Chem. Chem. Technol., 2017, Vol. 11, No. 2, pp. 214–219

Chemical Technology

DEVELOPMENT OF GLASS-CERAMIC HIGH-STRENGTH MATERIAL FOR PERSONAL ARMOR PROTECTION ELEMENTS

Oksana Savvova[1, *], Luidmyla Bragina[1], Gennadii Voronov[1], Yuliya Sobol[1], Olena Babich[1], Oksana Shalygina[1], Mykola Kuriakin[1]

https://doi.org/10.23939/chcht11.02.214

Abstract. The perspective of glass-ceramic high-strength materials used for personal armor elements has been established. The methodological approach has been developed and the choice of initial lithium aluminosilicate system for obtaining high-strength lightweight glass-ceramic materials has been substantiated. The glass formation area in the chosen system was studied, and model glasses were synthesized. Features of crystal structure formation during heat treatment of the developed model glasses were investigated. As a result, high-strength glass-ceramic materials have been developed. It has been determined that they possess high performance characteristics and can be used in manufacturing of modern composite armor.

Keywords: glass ceramic material, lithium aluminosilicate system, high-strength, mechanical properties, personal armor protection element.

1. Introduction

Rapid developments in the field of explosive substances, armaments and small-arm weapons contribute to the growth of ballistic risks faced by military and law-enforcement personnel. It is the reason for an urgent need in reliable and advanced materials for production of personal armor elements which provide increased level of their armor protection, and therefore save people's lives in conflict zones. Considering aforementioned, the studies aimed at finding and development of new high-strength lightweight materials are relevant.

Currently, various materials are being developed and used for manufacturing of armor protection elements. Specifically, flexible textile armor consisting of high-modulus and high-strength polyaramide or polyethylene fabrics or fibers is widely used for protection from low-energy weapons, such as melee weapons, revolver and pistol bullets [1]. Effective protection against high-energy weapons with high penetrative power, *e.g.* armor piercing rifle bullets with heat-treated slugs (5th and 6th classes according to Ukrainian standard DSTU V 4103-2002), is impossible without the use of hard elements like metallic alloys, ceramic and glass-ceramic materials (Table 1). The most notable of them are: high-strength armor steels MARS 300 (France), ARMOX 600S (Sweden), XH-206 (Germany), 44S (Russian Federation) [2], functional gradient materials (Italy) [3]; armor ceramics (Russian Federation) [4], glass-ceramic materials (Great Britain) [5].

Among the works dedicated to the synthesis problems of high-strength ceramic materials for personal protection there are a number of solid works by the scientists from Ukrainian institutions: National Technical University of Ukraine "Kyiv Polytechnic Institute" (NTUU "KPI") [10], Frantsevich Institute for Problems of Materials Science [11], "Keramtech LTD", Ukrainian State University of Railway Transport, V. Bakul Institute for Superhard Materials of NASU [12] and National Technical University "Kharkiv Polytechnic Institute" (NTU "KhPI") [13, 14].

Technology of ceramic-metallic materials with titanium matrix reinforced by ceramic titanium boride fibers, characterized by a tensile strength of 890 MPa and plasticity of more than 15 %, developed by NTUU "KPI" in cooperation with EO Paton Electric Welding Institute is of great interest. Moreover, they have developed a new generation of versatile superhard reinforced ceramics with armor protection class of 6. This product is both advanced and readily marketable in current conditions [10].

IPM NASU has also contributed significantly to design, technological development and adjustment of the production of armored ceramic-polymer items. Also, for the first time in Ukraine they have created the manufacturing line for production of mosaic-structured ceramic-polymer armor blocks using method of reaction sintering of silicon carbide ceramics. [11].

[1] National Technical University "Kharkiv Polytechnic Institute", 21 Frunze St., 61002 Kharkiv, Ukraine
* *savvova_oksana@ukr.net*

