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Journal of Materials Research and Technology
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Review article

Transparent glass–ceramics for ballistic protection: materials and challenges



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ARTICLE INFO

Article history:

Received 21 September 2018

Accepted 6 May 2019

Available online 20 May 2019

Keywords:

Transparent glass–ceramic

Ballistic protection

Add-on armor

ABSTRACT

The military ballistic protection market has reached approximately US\$ 10 billion/year, and the civil market is also very significant and is steadily increasing, which drives research for new ballistic protection alternatives. Materials currently used and under development as transparent ballistic protection devices include glasses, glass–ceramics, single and polycrystalline ceramics, and polymer–composites. Glass–ceramics are a less expensive, versatile alternative to currently used transparent ceramics. Glass–ceramics are generally harder, stiffer, tougher, and stronger than glasses, and can be made transparent or opaque, according to the needs of the protective system. They can be easily shaped in simple or complex forms, are much less expensive than carbides and nitrides, and are less dense than transparent alumina or spinel. This positive combination of properties makes glass–ceramics suitable for a wide range of applications. However, for an effective development of new transparent glass–ceramics (TGC), it is vital to understand which key properties must be optimized. In this review, we compile information on the role of each material in multi-layer ballistic systems, give a brief description of ballistic impact, and the properties related to it, and discuss the development of TGC to be used as ballistic protection. Our aim is to describe the most important ballistic protection materials and to indicate the pathways that research on TGC for ballistic protection have taken. We finish by concluding that there are still several opportunities that warrant further research on this particular application of glass–ceramics.

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<https://doi.org/10.1016/j.jmrt.2019.05.006>

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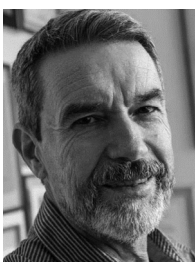
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1. Introduction

Dynamics of materials research in a highly sensitive sector, such as ballistic protection, differ from other industry segments, due to security reasons. To understand how the development of new ballistic protection materials is performed, one must understand who the players are and what type of research is being and has been conducted; although it is fair to assume that most are kept as industrial secrets. The armament industry can be roughly divided into research on arms and ammunition, and ballistic protection. Arms and

ammunition involve an order of magnitude more funds than ballistic protection. To carry out efficient development work, it is important to review the fundamentals on the subject, such as protection levels, add-on armor, the physics of the ballistic impact, the most important materials properties to be optimized, etc. This paper focuses on presenting the most important properties related to ballistic protection and analyzes the existing transparent glass-ceramics (TGC). A broader view on how to evaluate and analyze the individual properties, rather than the ongoing industrial development can be found elsewhere [1].

This paper is divided into: (i) the world market – to provide an overview for the reader on the numbers regarding research on ceramic and glass-ceramic materials used as ballistic protection. Secondly, (ii) the fundamentals about ballistic protection. In this section, we present various protection levels; the concept of ceramic armor; the role of materials and microstructure; the processing and properties of TGC, and some recent research on TGC. Finally, (iii) we present the conclusions and research perspectives for this niche application of glass-ceramics.

2. Market and research

The production of armament is, unfortunately, a key industry for several countries. In 2016, the top 100 (excluding China) combat armament producing and military services companies earned approximately 375 billion dollars, 38% more than in 2002 [2]. The ballistic protection segment on its own was valued at almost 8 billion dollars in 2013 and is expected to be worth 11 billion dollars by 2020 [3].

It is well known that this is an enormous market, however published research on transparent glass-ceramics for ballistic protection has been modest (obviously we cannot access results that are kept as industrial secrets, which could be very significant in this particular field). A search on the Web of Science database [4] for papers published until December 2017 related to TGC to be used as ballistic protection reveals only 9 documents [1,5–12], whereas the similar search for transparent ceramics resulted in 104 papers. It is worth noting that among those nine papers on TGC, none of them investigates their ballistic performance.

A similar search for patents related to TGC for ballistic protection at the Derwent Innovations Index database [13], until December 2017, reveals 22 deposited patents (not all patents indicate the chemical compositions). On the other hand, there were 1096 deposited patents on ceramic materials for ballistic protection, and 62 for transparent ceramics. Thus, there has been an intense search for new transparent ceramics but published research on TGC for ballistic protection has been scarce.

3. Fundamentals about ballistic protection

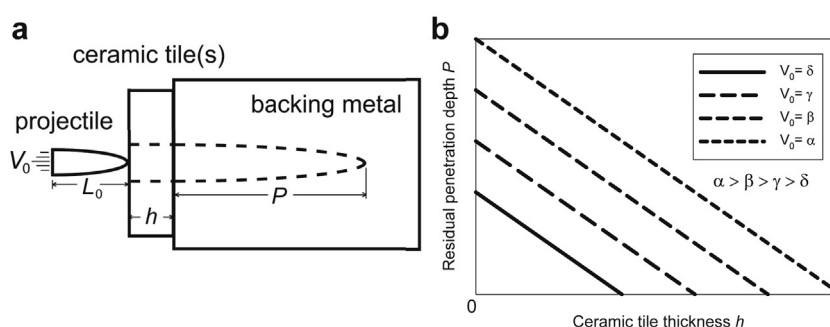
In this section, we describe the main aspects of ballistic protection and the main properties and characteristics of TGC for ballistic protection. Section 3.1 presents the protection levels and the correspondent ammunition that can be blocked by each level of protection. Section 3.2 shows the concept of

Table 1 – Protection level, weapon and corresponding ammunition, velocity, weight and kinetic energy. Adapted from Ref. [17]. The complete table can be found in that reference.

