d) $FeTa_3B_{13.5}$; e) $FeTi_5B_{13.5}$

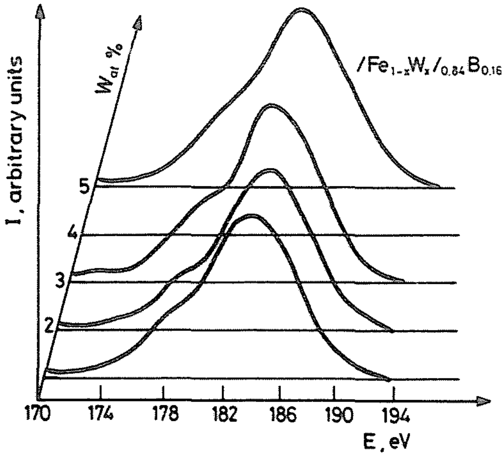

Fig. 2. The B K_α spectra of some $Fe_{0.84-x}W_xB_{0.16}$ ($0 \leq x \leq 0.05$) amorphous alloys

electronic density of states (K. Suzuki et al. (1980)) the changes in the Fe-spectra are negligible, only the B K_α was influenced by the alloying process. The average mass centres of spectra (centroid position), which could be a good indication of stabilization (P. Oelhafen (1984)), are monotonously depending on the *d*-electron number.

On the DTA-curves we have observed the well known features (T. Kemény et al.), a peak corresponding to the α-Fe precipitation and another one, the amorphous-crystalline phase transition (Fig. 3). Some series of DTA-curves of the different samples are summarized in Fig. 4.

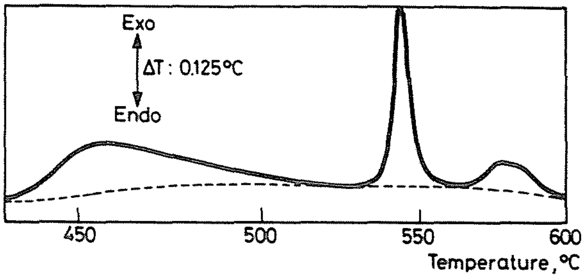

Fig. 3. An example DTA-curve of the $FeTa_3B_{0.135}$ sample

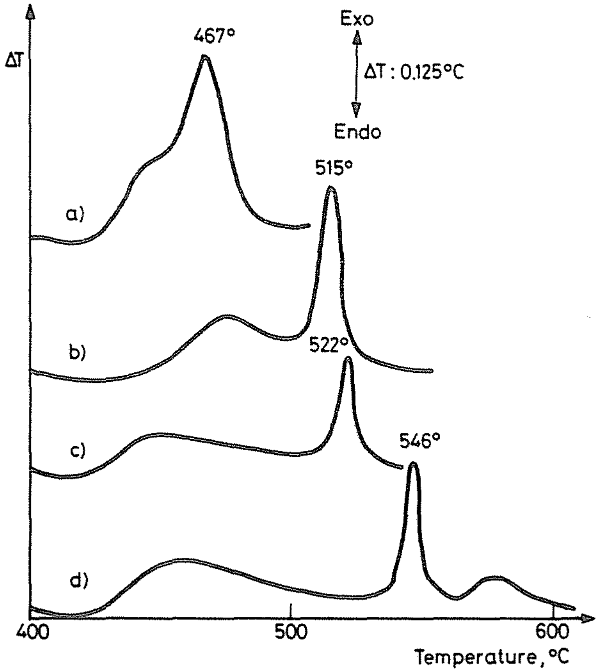

Fig. 4. The series of DTA-curves of different $Fe_{1-x-y}TM_xB_y$ ($0 \leq x \leq 0.05$; $0.135 \leq y \leq 0.25$) alloys. a) $FeCr_5B_{13.5}$; b) $FeW_3B_{13.5}$; c) $FeMo_3B_{13.5}$; d) $FeTa_3B_{13.5}$