Table 1

Characteristics of armor protection

Property	Metallic alloys [2, 6]		Ceramics [2, 3, 7]			Glass-ceramics [8, 9]	
	44S	VT14	Al_2O_3	B_4C	SiC	lithium alumi nosilicate	lithium silicate
Density ρ, kg/m^3	7900	4520	3600–3900	2450–2520	3200–3300	2410	2350– 450
TCLE, $\alpha \cdot 10^7$ K^{-1}	–	87.0	84	55.4	51.2	5 – 17	50–114
Bending strength σ_{bend}, MPa	–	–	200–400	200–360	600 –730	100 –137	38–40
Bending strength σ_B, MPa	2250–2350	835–1300	–	–	–	–	–
Compressive strength $\sigma_{compress}$, GPa	–	–	2.07–6.6	2.9–6.97	1.7–5.84	–	–
Tensile strength σ_{tens}, MPa	–	–	260–300	155	310	–	–
Hardness *HV*, GPa	–	–	12–18	29 – 36	28	–	5.8
Hardness *HB*, MPa	55–57	25.5–38.8	–	–	–	–	–
Microhardness *H*, MPa	–	–	–	–	–	5700 9300	6800
Young's modulus *E*, MPa	216	110	300–450	440–460	440–476	94–95	94
Poisson ratio μ	–	–	0.22	0.19	0.19	0.28	0.27
Sound velocity *c*, km/s	–	–	9.5–11.6	13.0–13.7	11.2–12.0	6.0–6.4	6.0
Thermal conductivity λ, W/(m·K)	–	13.82	35	28	41	1.7–2.3	–
Stress intensity K_{1C}, MPa·m$^{0.5}$	–	–	4.5	3.2	4.0	–	1.6–1.8
Impact strength KCU, kJ/m^2	50.0–60.0	200–500	–	–	–	2.2–6.0	–

Scientist of TOV “Keramtekh LTD” (Ukraine) have established manufacturing of experimental armor plate specimens using efficient high-density composite material on the base of refractory powders of oxides and carbides with high strength characteristics [12].

Studies conducted in NTU “KhPI” allowed to significantly improve characteristics and reliability of armor and aviation products by using valve metals with microarc oxidation treatment as the materials for elements of military vehicles, which can also be an effective mean of personal protection [14].

Analysis of currently available materials used as protective elements in bullet-proof vests in terms of performance and cost characteristics allowed to elicit their advantages and disadvantages.

While having functional efficiency, the armor steels and ceramic materials are heavy, which limits their use. The use of B_4C ceramics with low density is limited by high costs and complexity of manufacturing technology. Titanium alloys are susceptible to localized shear plastic strains due to their low heat conductivity at intense dynamic load [2]. One of the solutions of this problem is development of high-strength lightweight glass-ceramic materials for the use in the elements of personal protection with high performance characteristics.

For that reason in Ukraine there exists a further need in studies related to technological development of relatively low-cost glass-ceramic materials.

The aim of the work is development of glass-ceramic high strength materials for the elements of personal protection.

2. Experimental

2.1. Objectives and Research Methods

To achieve the aim of the research the following objectives were set:

– to analyze best practices in developing of materials used as the elements of personal protection;

– to devise methodological approach for development of high strength glass-ceramic materials;

– to substantiate the choice of oxide system for obtaining glass-ceramic materials, investigate glass formation in it and synthesize model glasses;

– to determine the effect of phase composition on functional properties which provide high strength of the materials;

– to develop compositions of glass-ceramic materials for the elements of personal protection.

Following physico-chemical research methods, which allowed to investigate processes that take place during heat treatment, have been used in the work: differential-thermal (DTA), gradient-thermal, petrographic and dilatometric analysis methods. Values of mechanical characteristics were measured with PMT-3 and TMV-1000 hardness testers, and static-method elasticity tester.

2.2. Development of Methodological Approach for Obtaining High-Strength Lightweight Glass-Ceramic Materials for Elements of Personal Armor

The problem of obtaining a material for reliable personal protection creates the need to devise methodological approach consisting in determining a certain complex of requirements for the material being developed (Table 2) and its functional role.

Armor element must have two important properties: a high strength of surface layer, capable of breaking sharp nose of bullet slug, and required viscosity to absorb impact energy of bullet without formation of cracks and fracture [11].

Velocity of impact wave in armor material depends on its density and elasticity modulus. High velocity of advance of sound wave is important due to the following reasons:

i) impact energy is quickly dissipated throughout a large area;

ii) extent of projectile destruction increases.

The higher the difference between the velocity of sound wave in the projectile material and in the armor material, the more damage will the projectile receive. For ceramic materials, the velocity of sound wave increases with increasing elasticity modulus. However, for glass-ceramic materials the highest values of the velocity of sound wave belong to the compositions based on lithium aluminosilicates, elasticity modulus of which is 79–94 GPa. This can be attributed to the presence of vitreous phase in the structure of glass-ceramic materials, which provides relaxation of mechanical microstresses that occur due to thermal factors, and heal fractures that develop under impact. Presence of elastic glass matrix, which provides relaxation of stresses and dissipation of impact energy, allows to use this material not only as destructive, but also as damper layer. For this reason, brittle materials such as glass-ceramics have better protective action than it could have been expected on the base of simple calculations of the advance of sound wave.