Protection level	Test bullet ^a	Bullet mass (g)	Conditioned armor test velocity (m/s) ^b
II-A	9 mm FMJ RN	8	355
	.40 S&W FMJ	11.7	325
II	9 mm FMJ RN	8	379
	.357 Magnum JSP	10.2	408
III-A	.357 SIG FMJ FN	8.1	430
	.44 Magnum SJHP	15.6	408
III	7.62 × 51 NATO FMJ	9.6	847
IV	.30 AP	10.8	878

^a AP, armor piercing; FJ, full jacketed; FMJ, full metal jacket; RN, round nose; FN, flat nose; JSP, jacketed soft point; LRHV, long rifle high velocity; NB, nato ball; RN, round nose; SWC, semi wadcutter; S&W, Smith & Wesson; SJHP, semi jacketed hollow point; NATO, north Atlantic trade organization.

^b The impact velocities must be within ± 9.1 m/s.

**Fig. 1 – (a) Ballistic impact on a ceramic tile. (b) Depth of penetration for different impact velocities, V_0 [19].**

add-on armor and how the ballistic impact interacts with it. Discussions on the role and microstructure of the constituents are given in Section 3.3. Section 3.4 presents the processing and property analysis of TGC for ballistic protection.

3.1. Protection levels

Ballistics can be defined as “the scientific study of things that are shot or fired through the air, such as bullets and missiles” [14]. The arms industry is divided in two aspects: research and development of weapons – guns, rifles, cannons, and development of ballistic protection – shields, body and vehicle armor, and helmets, for instance [15].

The development of ballistic protection materials is conducted based on two main factors: what is to be protected and the desired protection level [16]. Table 1 presents the division levels of the personal body armor, proposed by the US National Institute of Justice. This table is only part of Table 4 presented at NIJ standard 0101.06 [17]. Typically, different materials are assembled so as to meet the protection proposed.

3.2. Add-on armor and ballistic impact

A ballistic protection can be defined as a single material or a set of materials, which is known as composite armor. In the latter case, materials from different classes are used to form the protection system. Hard materials, such as ceramics are used as add-on armor or the strike face, and a high-resistance plastically deformable material, such as certain special polymers

or metals, are used as main armor or backing face. The strike face and backing material are bonded together using polymer adhesives. The use of different materials, as well as complementary properties, aims to obtain a protection system with enhanced performance [18]. Obviously, the thicker the ceramic or glass-ceramic plate, the smaller the residual penetration depth in the backing material. Fig. 1 [19] depicts this process.

When the application requires visibility through the multi-layer system, for instance, visors of law enforcement helmets, sport arenas, vehicle and building windows, transparent materials, such as TGC and single-crystal ceramics must be combined with ballistic grade polymeric materials. Fig. 2 shows schematic diagrams of opaque and transparent composite ceramic armors.

Ballistic protection systems can be assembled on vehicles and aircraft windows and bodies. The strike face can be made of glass, ceramics or glass-ceramics. Transparent ceramics traditionally used for ballistic protection can be divided into monocrystalline, e.g., sapphire (Al_2O_3) or polycrystalline, e.g., magnesium spinel ($MgO \cdot Al_2O_3$) and ALON ($Al_2O_3 \cdot N_5$) [20–22]. Details on the state-of-the-art research on these materials can be found elsewhere [20–25].

Concerning ductile materials, stresses higher than the rupture stress are released through localized plastic deformation. Ceramics, on the other hand, do not show significant plastic deformation. Thus, when a ballistic impact occurs, the role of the ceramic plate is to crack and break, dissipating the kinetic energy of the projectile [18], and this is the reason why hard materials are used, i.e., to dissipate the highest possible

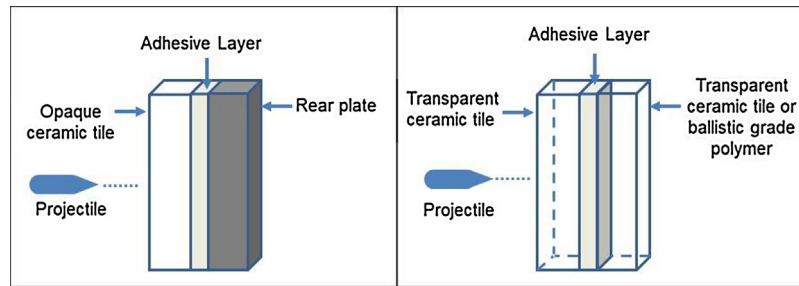


Fig. 2 – Schematics of (a) opaque composite ceramic armor, and (b) transparent composite ceramic armor.

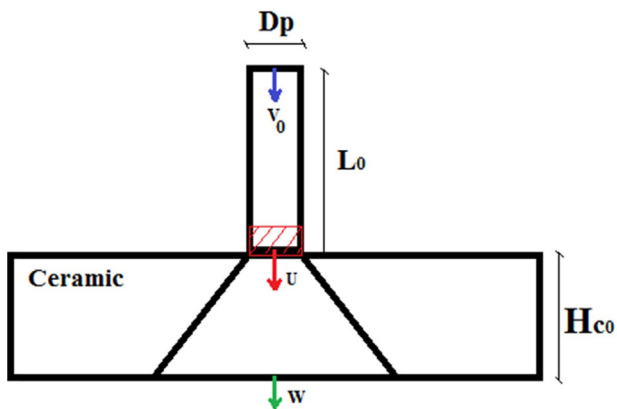


Fig. 3 – Schematics of the impact of a projectile on a ceramic tile.

Source: Adapted from Ref. [27].

amount of kinetic energy. The residual energy is absorbed by a highly resisting (backing) material that also absorbs the fragments generated by the cracking of the armor plate [26]. Fig. 3 [27] presents a schematic of a projectile impact on a ceramic tile. The projectile of length L_0 and diameter D_p , having a velocity V_0 , impacts a ceramic tile of width H_{c0} and the projectile will lose velocity. The tip velocity, u , is smaller than the projectile impact velocity, V_0 , which initially promotes severe plastic deformation in the projectile. A cone crack will be created, and the bruised material will initially have the same speed as the projectile tip, i.e., u , but later will be diminished to w .

