"Role of atomic packing in glass forming ability and stability of ternary and some quaternary bulk metallic glasses"

Dmitri V. Louzguine-Luzgin

WPI Advanced Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan

Abstract

In this work we study the influence of atomic packing efficiency on glass-forming ability of bulk (defined as 3-dimentional massive glassy articles with a size of not less than 1 mm in any dimension) metallic glasses by the analysis of a database of ternary and quaternary bulk metallic glasses. An extensive dataset on the composition and stability (critical thickness, glass-transition temperature, crystallization temperature and liquidus temperature) of ternary and quaternary metallic glasses has been obtained from the literature data. The results indicate that glassy alloys compositions are distributed in a highly non-uniform way in the compositional area and tend to prefer specific values of fraction and atomic size ratios. For example in ternary alloys clear maxima are seen at about $A_{65}B_{15}C_{20}$, $A_{70}B_{10}C_{20}$, $A_{65}B_{10}C_{25}$, $A_{40}B_{18}C_{38}$, $A_{45}B_{17}C_{28}$ and $A_{58}B_{13}C_{45}$ compositions. Clear minimum at $A_{50}B_{25}C_{25}$ corresponds to the A_2BC compound, while $A_{60}B_5C_{35}$ and $A_{75}B_5C_{20}$ compositions are close to A_2C and A_3C binary compounds, respectively. Glass-forming ability is shown to increase with increasing the number of alloying elements. According to the statistical analysis one can anticipate that the difference in D_c among binary, ternary and quaternary alloys is meaningful which confirms the first Inoue's principle for achieving high GFA. Quaternary bulk glass-forming alloys with large critical diameter in general have larger ΔT_x than those of ternary alloys and are preferable for shaping in SCLR. As T_g and T_x for ternary and quaternary alloys nearly linearly depends on T_l, one may anticipate that it is not a coincidence but real physical meaning on structural unity of the bulk-glass-forming alloys.

The data on glass-forming ability and thermal stability were collected for ternary and quaternary bulk metallic glasses. Only metallic glasses produced by solidification from the melt are considered. The data for binary bulk metallic glasses have been taken from our earlier paper[1]. Data for similar alloys from different literature sources with slightly different reported properties were also collected. The data retrieved from the literature separately for ternary and quaternary alloys include alloy composition, critical thickness (rod sample diameter) for single glassy phase formation, the glass-transition, crystallization temperatures and liquidus temperatures, namely T_g, T_x and T_l, respectively. The compositions used in the present review are usually nominal compositions given by the pre-melting weight of the elements. Common thermal stability parameters, including $T_{rg}=T_g/T_l$, $\Delta T_x=T_x-T_g$ and $\gamma=T_x/(T_g+T_l)$ were calculated from T_g, T_x and T_l. We collected the data from an extensive number of literature sources on ternary (709 data points - Fig. 1 represents the final part of the database) and quaternary (418 data points - Fig. 2 represents the final part of the database) bulk metallic glassy alloys to find relation between the glass-forming ability (GFA), alloy composition and other parameters. The number of data points containing critical diameter was 93 and 212, respectively.

The efficient cluster packing (ECP) model was used to establish the role of defect state and packing efficiency on metallic glass stability. Analysis of defects was also possible in the ECP structure, the most important are those associated with the filling of the inter-cluster sites. Structure and topology are inter-related in the ECP model to give a self-consistent description for a particular metallic glass. The structure of metallic glasses is related these to the glass stability and formability. Topological structure is obtained from the composition of the metallic glass, which gives both the atomic species (and hence atomic sizes) and concentrations. The critical diameter of ternary bulk glassy sample is plotted in Fig. 3 as a function of element B and C content in A-B-C alloys. Some clear maxima are seen at about $A_{65}B_{15}C_{20}$, $A_{70}B_{10}C_{20}$, $A_{65}B_{10}C_{25}$, $A_{40}B_{18}C_{38}$, $A_{45}B_{17}C_{28}$ and $A_{58}B_{13}C_{45}$ (less clear) compositions. One can also mention clear minima at the following compositions: $A_{50}B_{25}C_{25}$, $A_{60}B_5C_{35}$, $A_{55}B_{15}C_{30}$, $A_{46}B_7C_{47}$ and $A_{75}B_5C_{20}$. $A_{50}B_{25}C_{25}$ corresponds to the A_2BC compound, while $A_{60}B_5C_{35}$ and $A_{75}B_5C_{20}$ compositions are close to A_2C and A_3C binary compounds, respectively.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
29 MAR 2010	**Final**	**11-03-2009 to 25-03-2010**