Therefore, as a result of the combination of performance characteristics, glass-composite materials of glass-ceramic type can be used as a component of armor compositions “metal alloy (energy-destructive layer) – ceramics (energy-destructive layer) – glass-ceramics (energy-destructive and energy-damping layer) – polymer (energy-damping layer)”. Structural scheme of a composite armor element is shown in Fig. 1.

Achieving high values of strength and fracture viscosity in conjunction with low values of density and elasticity modulus of the armor elements can be provided by designing required initial composition of glasses and formation of nano- and microstructure of high-strength compounds in them during the low-temperature heat treatment. As a result, a significant number of fine crystals, which are partly intergrown, is formed. Main mechanisms of energy absorption and dissipation by glass ceramics consist in formation of significant number of new surfaces and finely fragmented particles of the material (up to 1 μm in size), acceleration of fragmented mass and conduction of heat energy.

Table 2

Values of criteria for glass-ceramic materials determined according to standards

Criteria	Value	Standard
Physical properties		
Density, g/cm^3	2.3–2.45	GOST 9553-74
Fracture toughness, $MPa{\cdot}m^{0.5}$	2.5–4.0	GOST 25.506-85
Impact strength, kJ/m^2	5.0–6.0	GOST 11067-2013 (EN1288-1:2000)
Bending strength, MPa	400–500	GOST 32281.1-2013
Young’s modulus, GPa	80.0–120	GOST 9900-2013
Hardness		GOST ISO 9385
Knoop *HK*	800–1000	
Vickers *HV*, MPa	7000–8000	
Microhardness, MPa	7000–8000	GOST 9450-76
Heat treatment temperature, K	≤1073	
Heat resistance, K	1073–1273	GOST 4069-69
Penetration		
Explosion resistance, class	ER1–ER4	GOST 13541-2013
Bullet resistance, class	Br1–Br6	GOST 32362-2013
Protection level of composite armor element, class	4–5	DSTU B 4104-2002
Cost, USD/kg	less than 150	

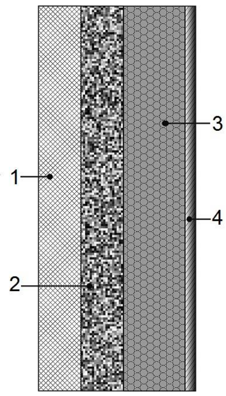

Fig. 1. Structural scheme of composite armor element: metal alloys (1); ceramics layer (Al_2O_3, SiC) (2); layer of glass-ceramic material (spodumene, cordierite, anorthite glass ceramics) (3) and polymer layer (polyaramide fibers, ultra-high-molecular-weight polymer) (4)

Experimental embodiment of these provisions will allow the necessary armor rating (classes 4–6 according to Ukrainian standard DSTU V 4104-2002) by using armor glass ceramics as a part of composite armor element. Additionally, the mass and cost of such armor elements must be significantly lower than those of the fully ceramic armor elements.

2.3. Choice of Core Oxide Systems and Synthesis of Model Glasses on their Base

Distinguishing characteristic of glass ceramic materials is the combination of high mechanical strength needed for provision of resistance to the action of energy-destructive constituents and ability to absorb and dissipate impact stresses with low density and relatively low cost.

It is known that thermal-resistant high-strength composite materials with high mechanical parameters, which may be used as armor elements, are obtained mainly on the base of spodumene and cordierite glass ceramics with thermal coefficient of linear expansion $\alpha = (1–125)\cdot10^{-7}\ K^{-1}$, bending strength of 175–441 MPa, elasticity modulus E = 88–150 GPa and hardness HK = 535–1100 [8, 15].

However, glass ceramic materials on the base of $MgO–Al_2O_3–SiO_2–TiO_2$ system are characterized by higher values of density as opposed to the glass ceramic on the base of $Li_2O–Al_2O_3–SiO_2–TiO_2$ system, which prevents from obtaining low-weight glass ceramics on its base. In Ukraine the development of spodumene glass ceramics is mainly focused on materials for catalysts for ammonia oxidation [16].

To establish the field of occurrence of glasses for synthesis of lithium aluminosilicate materials for elements of personal armor the system $R_2O–RO–RO_2–R_2O_3–LiF–CaF_2–P_2O_5–SiO_2$ was chosen, where R_2O – Na_2O, Li_2O, K_2O; RO – CaO, MgO, ZnO; RO_2 – ZrO_2 TiO_2; R_2O_3 – Al_2O_3, B_2O_3. The glass formation area was confined and investigated in the experimental system, compositions of model glasses of SP series were synthesized as a base for obtaining spodumene glass-ceramic materials, and synthesized model glasses of SL series were a base for obtaining materials based on lithium disilicate.