Furthermore, the chemical nature (oxide or non-oxide) and thickness, the type of confining material, the backing layer, and the geometry of the projectile all influence the performance of the protection system [28]. Moreover, 7–9 mm thick ceramic plates, bonded with aramid-fiber plates, such as Kevlar[®], from DuPont, or Twaron[®] from Teijin, can stop a variety of projectiles [26]. These plates are generally covered by ballistic-grade polyamide bonded with stress-resistant materials [29]. For instance, Monteiro et al. [30] observed that, in addition to the high ballistic resistance of aramid fibers, the debris of the projectile and the armor material generated during impact impregnate into the fibers, increasing the overall ballistic resistance of the multilayer system. During a ballistic impact there is energy transfer to the ballistic protection system in three ways [31]:

- i. Projectile penetration, armor perforation and projectile ejection, with a residual velocity, which indicates that its kinetic energy was higher than the armor could absorb.
- ii. The projectile partially penetrates the armor, indicating that its kinetic energy was smaller than the armor could absorb.
- iii. The projectile completely penetrates the armor, having zero residual velocity when it reaches the opposite face of the armor. In this case, the initial velocity of the projectile is called ballistic limit.

The mechanics of projectile penetration can also be divided in three steps [28,29,31,32]:

- i. Destruction of projectile's tip and the formation of a cone crack in the ceramic plate. In this point, the projectile's tip is eroded and the kinetic energy and perforation capability are drastically reduced.
- ii. Projectile penetration in the ceramic plate and the cone crack propagates, spreading ceramic debris. The main armor deforms elastically.
- iii. Plastic deformation of the main armor and absorption of the residual kinetic energy of the projectile.

The ceramic plate plays a major role on the first two steps.

The add-on armor on a protection system is thus a hard material that acts to diminish the penetration power of the projectile [18]. Ceramics are suitable to be used as add-on armor because they increase the dwell time of the projectile inside the armor system, diminishing its penetration power. The usually high values of compression charges sustained by ceramics make them a suitable material, but their low resistance to multiple hits is a disadvantage [33,34].

The ballistic impact is an event that occurs very fast in a very small region of the embodiment. Only a small amount of the projectile's kinetic energy ($\sim 0.2\%$) is spent on crack formation at the ceramic body; most of it (45–70%) is transferred in the form of ceramic debris [24].

The development of add-on armor can be performed through analytical modeling, numerical simulation or empirically [15]. A search on article databases regarding the analytical modeling of ceramics for ballistic protection shows over 1000 articles. Considering numerical simulations, a similar search results in almost the same number of papers. In both cases, the projectile–ceramic interaction is considered, which makes any result specific for each configuration. Once

the parameters of the system, such as mass and velocity of the projectile or thickness and crystallinity of the glass–ceramic plate, change, there is no guarantee that the material will maintain its performance in practice. Regarding empirical studies, the ballistic test is not simple to be arranged, as they demand not only trained personnel, but also a ballistic tunnel and consume a large number of samples. For these reasons, it is not a test to be used as an initial criterion to materials selection, but rather a test to confirm the efficiency of the developed material.

3.3. Backing material and strike face: composition and microstructure

The search for materials that can be used as the strike face on protection systems lies in ceramic materials. Budd and Darrant point out that the properties that make ceramic materials suitable to be used as the strike face are their high hardness, high compressive strength and lower density than metals [35]. The main advantages of ceramics over the other classes of materials are lower densities than metals, and higher hardness than metals and polymers. Besides, ceramics increase the dwell time of the projectile, diminish the penetration ability and fracture in a way that spreads energy through its cracked surface.

Among oxide ceramics, the most common is polycrystalline alumina, whereas among non-oxides, silicon and boron carbides [36] and also aluminum and titanium nitrides [26,28,29] are widely used. Concerning glass–ceramics, most research focuses on the $\text{Li}_2\text{O-SiO}_2$ (LS) system, having lithium disilicate as major crystalline phase [33,35,37–41]. Glass–ceramics from this system can present hardness up to 635 HK [37] and fracture toughness on plane strain

(K_{IC}) up to $3.3 \text{ MPa m}^{1/2}$ [42]. Research on lithium disilicate is preferred since $\text{Li}_2\text{O-SiO}_2$ is one of the few glass systems that presents spontaneous bulk nucleation without adding nucleating agents [43], making it easier to control the microstructure. However, a more in-depth discussion on glass crystallization will be presented in the next section.

Although there is consensus in the ballistics area that the better the mechanical properties, the better the performance of such material for ballistic protection, some cases show that care should be taken when choosing a material for this specific application. Three of the most common transparent ceramic materials used as add-on armor are sapphire (monocrystalline Al_2O_3), monocrystalline magnesium spinel ($\text{MgO}\cdot\text{Al}_2\text{O}_3$) and polycrystalline alumina (Al_2O_3). Despite the fact that sapphire presents better mechanical properties, such as higher Young's Modulus (E), Vickers hardness, fracture toughness and four-point bending strength, sapphire's ballistic performance is lower than the others [23,25]. After a series of dynamic indentations, it was observed that sapphire presents a higher dynamic brittleness than spinel. Hence, the former is more willing to crack and break during impact than the latter. This also explains spinel's better performance in multiple hits.

Correlation between material properties and ballistics plays an important role in its ballistic performance but are not straightforward. Although Woodward initially proposed hardness as the key property to select a ballistic material [44], Krell and Strassburger observed that when materials of different hardness are tested, the best performance lies in the one with highest elastic modulus, regardless of the hardness value [24]. A test was conducted using either spinel (that presents small debris after fracturing) or alumina (that presents large debris after fracturing) with a projectile with steel core (velocity of 850 m/s) both having aluminum as backing material. Alumina