4. TITLE AND SUBTITLE
Role of atomic packing in glass forming ability and stability of ternary and some quartenary bulk metallic glasses

5a. CONTRACT NUMBER
FA23860914032

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Dmitri Louzguine

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Tohoku University,2-1-1 Katahira, Aoba-Ku,,Sendai,Japan,JN,980-8577

8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Asian Office of Aerospace Research & Development, (AOARD), Unit 45002, APO, AP, 96338-5002

10. SPONSOR/MONITOR'S ACRONYM(S)
AOARD

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AOARD-094032

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

In this work we study the influence of atomic packing efficiency on glass-forming ability of bulk (defined as 3-dimentional massive glassy articles with a size of not less than 1 mm in any dimension) metallic glasses by the analysis of a database of ternary and quaternary bulk metallic glasses. An extensive dataset on the composition and stability (critical thickness, glass-transition temperature, crystallization temperature and liquidus temperature) of ternary and quaternary metallic glasses has been obtained from the literature data. The results indicate that glassy alloys compositions are distributed in a highly non-uniform way in the compositional area and tend to prefer specific values of fraction and atomic size ratios. For example in ternary alloys clear maxima are seen at about A65B15C20, A70B10C20, A65B10C25, A40B18C38, A45B17C28 and A58B13C45 compositions. Clear minimum at A50B25C25 corresponds to the A2BC compound, while A60B5C35 and A75B5C20 compositions are close to A2C and A3C binary compounds, respectively. Glass-forming ability is shown to increase with increasing the number of alloying elements. According to the statistical analysis one can anticipate that the difference in Dc among binary, ternary and quaternary alloys is meaningful which confirms the first Inoue?s principle for achieving high GFA. Quaternary bulk glass-forming alloys with large critical diameter in general have larger DTx than those of ternary alloys and are preferable for shaping in SCLR. As Tg and Tx for ternary and quaternary alloys nearly linearly depends on Tl, one may anticipate that it is not a coincidence but real physical meaning on structural unity of the bulk-glass-forming alloys.