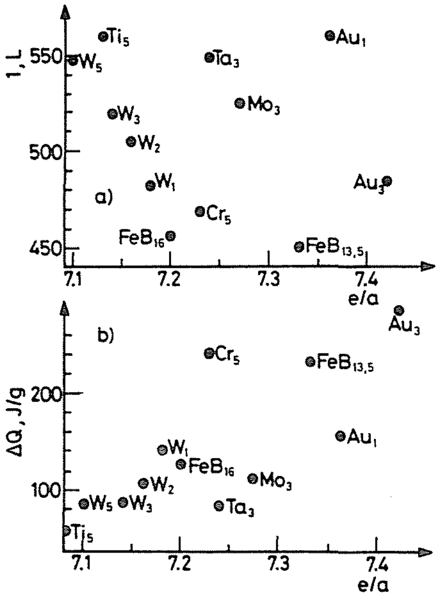

Fig. 5. The dependence of the crystallization temperature T_c) (a) and of the transition heat (ΔQ) (b) on the total electron concentration (e/a)

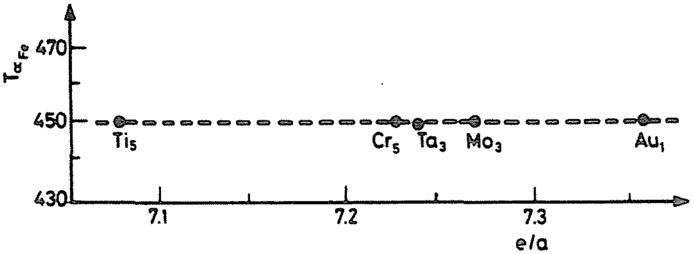

Fig. 6. The temperature of α-Fe precipitation versus (e/a)

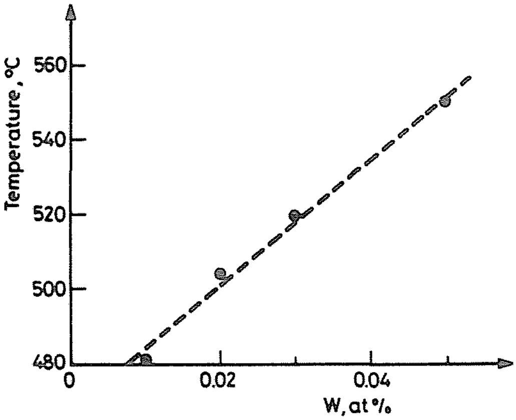

Fig. 7. The concentration dependence of crystallization temperature in the case of $Fe_{0.84-x}W_xB_{0.16}$ $(0 \leq x \leq 0.05)$

The dependences of the transition temperature and of the transition heat on the electron-atom ratio (*e*/*a*) are opposite (Fig. 5a, b). The peak characterizing the α-Fe precipitation in the case of $y = 0.135$ boron content does not depend on *e*/*a* using different TM metals as the alloying element (Fig. 6). An increase in the concentration of W leads to an increases in the temperature of crystallization in $Fe_{1-x-0.16}W_xB_{0.16}(0 \leq x \leq 0.05)$, (Fig. 7).

Discussion

The low-boron content ($y \leq 0.18$) $Fe_{1-y}B_y$ alloys are not well understood in the literature (Y. Waseda et al. (1978), T. Fujiwara et al. (1981)). Alloying transition metals have no effect on the stability of the very dilute amorphous alloys ($x \leq 0.03$) $Fe_{1-x-y}TM_xB_y$ as it may be calculated from the precipitation of Fe into α-Fe phase (Fig. 6). It suggests a non-changed chemical driving force forming the Fe_3B-type equilibrium state. The excess iron precipitates as the pure metal unaffected by the other transition metal (TM) components. On the other hand the effect of TM content is well observable on DTA peaks characterizing the crystallization (T_c and ΔQ, Figs 5/a and 5/b) which do not show any regularity between (*e*/*a*) and T_c^0 and ΔQ.

From the unchanged DTA peak characterizing the α-Fe precipitation we can assume that the transition metal atoms are in the non-precipitated part of the material and only the excess pure α-Fe has been precipitated. In our case in Fe-TM-$B_{0.135}$ the TM concentration relative to Fe is about 3.5%, so for a homogeneous spatial distribution of TM-atoms, about every 20th atom is TM, which means that every second coordination sphere of Fe will contain a TM-atom. Therefore the second coordination sphere has not a large influence on α-Fe precipitation. On the other hand the effect of the transition metal is large on the second phase transition (the amorphous-to-crystalline one) when the relative concentration of TM to Fe is about 8%. Assuming a homogeneous distribution of TM atoms in this stage as well, and knowing the fact that the coordination number of the nearest-neighbour Fe atoms for Fe is about the typical close-packed structure value of 12 (T. Fujiwara (1981)), every first coordination sphere of Fe will contain one of the TM atoms. It means that the TM-Fe interaction can become essential and not any more negligible. Accepting the general 'covalent-bond' model (P. Oelhafen (1983)) the B 2*s* state hybridizes with transition metal (Fe and TM) *s* and *p* states, as well as a bonding state created between B 2*p* and *d*-states of transition metals.