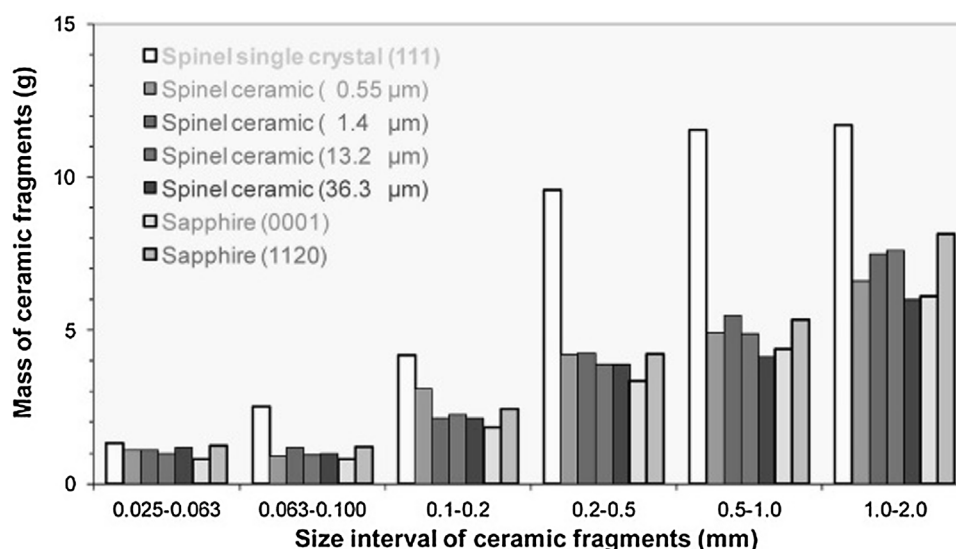


Fig. 4 – Size interval of ceramic fragments after the impact of $7.62 \times 51 \text{ mm}$ bullet for several single- and polycrystalline ceramic materials. Average grain size in indicated in parenthesis for polycrystalline materials. For monocrystalline materials, the crystallographic plane in indicated. Source: Adapted from Ref. [25].

has $E = 380$ GPa and presents a depth of penetration of about 4.0–6.5 mm, whereas spinel has $E = 280$ GPa and presented a depth of penetration of about 8.0–8.3 mm.

Mono- and polycrystallinity also play a role in the performance of a given material [24,25]. Researchers have observed that polycrystalline alumina and fine grain spinel can stop a 7.62×51 mm projectile (850 m/s) and that single crystal alumina (sapphire) would only stop the same projectile with twice the plate thickness. When sapphire cracks, it shatters into smaller debris, but it causes less damage to the incoming projectile than the one generated after the cracking of polycrystalline alumina. This behavior might be explained by the anisotropy of sapphire. Opposed to polycrystalline alumina, which presents homogeneous K_{IC} values, sapphire presents great toughness anisotropy. In this case, cracks would have a preferential path through the low- K_{IC} parts, consuming less energy during cracking. Krell et al. [25] analyzed the size of the debris of different ceramic plates under

an impact of a 7.62×51 mm bullet. Fig. 4 shows that the distribution of the size of the ceramic fragments (X-axis) changes according to the mean grain size of the ceramic plate (for polycrystalline materials) or crystallographic plane (for monocrystalline materials), therefore showing that the debris size is a function of the ceramic microstructure. The mean grain size or crystallographic planes are indicated in parentheses, in front of the material's name.

However, presuming that a monocrystalline version of a material would always present a worse performance than a polycrystalline counterpart is not always correct. Each case must be analyzed individually. Considering spinel for instance, in [24] the authors observed an improved ballistic performance for the monocrystalline version compared to a polycrystalline material. Fig. 5 [25] presents two graphs of depth of penetration of a 7.62×51 mm projectile when hitting different ceramic plates, having the same areal density, but different thickness, with aluminum as backing material.