15. SUBJECT TERMS
Metallic glasses

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**5**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	System	EL1	EL2	EL3	AT% 1	AT% 2	At% 3	D-crit	Tg, K	Tx, K	Tl, K	Tm, K	dTx	Trg	Gamma	REF
673	Zr-Ni-Al	Zr	Ni	Al	60	22	18	2	720.1	766.6	1289.9	1181.9	46.5	0.5583	0.3814	60WANG
674	Zr-Ni-Al	Zr	Ni	Al	60	23	17	5	715.8	767.1	1279.6	1179	51.3	0.5594	0.3844	60WANG
675	Zr-Ni-Al	Zr	Ni	Al	54	24	22		751	813	1284	1183	62	0.5849	0.3995	117DONG
676	Zr-Ni-Al	Zr	Ni	Al	55.8	24.8	19.4		735	805	1277	1184	70	0.5756	0.4001	117DONG
677	Zr-Ni-Al	Zr	Ni	Al	60	25	15						77			8INOUE
678	Zr-Ni-Al	Zr	Ni	Al	55	25	20		760	810			50			51INOUE
679	Zr-Ni-Al	Zr	Ni	Al	60	25	15		710	790			80			51INOUE
680	Zr-Ni-Al	Zr	Ni	Al	65	25	10	2	681.7	721.7	1253	1177	40	0.5441	0.373	60WANG
681	Zr-Ni-Al	Zr	Ni	Al	63	25	12	2	691.3	744.9	1219	1180	53.6	0.5671	0.3899	60WANG
682	Zr-Ni-Al	Zr	Ni	Al	60	25	15	5	715.4	770.2	1261	1179	54.8	0.5673	0.3897	60WANG
683	Zr-Ni-Al	Zr	Ni	Al	58	25	17	5	728.8	790.2	1303	1185	61.4	0.5593	0.3889	60WANG
684	Zr-Ni-Al	Zr	Ni	Al	55	25	20	2	757.1	803.3	1247	1177.5	46.2	0.6071	0.4008	60WANG
685	Zr-Ni-Al	Zr	Ni	Al	55	25	20		757	803			46			63ILLEK
686	Zr-Ni-Al	Zr	Ni	Al	60	25	15		670							64KIM
687	Zr-Ni-Al	Zr	Ni	Al	55	25	20		725							64KIM
688	Zr-Ni-Al	Zr	Ni	Al	65	25	10		640							64KIM
689	Zr-Ni-Al	Zr	Ni	Al	60	25	15		696	787	1230		91	0.5659	0.4086	71YOKO
690	Zr-Ni-Al	Zr	Ni	Al	55	25	20		733	818	1305		85	0.5617	0.4014	71YOKO
691	Zr-Ni-Al	Zr	Ni	Al	55	25	15									94INOUE
692	Zr-Ni-Al	Zr	Ni	Al	55	25	20									117DONG
693	Zr-Ni-Al	Zr	Ni	Al	60	25	15									117DONG
694	Zr-Ni-Al	Zr	Ni	Al	65	25	10									138INOUE
695	Zr-Ni-Al	Zr	Ni	Al	60	25	15									138INOUE
696	Zr-Ni-Al	Zr	Ni	Al	57.5	25.6	16.9		721	801	1280	1186	80	0.5633	0.4003	117DONG
697	Zr-Ni-Al	Zr	Ni	Al	52	26	22									63ILLEK
698	Zr-Ni-Al	Zr	Ni	Al	66	26	8		672	707.6	1251		35.6	0.5372	0.368	79LU
699	Zr-Ni-Al	Zr	Ni	Al	66	26	8		672	707.6		1188.5	35.6			91WANG
700	Zr-Ni-Al	Zr	Ni	Al	58.6	26	15.4		707	789	1274	1188	82	0.5549	0.3983	117DONG
701	Zr-Ni-Al	Zr	Ni	Al	58	27	15	2	724.9		1274.2	1179		0.5689		60WANG
702	Zr-Ni-Al	Zr	Ni	Al	57	27	16									63ILLEK
703	Zr-Ni-Al	Zr	Ni	Al	62	28	10	2	696.5	736.1	1218.3	1177	39.6	0.5717	0.3844	60WANG
704	Zr-Ni-Al	Zr	Ni	Al	61	29	10	2	697.5	738.6	1210.6	1179.8	41.1	0.5762	0.3871	60WANG
705	Zr-Ni-Al	Zr	Ni	Al	55	30	15		750	790			40			51INOUE
706	Zr-Ni-Al	Zr	Ni	Al	58	30	12	2	717.9	769.1	1233.5	1178.9	51.2	0.582	0.3941	60WANG
707	Zr-Ni-Al	Zr	Ni	Al	55	30	15		743	790			47			138INOUE
708	Zr-Ni-Al	Zr	Ni	Al	55	35	10		740	770			30			138INOUE
709	Zr-Ni-Ti	Zr	Ni	Ti	40	37	23			531						13PARK