There are some observable contradictions with Nagel—Tauc's stabilization theory (T. Fujiwara (1982)) (Th. Paul et al. (1985)), because the Fermi energy (E_F) is generally situated near the maximum of the DOS. In the case of the chemically required stoichiometric composition ('Fe_3B') the picture is basically changed, the E_F position is just corresponding to a minimum of the DOS. (T. Fujiwara (1982)), in agreement with the behaviour predicted by the Nagel—Tauc's theory. It means that after the precipitation of the excess Fe from the alloy to α-Fe the materials is in chemical equilibrium, in 'Fe_3B' stoichiometric form, but in non-equilibrium state structurally and topologically. It means that the contradiction with the Nagel—Tauc prediction is only apparent, and the real crystallization proceeds from the 'Fe_3B' structure in all cases, which is stabilized by the electronic band structure. The B 2*p*- and *d*-states hybridization can become important for low TM-content amorphous 'Fe-B' alloys, having TM-atoms in every first coordination sphere of Fe and the stability will decrease with increasing *d*-state band-splitting. In the case of higher TM-concentrations this stability decrease (for pure electronic-structure stabilization effects) is more obvious (A. Mogro—Camparo et al. (1981)). We should note that the relatively large effect of TM-atoms is in agreement with the assumption that in the amorphous Fe-B-system the chemical bonds are stronger among Fe (or TM) atoms than in its crystalline counterpart in these dilute alloys (M. DeCrescenzi et al. (1983)).

The thermodynamic information (DTA) is in fair agreement with the electronic ones (SXS spectra) where the stability is monitored by the centroid position of the curves (A. Szász et al. (1985), N. Z. Negm et al. (1987)). In our

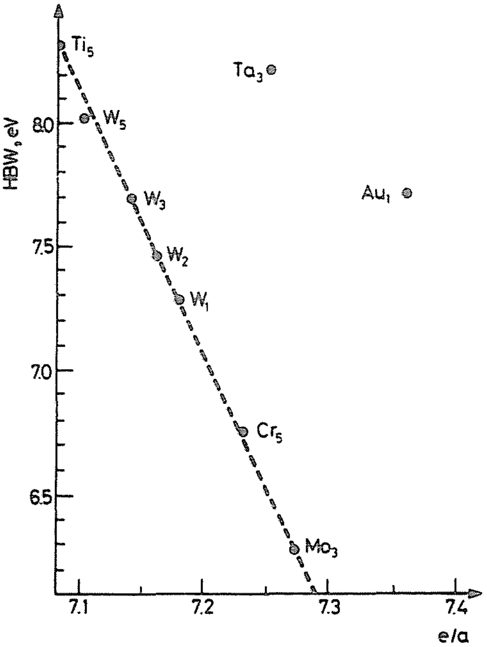

Fig. 8. The half-band width of SXFS spectra plotted against *e*/*a*

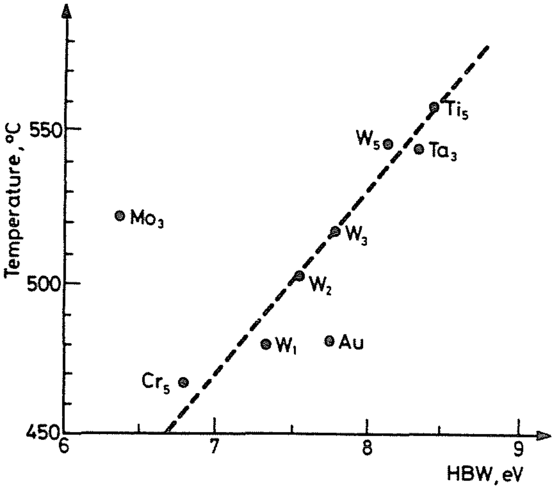

Fig. 9. The correlation of crystallization temperatures (measured by DTA) and HBW (measured by SXS)