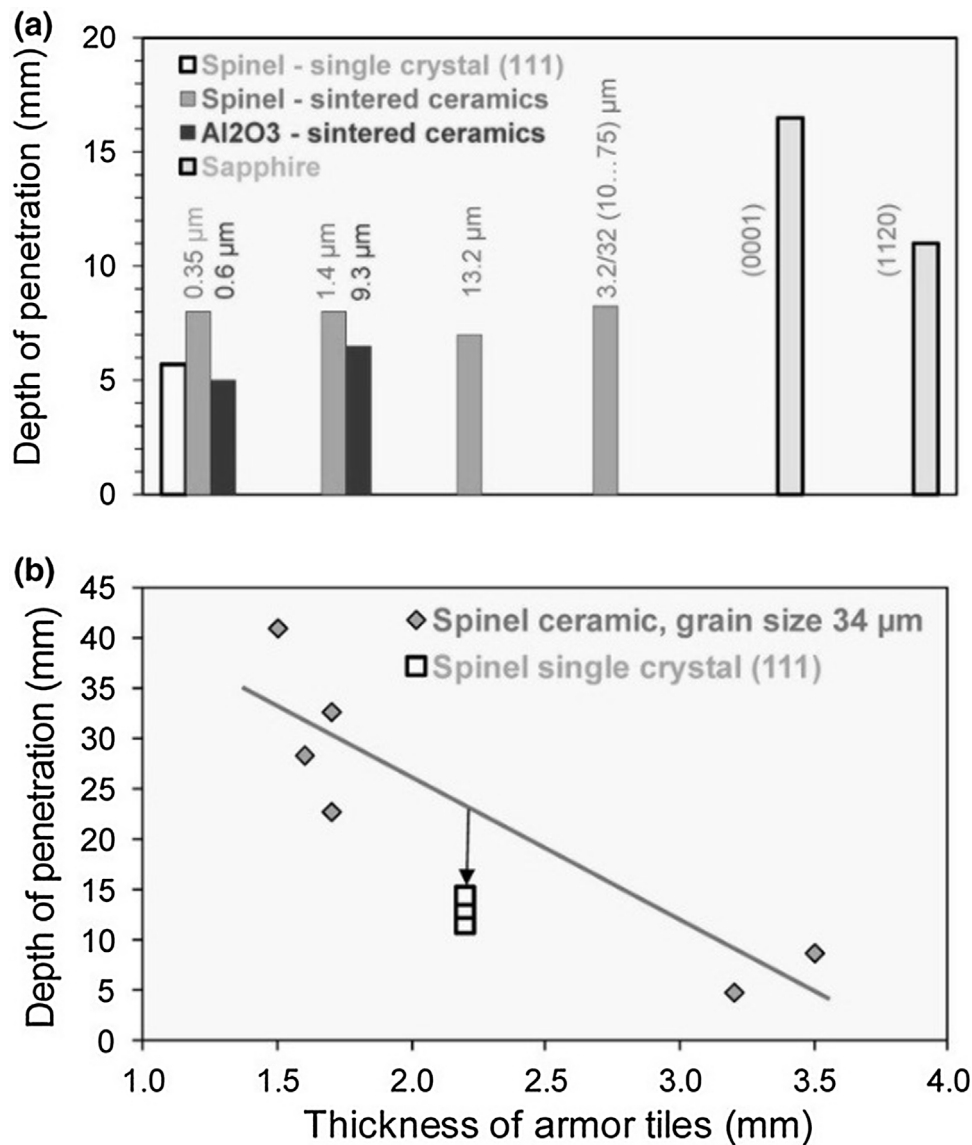


Fig. 5 – Depth of penetration analysis of several single- and polycrystalline ceramics (a) with Al as backing material and (b) with glass as backing material [25].

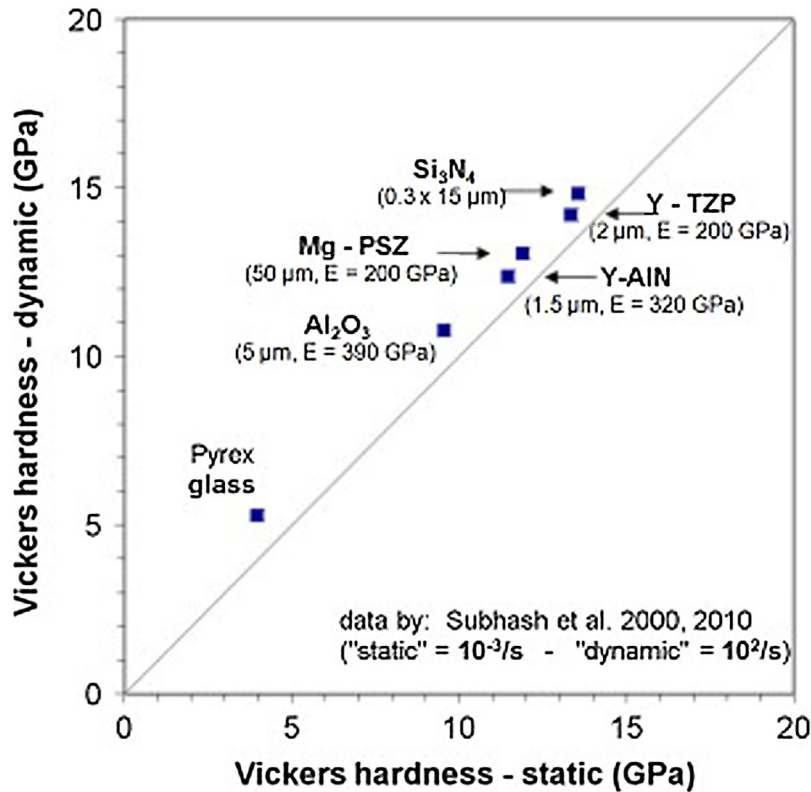


Fig. 6 – Difference between dynamic and static Vickers hardness for selected ceramic materials [24].

Both single and polycrystalline configurations of Al₂O₃ were tested. The single crystals showed a slightly superior performance. The authors associated the higher performance of the former material with a coarser fragmentation, which would cause higher damage to the projectile. All these particularities show how difficult it is, independently or collectively, to analyze how each mechanical property affects the ballistic performance of a given material.

When analyzing material properties, it is important to have in mind that in most of available data, a static property is quantified. This is mostly due to the ease of measurement or equipment availability. The imprint generated after a hardness test is proportional to the energy and geometry of the indenter. For this reason, hardness tests are generally carried out under slow loading rate. Also for this reason, hardness can be measured under static (slow loadings) or dynamic conditions (fast loadings). Since ballistic tests are extremely fast, dynamic properties, rather than static, should be known. Although small differences are typically detected for one given property alone, combining these differences in all properties might lead to unexpected results. For instance, Fig. 6 shows the difference of dynamic Vickers hardness results compared to static measurements, for a glass and some polycrystalline ceramics [24]. These results show and the authors pointed out that, for hardness, the use of static values should not lead to a misinterpretation of the performance of a ceramic material to be used as strike face.

3.4. Transparent glass-ceramics: processing and properties analysis

As proposed by Zanotto and Mauro [45]: “glass is a nonequilibrium, noncrystalline condensed state of matter that exhibits a glass transition. The structure of glasses is similar to that of their parent supercooled liquids (SCL), and they spontaneously relax toward the SCL state. Their ultimate fate, in the limit of infinite time, is to crystallize”. The crystallization process can happen homogeneously or heterogeneously [43]. In the former case, the probability for the nuclei to appear either on the surface or in any region of the glass sample interior is the same. In the latter case, which is much more common, the probability of the nuclei to be originated on the solid impurities on the surface, and flaws, such as inner cracks or bubbles, are higher than in the glass interior. However, using nucleating agents, bulk nucleation can be induced in systems that would only present measurable surface nucleation.