Fig. 1. Database for ternary alloys.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	**System**	**EL1**	**EL2**	**EL3**	**El4**	**AT% 1**	AT% 2	At% 3	At% 4	**Critical Diam**	**T_g, K**	**T_x, K**	**T_l, K**	**Tm, K**	**Ref**
384	Zr-Cu-Ag-Al	Zr	Cu	Ag	Al	50	36.7	7.3	6				1147	1055	43JIANG
385	Zr-Cu-Ag-Al	Zr	Cu	Ag	Al	48	38.3	7.7	6			767	1124	1124	43JIANG
386	Zr-Cu-Al-Ni	Zr	Cu	Al	Ni	55	30	10	5		690	780			93Inoue
387	Zr-Cu-Al-Ta	Zr	Cu	Al	Ta	44	35.2	8.8	12		701				103Inoue
388	Zr-Cu-Al-Ta	Zr	Cu	Al	Ta	45.5	36.4	9.1	9		702				103Inoue
389	Zr-Cu-Al-Ta	Zr	Cu	Al	Ta	47	37.6	9.4	6		703				103Inoue
390	Zr-Cu-Al-Ta	Zr	Cu	Al	Ta	48.5	38.8	9.7	3		705				103Inoue
391	Zr-Cu-Fe-Al	Zr	Cu	Fe	Al	59.2	25.4	9.1	6.3		661	745	1238	1130	55LIU
392	Zr-Cu-Fe-Al	Zr	Cu	Fe	Al	55.2	25.4	9.11	10.3						55LIU
393	Zr-Cu-Fe-Al	Zr	Cu	Fe	Al	58	22	8	12	5.0	677	761			65HONO
394	Zr-Cu-Fe-Al	Zr	Cu	Fe	Al	59.2	24.8	8.9	6.9		658	747	1231	1132	55LIU
395	Zr-Cu-Fe-Al	Zr	Cu	Fe	Al	59.2	23.6	8.4	8.1		667	757	1206	1133	55LIU
396	Zr-Cu-Fe-Al	Zr	Cu	Fe	Al	59.2	22.9	8.2	8.7		667	759	1201	1134	55LIU
397	Zr-Cu-Fe-Al	Zr	Cu	Fe	Al	59.2	24.2	8.6	7.5		679	777	1223	1134	55LIU
398	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	62	17	13	8		657	726			51PARK
399	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	52	32	4	12		703	792	1118		23INOUE
400	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	52	30	6	12		709	792	1103		23INOUE
401	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	50	26	12	12		712	793	1106		23INOUE
402	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	50	34	4	12		714	804	1118		23INOUE
403	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	48	32	8	12		715	804	1110		23INOUE
404	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	50	32	6	12		716	800	1126		23INOUE
405	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	52	28	8	12		716	796	1107		23INOUE
406	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	50	30	8	12		723	794	1123		23INOUE
407	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	46	34	8	12		725	796	1138		23INOUE
408	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	48	28	12	12		725	789	1160		23INOUE
409	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	48	34	6	12		725	800	1140		23INOUE
410	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	50	28	10	12		726	792	1118		23INOUE
411	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	48	30	10	12		727	790	1148		23INOUE
412	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	48	30	10	12		729	795	1157		23INOUE
413	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	52	26	10	12		729	788	1144		23INOUE
414	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	44	34	10	12		730	796	1158		23INOUE
415	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	46	30	12	12		733	790	1144		23INOUE
416	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	44	32	12	12		738	791	1168		23INOUE
417	Zr-Cu-Ni-Al	Zr	Cu	Ni	Al	55	30	5	10	30.0					90Inoue
418	Zr-Cu-Ni-Al	Zr	Cu	N i	Al	65	17.5	10	7.5		633				48PERE

Fig. 2. Database for quaternary alloys.

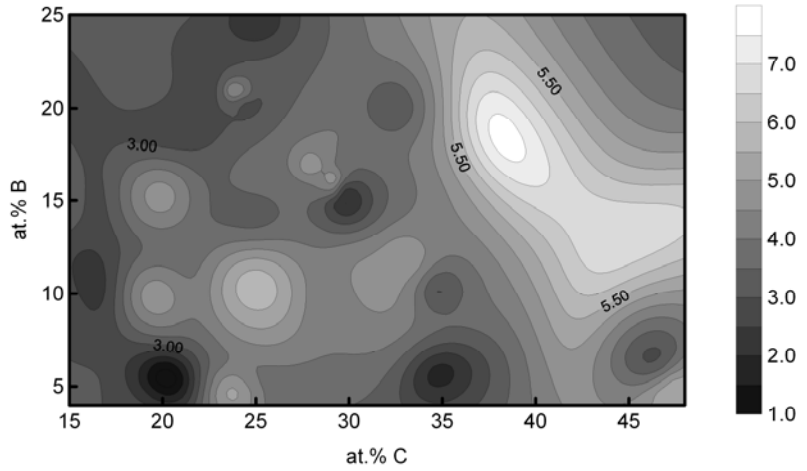

Fig. 3. Critical diameter of ternary bulk glassy sample as a function of B and C content in A-B-C alloys

The critical diameters of bulk glassy samples are shown as a function of both T_{rg} and $\Delta T_x/100$ for ternary (Fig. 4) and quaternary (Fig. 5) alloys. There is no apparent correlation between T_{rg}, ΔT_x and critical diameter for ternary alloys. Systematic absence of bulk glassy alloys seems to occur in quaternary alloys when T_{rg} is less than about 0.54 and ΔT_x is less than about 50 K, and when T_{rg} is less than about 0.56 and ΔT_x is greater than about 105 K. Quaternary alloys with critical diameters in excess of about 15 mm in general have larger ΔT_x values. Thus, quaternary bulk glass-forming alloys are preferable for shaping in the supercooled liquid region (SCLR). One can also conclude that the addition of 4-th alloying elements not only enhances the GFA but stabilizes the SCLR.