case the centroid position can be replaced by the half-band-width (HBW), because E_F is fixed to the vacuum level. The change of HBW versus *e*/*a* is given in Fig. 8. This is in good agreement with the calculation of the difference between E_F and the centroid position of DOS, being −2.01 eV and −2.92 eV for a-$Fe_{85}B_{15}$ and a-$Fe_{75}B_{25}$, respectively (T. Fujiwara (1982)). It means that the covalent bond conception (P. Oelhafen (1983)) needs some refinement because of the really large differences between the stabilities of alloys containing a small proportion of different TM-s. More confusing is the fact that slight concentration increase of the same TM, led to an increase in stability which was demonstrated by DTA curves (Fig. 7) and correlated rigorously with the HBW of SXS spectra (Fig. 9) as well.

The effect of the stabilization of the electronic structure is discussed in terms of the structural concept (A. Szász et al. (1988)) and it is observed in the case of different metastable phases (A. Szász et al. (1985), N. Z. Negm et al. (1987), A. Szász et al. (1988)). We suggest for these ternary Fe—TM—B systems the same effect; the stabilization of these states is due to the electronic structure of these materials.

Assuming that the precipitated α-Fe does not play a role in crystallization stability, a reduced (*e*/*a*) can be defined based on one of the following assumptions:

— The amount of the precipitated α-Fe is calculated on the assumption that part of the Fe atoms are replaced by TM in the intermetallic compound 'TM_3B':

$$Fe_{1-x-y}TM_xB_y \rightarrow (\alpha\text{-Fe})_{1-4y} + Fe_{3y-x}TM_xB_y \tag{1}$$

The corresponding (e/a) will be denoted as

$$(e/a)_r = \frac{8(3y-x)+tx+3y}{4y} = \frac{(27y+x(t-8))}{4y}$$

where t is the number of $3d$ and $4s$ electrons of TM.

— The amount of the precipitated α-Fe is calculated on the assumption that the intermetallic compound is formed as $Fe_{3y}TM_xB_y$:

$$Fe_{1-x-y}TM_xB_y \rightarrow (\alpha\text{-}Fe)_{1-4y-x} + Fe_{3y}TM_xB_y \qquad (2)$$

and the corresponding (e/a) will be:

$$(e/a)_{rt} = \frac{(24y+tx+3y)}{4y+x} = \frac{(27y+tx)}{4y+x}$$

Analyzing the HBW, ΔQ and T_c versus the different electron concentrations (Fig. 10, 11 and 12 and Table 2) the following observations were made:

1. HBW is in linear relationship with $(e/a)_r$ and $(e/a)_{rt}$, where "e" denotes the number of the outermost d-electrons, and it is almost independent on the boron content or the concentration (in this dilute range) of TM.

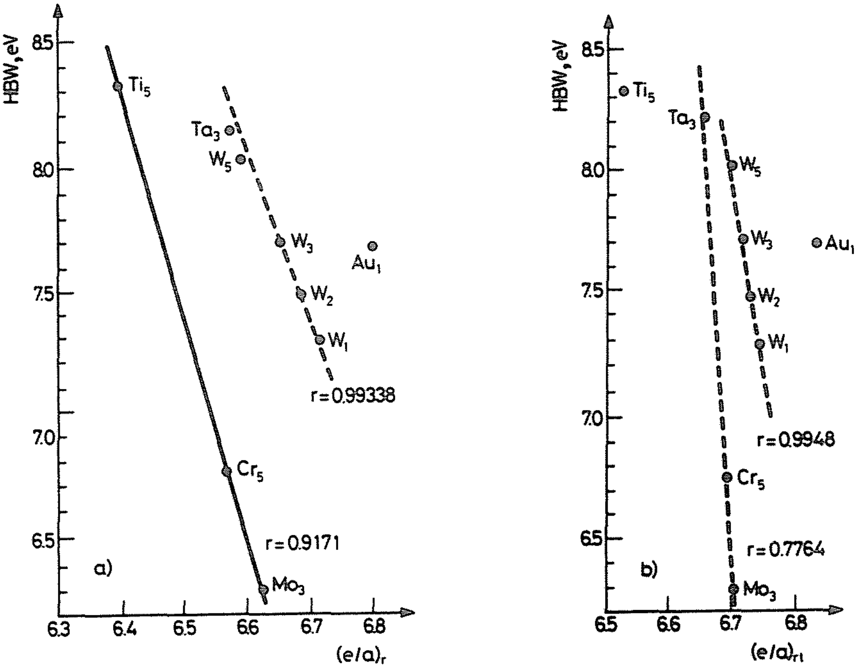

Fig. 10. The dependence of HBW on different (e/a)-s:
a) $(e/a)_r$; b) $(e/a)_{rt}$