The crystal size of glass-ceramics is controlled through nucleation and crystallization processes. These processes occur at different temperatures for most glass compositions. At lower temperatures, nucleation is favored whereas at higher temperatures, crystal-growth predominates. The longer the nucleation time, the higher the crystal density, and the smaller the final crystal size. In fact, with a higher crystal number density, during crystallization at higher temperatures, the crystals will impinge on each other, limiting

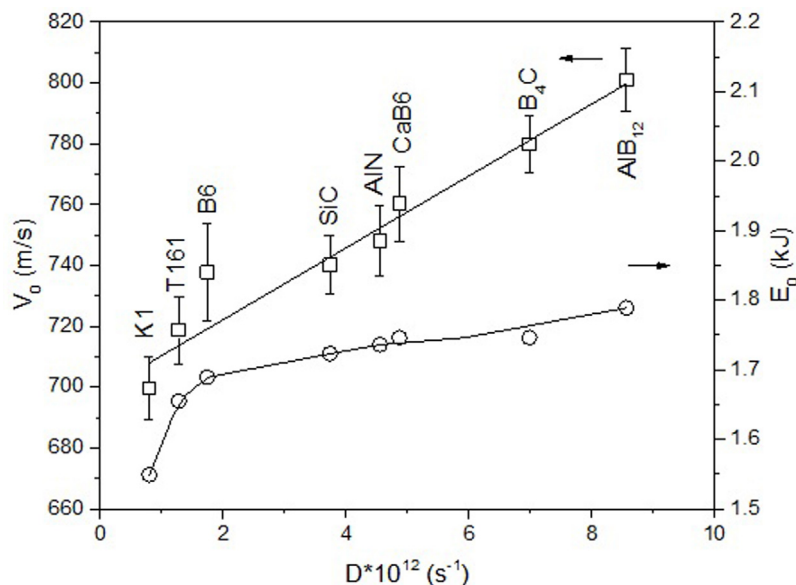


Fig. 7 – The D-criterion dependency on the critical fracture energies (right Y) and the critical penetration velocities (left Y), as published by Neshpor [50]. The lines connecting the points are just eye guides.

their growth and final size. If the crystal density is in the order of 10^{21} crystals/m³, the glass–ceramic body will be transparent [35]. When crystallizing a glass intended for ballistic protection, one seeks for the highest crystallized fraction possible, since crystals generally show higher mechanical properties when compared to their parent glass. The crystallized fraction of a glass–ceramic is thus limited by the crystallization process. In most cases, during crystallization, the residual glass composition changes and it is hard to crystallize a glass up to 100%. Transparency may be attained in glass–ceramics with very low or very high, up to 99%, crystallized volume fraction [11].

To be able to design TGC to be used as ballistic protection, it is important to know the key properties they must present and their desirable values. High mechanical properties are a precondition for selecting a material to be used as ballistic protection. It is known to experts that ceramics with high hardness [11,36,37,46,47] and high sound propagation speed, which relate to a high elastic modulus [48,49], are good candidates for add-on armors. Some researchers also pointed out that tough materials would have, in principle, a better performance than those with lower K_{IC} [23,46]. Considering combined properties of the employed ceramic materials, to the best of our knowledge, there is only one published model that is intended to predict materials performance under ballistic impact, the D-criterion, proposed by Neshpor [50] which is defined as:

$$D = \frac{0.36H_V C_L E}{K_{IC}^2} \quad (1)$$

where H_V is the Vickers hardness, E is the elastic modulus, C_L is the longitudinal sound wave propagation velocity, and K_{IC} is the fracture toughness. According to this criterion, the higher

the D value, the higher the performance under ballistic impact. Fig. 7 presents the D-criterion calculated and published by Neshpor for eight different materials: K1; T-161; B6; SiC; AlN; CaB₆; B₄C and AlB₁₂. K1 is a composite material containing B₄C, aluminum boron carbides and metallic Al with aluminum boron carbide, nitride and oxide inclusions. T-161 is a material containing 78% of Al₂O₃ with a glassy binder obtained by cold pressing followed by sintering at 1300–1400 °C. B6 is a material containing 96% Al₂O₃.

Interestingly, this criterion indicates that low- K_{IC} materials are better for protective systems, which is contradictory to what some researchers propose [23,46].

The idea that higher hardness leads to a higher performance comes from the fact that these materials are more resistant to projectile penetration. Moreover, harder materials break the projectile into many small pieces, dividing its kinetic energy. According to Haney and Subhash [23], Raymond L. Woodward was the first to propose hardness as a key property to predict the ballistic performance of a material. LaSalvia [36] acknowledges the role of hardness in ballistic protection, but reminds on the importance of K_{IC} and fracture strength.

Nonetheless, Eq. (1) is rather simplistic, because the dynamics of a ballistic impact is very complex and not fully understood so far. A more precise and complete relationship between properties, similar to Eq. (1), is still an open-ended question. Although the D-criterion is intended to predict performance, it does not always successfully rank different materials, as pointed out by Budd and Darrant [35]. They tested 5 different glass–ceramic compositions. Their physical properties are presented in Table 2. The D-criterion is also presented, to compare its prediction with the obtained ballistic results.

Table 3 shows the ranking of the glass–ceramics according to their properties, the ballistic limit and the D-criterion,

Table 2 – Glass–ceramic physical properties [35] and calculated D-criterion.

Glass–ceramic	α	β	γ	δ	ε
Hardness (GPa)	6.3	8.5	6.7	11.1	11.4
3-pt bending (MPa)	120	167	172	149	119
E (GPa)	126	101	88	94	96
K_{IC} (MPa m ^{1/2})	2.4	2.3	2.1	1.7	1.9
ρ (g/cm ³)	2.61	2.53	2.56	2.76	2.73
Relative ballistic limit ^a	1.13	1.18	1.17	1.16	1.16
D-criterion ^b	4	3	5	1	2

^a The ballistic limit was taken relatively to the ballistic limit values of soda-lime-silica glass. It is the ratio between the projectile's speed that results in total perforation in the glass–ceramic to the projectile's speed that results in total perforation in the glass.

^b Calculated in the present paper.

Table 3 – Ranking of the glass–ceramics according to their physical properties.

Rank	1	2	3	4	5
Ballistic limit	β	γ	δ and ε	–	α
HV	ε	δ	β	γ	α
3-pt bending	γ	β	δ	α	ε
E	α	β	ε	δ	γ
K_{IC}	α	β	γ	ε	δ
ρ (g/cm ³)	δ	ε	α	γ	β
D-criterion	δ	ε	β	α	γ

Table 4 – Mechanical properties and their relevance to ballistic impact. The complete version can be found in the work of Haney and Subhash [23].