Frequency distributions of critical diameters in ternary and quaternary alloys are shown in Fig. 6. As non-integer values of critical diameters were also reported for ternary and quaternary alloys the data were integrated at 1 mm steps. One of possible fitting ways of the data was log-normal distribution (Fig. 5 which led to coefficient of determination R^2 of 0.83 and 0.94 for ternary and quaternary alloys, respectively. It is also interesting to note that the fraction of alloys having critical diameter larger than 7 mm was 0, 9.6, and 22.5 in binary, ternary and quaternary alloys, respectively.

Fig. 7 illustrates the dependence of simple average critical diameter $\overline{D_c}$ from system complexity. Its natural logarithm increases linearly with the number of alloying elements in the alloy from 2 to 4 elements.

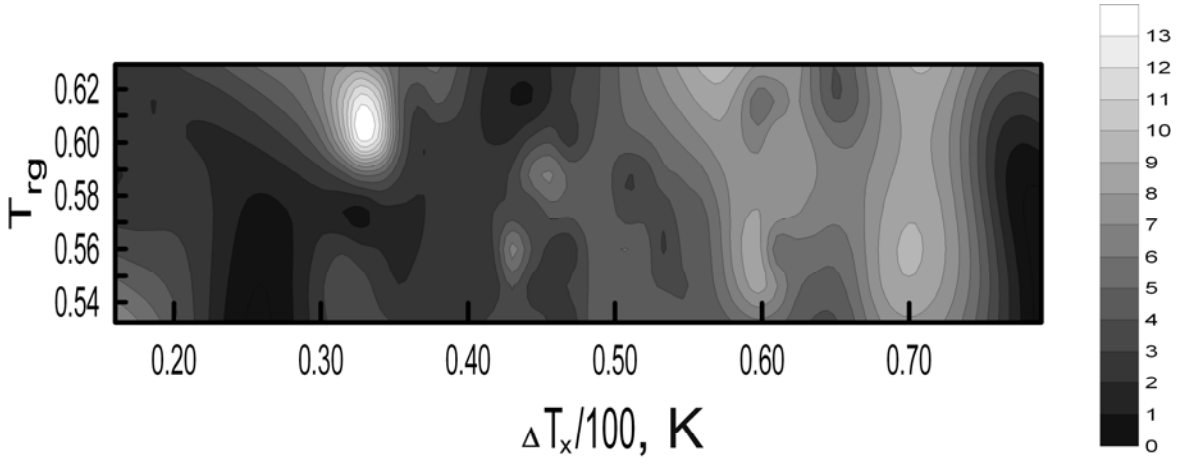

Fig. 4. Critical diameter of ternary bulk glassy sample as a function of both T_{rg} and $\Delta T_x/100$.

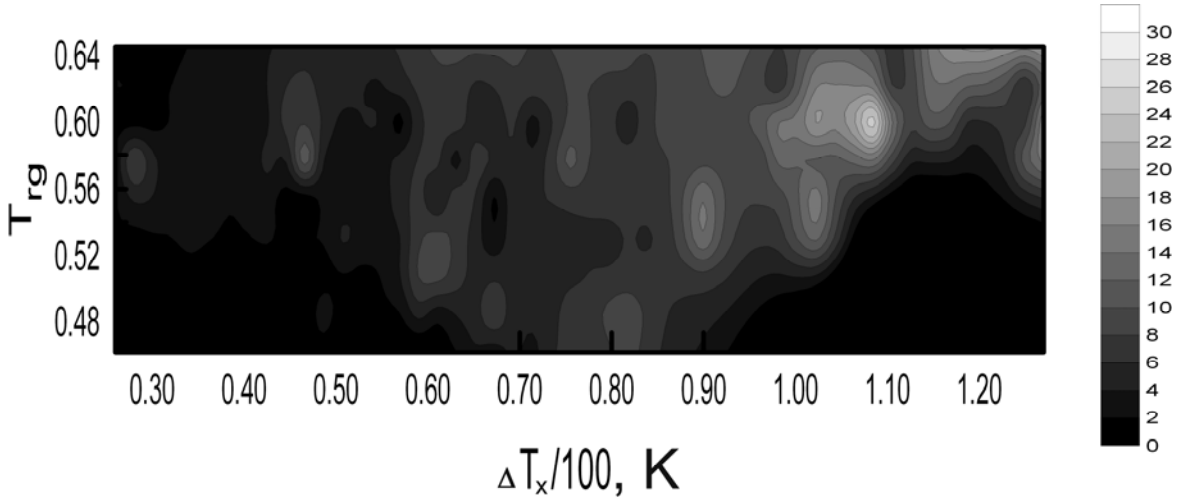

Fig. 5. Critical diameter of quaternary bulk glassy sample as a function of both T_{rg} and $\Delta T_x/100$. Largest Pd-Ni-Cu-P samples produced by fluxing were excluded.