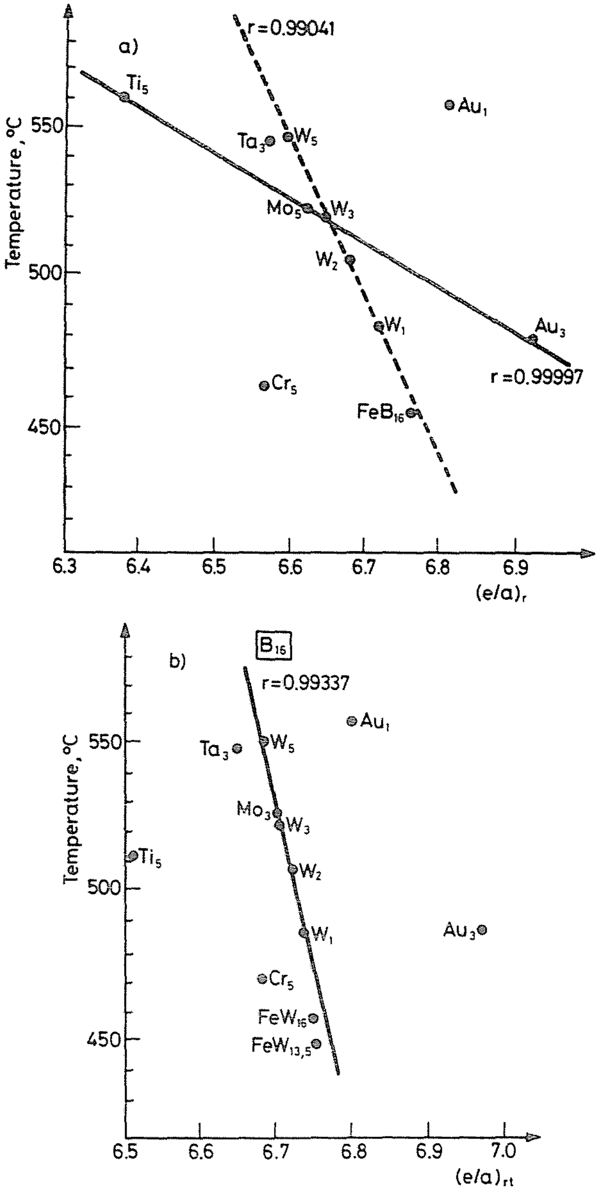

Fig. 11. The dependence of ΔQ on different (e/a)-s:
a) $(e/a)_r$; b) $(e/a)_{rt}$

2. The Q and T_c are in best fit with $(e/a)_{rt}$, and this linear relationship depends markedly on boron concentration.
3. The parameters of alloys without TM are under investigation.

These observations lead to the following conclusions:

a) The stabilization is due to the electronic structure.