Glasses of the aforementioned series were obtained by melting the glass batch consisting of conventional raw materials used in glass industry under identical conditions. The melting was carried out within the temperature range of 1523–1873 K in corundum crucibles with subsequent cooling of glass on a sheet of metal (Table 3). In the model glasses of SP and SL series the oxides were in ratios close to stoichiometric, which is required for crystallization of spodumene and lithium disilicate. Occurrence of these crystalline phases in the glass ceramic materials will provide their high performance characteristics.

In order to obtain the volume crystallized structure, conventional crystallization catalysts with different action mechanisms were used, *viz.* TiO_2, ZrO_2 and LiF. Part of the model glasses contained certain amounts of P_2O_5 and ZnO so that the fine-crystalline interconnected structure could be formed. At the same time, the presence of P_2O_5 in the structure of glasses allows to decrease specimen's strain and stresses which occur upon absorption of impact energy.

Table 3

Technological parameters and characteristics of the main crystalline phase for developed glass crystalline materials

Series of experimental material	Technological parameters		Characteristics of main crystalline phase
	Melting temperature, K Duration, h	Heat treatment	
SL	1523–1723 5–6	Stage I 853–893 K, 4 h Stage II 973–1073 K, 4 h	Lithium disilicate 80 vol %, 1 μm
SP	1723–1873 6–8	Stage I 813–833 K, 4 h Stage II 1073–1123 K, 4 h	β-Spodumene 80 vol %, 1 μm

3. Results and Discussion

Petrographic analysis of experimental glasses of the SL series has shown that all specimens are formed on the base of colorless anisotropic eutectic melt. This fact is the evidence that the structure of model glasses contains nonuniformities of fluctuation type, highly evolved near the eutectic points where the simultaneous nucleation of two phases is possible.

This allows to conclude that during heat treatment of materials on the base of the synthesized glasses, the fine crystalline structure will be formed by directed crystallization.

The presence of lithium metasilicate is typical of SP glasses, recrystallization of which into lithium disilicate at preliminary heat treatment leads to β-spodumene crystallization at 1073–1123 K.

According to the data obtained by gradient thermal analysis, crystallization ability of SL and SP glasses is determined by the ratio of phase-forming components, type and amount of crystallization catalysts in their structure. For example, simultaneous presence of TiO_2 and ZrO_2 in experimental glasses leads to crystallization of phases in the amount of 30 vol % after melting. This may lead to further enlargement and growth of crystals during heat treatment, and as a result, to strength degradation of the structure and decrease of materials mechanical properties. Introduction of fluorite and titanium(IV) oxide to glasses of SP series provides the occurrence of crystalline phase in the amount of 20 vol % in their structure after cooling, with further formation of fine structure containing approximately 60 vol % of crystalline phase at heat treatment. Similar trend is observed for model glasses of SL series as well, which, along with the presence of P_2O_5 in their composition is an important prerequisite of phase separation with subsequent formation of glass-ceramic structure in conditions of low-temperature heat treatment (Fig. 2).

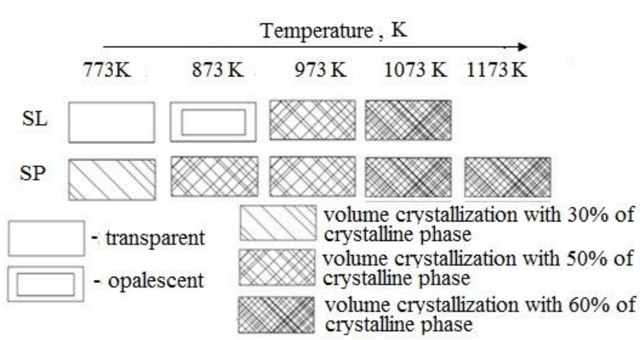

Fig. 2. Crystallization ability of model glasses

According to the DTA data for model glasses of SL and SP series, glass formation interval is determined by their melting characteristics and equal to 753–837 K (Fig. 3). Endothermic effect observed for these glasses within 573–653 K is related to elimination of residual stresses. Crystallization of glasses of SP series at 893 K is the evidence of possible formation of β-eucryptite. Upon the increase of the temperature to 1073 K, conditions favorable to the occurrence of the peak characteristic to β-spodumene are created. For the glasses of SL series in the temperature interval of 893–973 K a high exothermic peak is observed, which is typical of lithium disilicate crystallization.