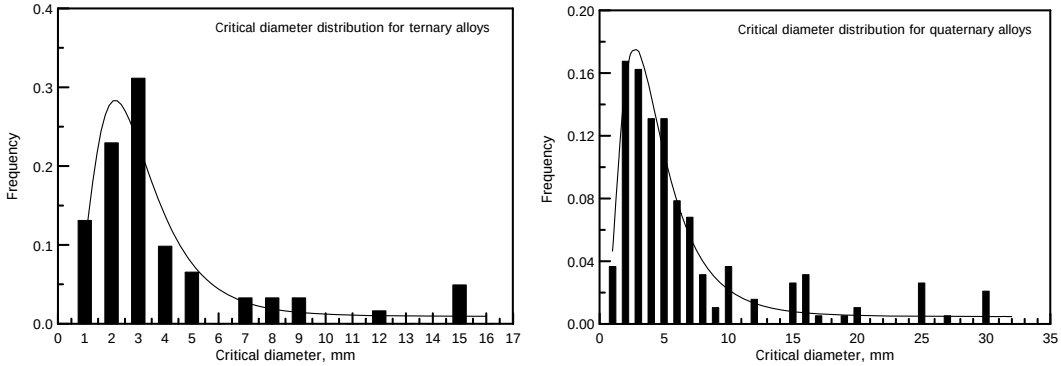

Fig. 6. Distribution of frequency number of alloys per 1 mm step as a function of their critical diameter. The fits represent log-normal distribution. Largest Pd-Ni-Cu-P samples produced by fluxing were excluded.

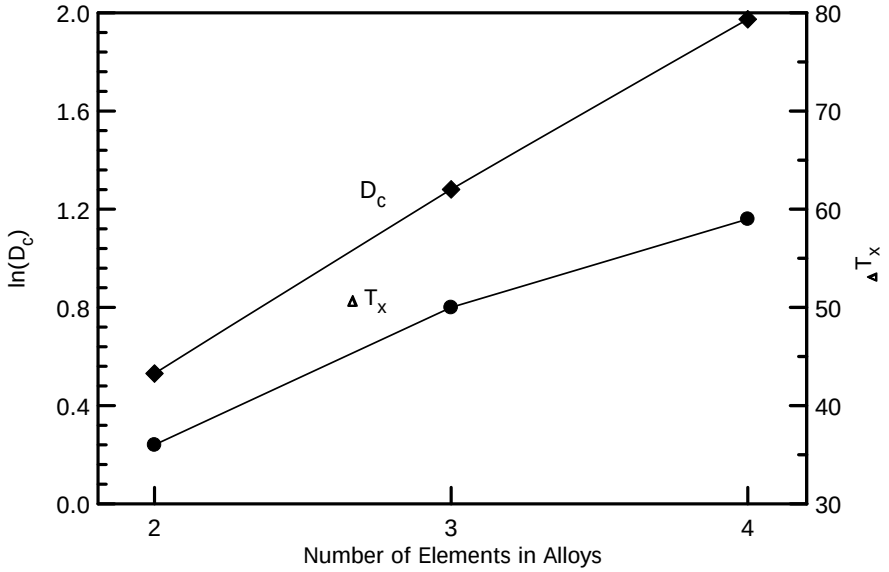

Fig. 7. Natural logarithm of simple average critical diameter $\ln(\overline{D_c})$, and average ΔT_x as a function of alloy system complexity. (b)

Simple average ΔT_x and T_{rg} for binary, ternary and quaternary alloys are 36 K and 0.56, 50 K and 0.585, 59 K and 0.577, respectively. As distribution of ΔT_x values can be fitted nearly equally well/bad with both normal and Log-normal distribution (R^2 for quaternary alloys, for example is 0.804 and 0.805, respectively) usage of simple average may be justified.