Property	Relevance to ballistic performance
Hardness	Blunts and erodes the projectile Promotes dwell Measure of performance potential
Fracture toughness	Increases resistance to penetration
Fracture strength	Compressive fracture strength relates to initial resistance to crack generation and growth
Elastic constants	Reduced propensity to cause cracking to the rear surface of the plate

highest-to-lowest values. This table clearly indicates that no single mechanical property ranks the different glass–ceramics in the same way as Neshpor's D-criterion. The relationship of the mechanical properties with the ballistic limit should also be noted. The best result for the ballistic limit test was obtained by the glass–ceramic β , which was not ranked in first place in any test, although it came in second in three of them (3-point bending, Young's Modulus and K_{IC}). Another key point to be observed is, once again, related to the D-criterion. Besides the fact of not accurately ranking the materials, it also mixed them up. The best result in ballistic limit tests, glass–ceramic β was ranked third according to the D-criterion. Moreover, the second-best glass–ceramic after the ballistic limit test, GC γ , was ranked last by the D-criterion.

Ultimately, it is important to call attention to the results regarding the fracture toughness. As pointed out before, its role in the ballistic impact is not clear, since according to Neshpor [50], its value should be low, whereas other authors [23,46] point in the opposite direction. Concerning the results presented in Table 4, the glass–ceramic with higher K_{IC} is the one that presented the worst result under a ballistic impact. However, the one with the second-higher K_{IC} , was the best glass–ceramic under a ballistic impact. The results concerning this small group of glass–ceramics alone show how difficult it is to foresee the ballistic response of a given material based on its properties.

It is, though, necessary to continue this type of research to gain a better understanding of the relationship between the mechanical properties and the ballistic performance of any material. Table 4 summarizes certain mechanical properties that are presented in patents and scientific papers and their relevance to the ballistic performance of materials. The table was compiled by E.J. Haney and G. Subhash and is partially presented here. The complete table can be found in [23].

Not only the mechanical properties of the ceramics or glass–ceramics (used as strike face) take a part on how the add-on armor will break, but also the material used as main armor (backing material) plays a role. A study [24] analyzed three different configurations of a protection system, all having alumina as the impact face. The backing materials were steel, aluminum and glass. Although they have very different E (210 GPa, 85 GPa and 70 GPa, respectively) the worst performance was obtained with aluminum as a backing material. This result was explained by the fact that alumina cracks in different ways for each backing material.

This study also observed the influence on the ballistic protection performance of other parameters, such as the impact face's E, hardness and fragment size. A higher E leads to a longer dwell time of the projectile, which is a benefit to the protection system [25]. Depth-of-penetration (DoP) tests on alumina having steel as backing material and a tungsten projectile with a velocity of 1250 m/s were conducted. Keeping E

constant, an increase in hardness of the strike face leads to a better performance of the protection system. Considering the grain size, a spinel test with glass as backing material showed that when the grain size had a bimodal distribution 3–75 μm (reported $H_V = 12.0 \pm 0.1$ GPa), the residual projectile velocity was 140 m/s. On the other hand, for a grain size of 0.35 μm (reported $H_V = 14.2 \pm 0.2$ GPa) the residual velocity dropped to 33 m/s.

Although it is known that the performance of the strike face will depend on the backing material, Grujicic et al. [51] observed that depending on the type of backing material, some properties will show a correlation with the performance of the strike face and some will not. When they analyzed a protection system having a stiff backing layer, it was observed a positive correlation between the ballistic mass efficiency (defined as the energy loss due to the impact divided by the areal density of the material) and the backing material's hardness. However, when analyzing the ballistic mass efficiency versus the bending strength, also for stiff materials, no correlation is observed.

Bless [6] tested a series of materials, a Corning glass-ceramic was among them, and it was observed that for blunt projectiles the performance of the materials tested is inversely proportional to their density. For sharp and hard projectiles, on the other hand, the material's compressive strength is more important. According to Talladay et al. [7] when the projectile changes its trajectory inside the glass-ceramic, the penetration capability is diminished.

4. Research on transparent glass-ceramics for ballistic protection

TGC used as ballistic protection is not something new. For example, GEC Alstom holds a patent back from 1995 of Transarm[®], a lithium disilicate ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$) based glass-ceramic [35]. Yet, research (as judged from the number of patents and articles) on transparent ceramics or TGC for ballistic protection remains much less significant than non-transparent ones.

Storch et al. [52] studied a new fabrication route for laminate glass to be used as ballistic protection. However, no new composition is proposed.

Gabel et al. [53] proposed a composition from the (lithium-aluminum-silicate – LAS) system to be used, among other possible applications, such as ballistic protection. The glass-ceramic plate comprises Keatite solid solution ($\text{Li}_{1-2x-2y}\text{Mg}_x\text{Zn}_y\text{AlSi}_2\text{O}_6\text{--Li}_{1-2x-2y}\text{Mg}_x\text{Zn}_y\text{AlSi}_4\text{O}_{10}$, with $0 \leq x \leq 0.5$; $0 \leq y \leq 0.5$ and $0 \leq x + y \leq 0.5$) as the main crystalline phase and high-quartz solid solution as the minor crystalline. In order to develop the desired microstructure, a double-stage heat treatment is applied. After the applied heat-treatment, the material becomes a transparent colored plate. However, no ballistic test is presented, though.

Pickup et al. [8] studied the dynamic behavior of Alstom's Transarm. Patel et al. [9] also used Transarm in a series of performance studies of transparent protection systems. In none of the cases a new TGC was proposed. The authors measured the dynamic shear strength of Transarm and borosilicate glass, observing the superiority of the former. They conclude

that Transarm has the potential to be used against low-caliber ammunition.

Senf et al. [10] tested Schott AG's Zerodur[®] under impact of pointed and blunt steel cylinders. They observed that this lithium aluminosilicate (LAS – $\text{Li}_2\text{OAl}_2\text{O}_3\text{--SiO}_2$) glass-ceramic fractures in a similar way to the glasses studied by the same authors. They observed that the glass-ceramic presented a slightly lower mass efficiency (the mass needed to stop the projectile) than the soda-lime silica glass, for the projectile-target configuration analyzed.