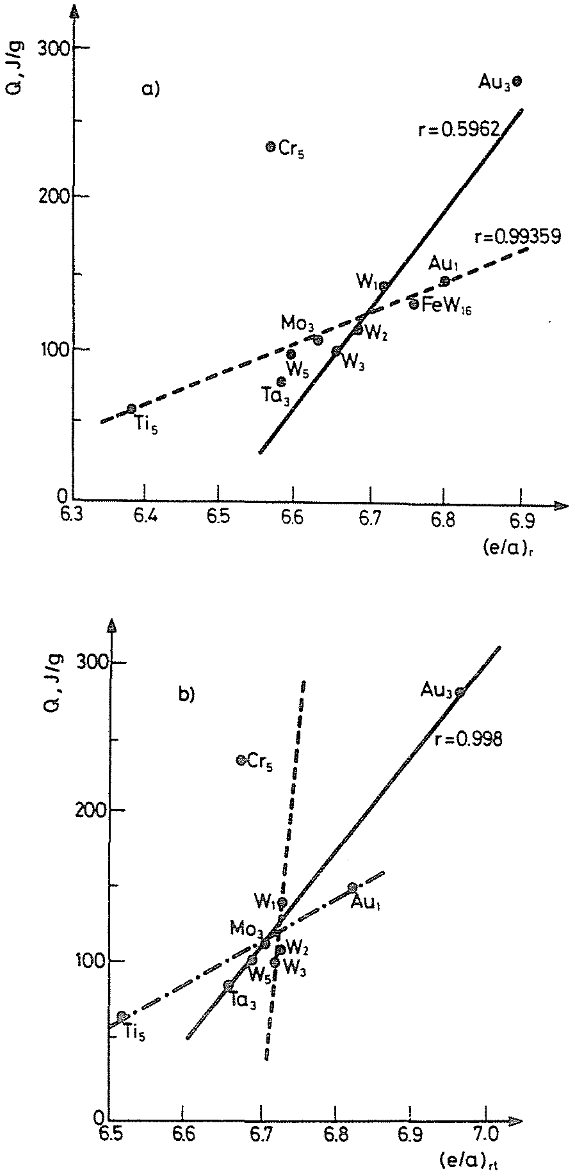

Fig. 12. The dependence of T_c on different (e/a)-s:
a) $(e/a)_r$; b) $(e/a)_{rt}$

b) The α-Fe precipitation temperature is independent of the TM content, but the amount of precipitated Fe is not.

c) The Fe—B-bond determines the crystallization process and the stability of these amorphous alloys.

Table 2

The correlation coefficients of different linear-regression fitting. (The numeration of alloys is in Table 1.)

Parameter	e/a	Alloys (Number from Table 1.)	Correlation coef.
HBW	e/a	4+5+7+8+9+10	0.9480
	$(e/a)_r$	6+7+8+9+10	0.99338
		4+5+6	0.9171
	$(e/a)_{rt}$	7+8+9+10	0.9948
		4+5+6	0.7764
Q	e/a	4+7+8+9	0.9657
		5+6+12	0.9857
		5+6+12	0.9156
	$(e/a)_r$	7+8+9+10	0.5962
		5+6+11	0.9935
		5+6+7+10+12	0.3536
	$(e/a)_{rt}$	7+8+9	0.8879
		3+5+11	0.9935
		5+6+10+12	0.9980
		4+5+7+8+9	0.4764
T_c	e/a	7+8+9+10	0.9917
		5+6+12	0.9534
		3+5+6+12	0.8947
	$(e/a)_r$	7+8+9+10	0.9904
		3+5+9+12	0.999976
	$(e/a)_{rt}$	5+7+8+9+10	0.9912
		3+6+10	0.8909
		1+2+6	0.9971
		6+10+11	0.9981

We have observed some similarities between our ideas and the popular stability theory of Buschow and others (K. M. J. Buschow (1980), M. Lasocka et al. (1984)).

It was shown that the stability of amorphous binary alloys can be described in terms of a simple kinetic model, where the activation energy for crystallization is taken to be proportional to the formation enthalpy of a structural hole (ΔH_h) (the size of the smaller type of atoms) (K. M. J. Buschow et al. (1980)), or it depends linearly on the average atomization enthalpy (ΔH_{ab}) (M. Lasocka et al. (1984)). Generally it can be shown (K. M. J. Buschow (1980)) that the vacancy formation energy and the sublimation enthalpy are proportional to each other, and the hole formation enthalpy can be expressed by the monovacancy formation enthalpies of the binary system. In the same way the vacancy formation energy is proportional to the average specific lattice energy of one atom (A. C. Damask (1963)). The vacancy formation is strongly related to the electronic structure (N. H. March (1976)), which means that the linear dependence of the stability of amorphous alloys on the *e/a* ratio is not surprising. Furthermore the centroid position (mass-center under the SXS-peaks, corresponding to the partial electronic DOS) could be defined by

$$E_{MC} = \int_0^{E_F} E \cdot n(E) dE$$

where E_{MC} the energy of the mass-center, E_F is the Fermi energy, $n(E)$ is the density of electronic states. According to the linear dependence of E_F on the vacancy formation (E_v) (F. G. Fumi (1955)),

$$E_{MC} = \int_0^{E_v} E' \cdot n(E') dE'.$$

So the stability criteria were observed in different measurements (thermodynamic and/or electronic) and they were found to be closely correlated.

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