Fig. 8 shows T_g and T_x values as a function of T_l for ternary and quaternary alloys. For ternary and quaternary alloys the dependency of T_g and T_x on T_l is considerably linear (R^2>0.9) and linear extrapolation approaches nearly zero at low temperature though a residual T_l exists when T_g or T_x is zero. This effect may be connected with the range of T_{rg} of 0.55-0.65 typical for bulk glass-formers compared to marginal glass-formers in binary alloys. In the case of ternary and quaternary alloys, the linear fit of T_x essentially intersects absolute zero at T_l of zero, but the extrapolated curve fit for T_g suggests that T_l is greater than zero when T_g is zero. It seems to have a clear meaning that a hypothetical alloy having T_l close to absolute zero will have a very close T_x while hypothetical BMG alloys with T_l close to 100-150 K will have no T_g and never can be vitrified remaining just a supercooled liquid if such a liquid could exist.

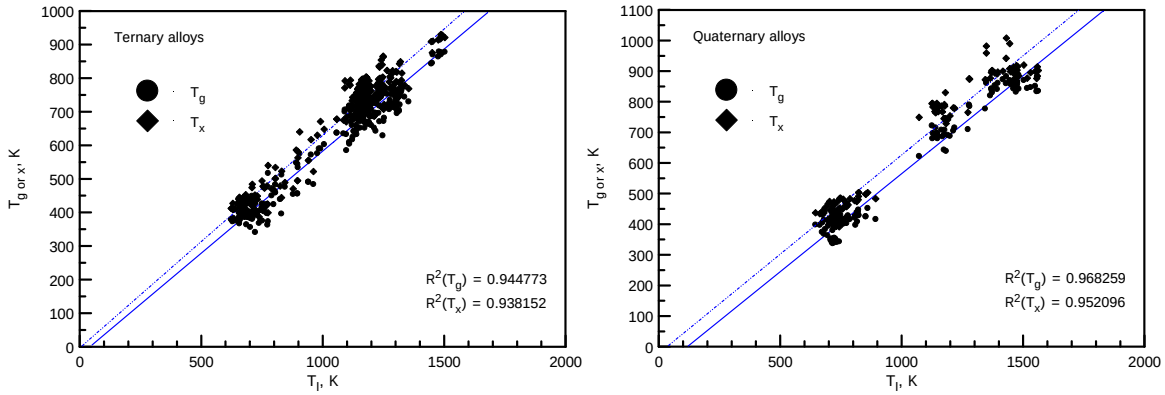

Fig. 8. T_g (solid line) and T_x (dashed line) as a function of T_l for binary, ternary and quaternary alloys.

In conclusion: The results indicate that glassy alloys compositions are distributed in a highly non-uniform way in the compositional area and tend to prefer specific values of F_a and RB/RA in case of binary alloys and critical diameters of bulk glassy alloys. For example, in ternary alloys clear maxima are seen at about $A_{65}B_{15}C_{20}$, $A_{70}B_{10}C_{20}$, $A_{65}B_{10}C_{25}$, $A_{40}B_{18}C_{38}$, $A_{45}B_{17}C_{28}$ and $A_{58}B_{13}C_{45}$ compositions. Clear minimum at $A_{50}B_{25}C_{25}$ corresponds to the A_2BC compound, while $A_{60}B_5C_{35}$ and $A_{75}B_5C_{20}$ compositions are close to A_2C and A_3C binary compounds, respectively. Glass-forming ability is shown to increase with increasing number of alloying elements. According to the statistical analysis one can anticipate that the difference in D_c among binary, ternary and quaternary alloys is meaningful which confirms the first Inoue's principle for achieving high GFA. Quaternary bulk glass-forming alloys with large critical diameter in general have larger ΔT_x than those of ternary alloys and are preferable for shaping in SCLR. One can conclude that the addition of 4th alloying element not only enhances the GFA but also stabilizes the SCLR. The T_x as a function of T_l plot crosses absolute zero in case of ternary and quaternary bulk metallic glasses. A scientific paper based on the present report in under preparation at present.

References:

[1] D. Miracle, D. V. Louzguine-Luzgin, L. Louzguina-Luzgina and A. Inoue, "An assessment of binary metallic glasses: Correlations between structure, glass forming ability and stability" International Materials Reviews, in press.