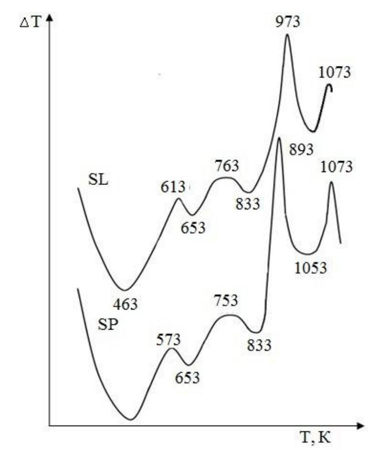

Fig. 3. Thermograms of model glasses

The choice of conditions of heat treatment for these glasses was based on generally accepted principles of designing glass-ceramics and considering the use of glass technology for their production [17]. The glass-ceramic materials of SL and SP series obtained under conditions of low-temperature treatment are characterized by volume fine crystallization of lithium disilicate or β-spodumene high-strength phases (Table 3).

It is due to the low-temperature heat treatment that the glass automatically “chooses” the metastable phases which are easily wetted by the glass, and as a result are strongly adhered to the glass. During long high-temperature exposures the recrystallization into stable phases takes place which will provide necessary performance characteristics of glass-ceramic material.

For the experimental materials of SL and SP series obtained after the two-stage heat treatment, the values of mechanical and thermal properties are typical of high-strength glass-ceramic materials (Table 4).

It has been established that formation of volume-crystallized fine structure of glasses that contain β-spodumene or lithium disilicate in the amount of 80 vol % provides elevated mechanical characteristics of the material. The combination of these characteristics along with low density will allow to use them as a base in developing materials used in composite armor elements, which will provide bullet and fragment protection and simultaneously act as a damper.

Table 4

Performance characteristics of developed glass-ceramic materials

Series of experimental material	Mechanical characteristics				$\alpha \cdot 10^7$, K^{-1}	ρ, g/cm^3
	H, GPa	K_{1C}, MPa·m$^{0.5}$	HV, GPa	E, GPa		
SL	6.75–6.95	2.85–3.0	6.8–7.1	84–90	22.5–60.0	2.38–2.40
SP	8.33–9.08	2.4–3.4	8.28–8.67	80–100	10.0–22.4	2.40–2.45

4. Conclusions

As a result of conducted investigations the methodological approach has been developed, which consists in determination of the complex of requirements to the created material and its functional role in the means of personal armor protection. The choice of initial lithium aluminosilicate R_2O–RO–RO_2–R_2O_3–LiF–CaF_2–P_2O_5–SiO_2 system has been substantiated, the fields of synthesis of model glasses of SP (spodumene) and SL (on the base of lithium disilicate) in this system have been confined. Technological parameters of obtaining high-strength lightweight glass-ceramic materials which include temperature and duration of melting, as well as low-temperature heat-treatment conditions needed to obtain the fine crystalline interconnected structure have been determined.

It has been found that developed glass-ceramic high-strength lightweight materials are characterized by low density of 2.38–2.45 g/cm^3 and high performance characteristics, *viz.* the value of microhardness of 6.75–9.08 GPa, Vickers hardness of 6.8–8.67 GPa, stress intensity of 2.4–3.4 MPa·m$^{0.5}$ and Young modulus of 80–100 GPa due to formation of volume-crystallized fine structure of glass containing β-spodumene or lithium disilicate in the amount of 80 vol %.

Therefore, improvement of the effectiveness of composite armor may be achieved by the use of glass-ceramic materials in its body that simultaneously acts as energy-destructive and energy-damping layer, which will allow for weight and cost decrease of armor element while retaining its protective characteristics.

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Received: February 18, 2016 / Revised: March 03, 2016 / Accepted: November 12, 2016

РОЗРОБЛЕННЯ СКЛОКРИСТАЛІЧНИХ ВИСОКОМІЦНИХ МАТЕРІАЛІВ ДЛЯ ЕЛЕМЕНТІВ ІНДИВІДУАЛЬНОГО БРОНЕЗАХИСТУ

Анотація. *Встановлена перспективність використання склокристалічних високоміцних матеріалів для елементів індивідуального бронезахисту. Розроблено методологічний підхід, обґрунтовано вибір вихідної літійалюмосилікатної системи при одержанні високоміцних полегшених склокристалічних матеріалів. Досліджено область склоутворення в обраній системі та синтезовано склади модельних стекол. Вивчено особливості формування кристалічної структури у розроблених модельних стеклах за термічного оброблення. Розроблено високоміцні склокристалічні матеріали, що характеризуються високими експлуатаційними властивостями, та можуть бути використані при створенні сучасної композиційної броні.*

Ключові слова: *склокристалічний матеріал, літійалюмосилікатна система, високоміцний, механічні властивості, елемент індивідуального бронезахисту.*