Herrmann et al. [52] analyzed a series of protection systems having glasses or glass-ceramics as strike face. Although the protective systems use glass-ceramics, a specific composition is not indicated.

Auchter-Krummel et al. [54] studied a protection system comprising layers of different materials, ceramics, glasses and glass-ceramics. The glass-ceramic face is the one which receives the impact. Its composition was not mentioned. According to the inventors, in this work, an enhanced transparency is achieved, not by polishing but by applying a polymer film on the surface of the plate. Ballistic tests were conducted using 7.62 mm caliber steel-core bullets. The results of the glass-ceramic of the invention were compared with other materials, such as floated borosilicate glass, commercial impact resistant poly methyl(methacrylate) and polyvinylbutyrate. Results showed that the glass-ceramic of the invention presented a lower weight per unit area than the laminates of other compositions.

Zachau et al. [55], on the other hand focused their research on a specific glass-ceramic, from the lithium aluminum-silica (LAS) system to be used in a protective system. Different glass compositions are given as examples. After nucleation at 750 ± 20 °C for 20 ± 15 min and crystallization at 900 ± 20 °C for 20 ± 15 min, the material has Knoop hardness ≥ 580 . In a different study [56], a LAS glass-ceramic composition was proposed, but the crystallization cycle was not revealed. The crystalline phase present is keatite ($\text{LiAlSi}_x\text{O}_y$ – where x is in the range from 2 to 4 and y is in the range from 6 to 10). The authors claim that this glass-ceramic material has a higher transparency than previous materials presented on the background of their patents.

Zachau and Corvers [57] presents a reactive armor. In the studied embodiment, the armor can contain different crystal phases, according to the selected system, from either $\text{Li}_2\text{O--Al}_2\text{O}_3\text{--SiO}_2$, $\text{MgO--Al}_2\text{O}_3\text{--SiO}_2$ or $\text{K}_2\text{O--Na}_2\text{O--Al}_2\text{O}_3\text{--SiO}_2$. The main crystal phases the glass-ceramics may contain are: high-quartz mixed crystals ($\text{Li}_{2-x}(\text{Mg}, \text{Zn})_{x/2}\text{Al}_2[\text{SiO}_4]_2$ ($0 \leq x \leq 1$)); keatite mixed crystals ($\text{Li}_2\text{O--Al}_2\text{O}_3 \cdot 4.8\text{SiO}_2$); lithium disilicate ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$) or lithium metasilicate ($\text{Li}_2\text{O} \cdot \text{SiO}_2$), nepheline ($\text{Na}_{8-x}\text{K}_x\text{Al}_8\text{Si}_8\text{O}_{32}$), spinel mixed crystals ($\text{Mg}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$), forsterite (MgSiO_4). The combination of phases varies depending on the composition of the parent glass. In all systems, nucleating agents (TiO_2 , ZrO_2 , SnO_2 and HfO_2) are present with a total amount between 0.5 and 15 wt%. The authors selected the glass-ceramic that contains at least one of the following phases: high-quartz mixed crystal, spinel mixed crystal, lithium disilicate and lithium metasilicate. Most preferably high-quartz mixed crystal and/or spinel mixed crystal. No new glass-ceramic is developed. The authors tested the reactive armor against a

grenade impact and it had a better performance against the non-reactive configuration.

Carberry et al. [47,58] presented a protection system that uses a LAS glass–ceramic as the strike face. The glass–ceramic material contains from 60 to 70% crystalline volume fraction, having a mean crystal size of 200 nm or less in one configuration. Higher values of crystal sizes are also possible, according to the researchers.

Carberry et al. [59] proposed a multilayer protection system where the layer and interlayer have the same refractive index, making the armor transparent. The authors state that one efficient way of diminishing penetration ability of a ballistic round is by making it spin while it penetrates the armor. They presented prior patents where the assembly of the pieces and their geometry made the projectile turn. It can be observed that using granular media and ceramic plates in the form of pyramids are some of the ways presented to make the projectile swirls during its course. However, all this is not suitable to transparent armors. The layers have non-homogeneous properties, which cause the incoming projectile to rotate within the material, diminishing its penetration capacity. According to the inventors, the glasses and glass–ceramics used may be from the following systems: borosilicate, aluminosilicate, LAS and combinations of them. The crystalline phases present may include β -quartz, spinel, β -willemitite (Zn_2SiO_4), forsterite (Mg_2SiO_4) and spinel solid solution. No new glass–ceramic was developed.

Leighton et al. [60] proposed a transparent protection system in which one of the layers may consist of glass–ceramic material. Neither a new type of glass–ceramic nor a specified system is proposed. The advantage of the presented material, according to the author, is the laminated edge seal of the assembly that improves the resistance against liquids and vapors.

Varshneya and Kreski [61] also presented a transparent protection system that incorporates a glass–ceramic material, but the specific composition was not detailed. The authors claim that their invention allows a higher absorption of kinetic energy, reducing the tensile stresses to which the armor is subjected, only by selecting different materials. No proposition of new composition is made. A similar situation was presented by Hartley [62].

Pinckney et al. [63] presented a protection system having glass with an anomalous behavior and a glass–ceramic as

strike face. The anomalous behavior is characterized by the formation of Hertzian-cone cracks during Vickers indentation, indicating that the material densifies during the process [64] (the glass–ceramic composition is not informed). The authors claim that using these anomalous glasses improves the ballistic performance due to densification. A different patent [65] proposed a protection system having a glass–ceramic layer containing spinel crystals and one or more glass layers bonded without using adhesives. The glass–ceramic composition and how to get spinel crystals are not informed in [65]. The aim of that work was to propose a way to bond the different layers of the composite armor without using a polymer. In fact, the authors claim that polymers can cause, through degradation, discoloration and delamination. The layers of glasses and glass–ceramics are thermally bonded together.

Pinckney et al. [66] also investigated a transparent protection system composed of multiple layers capable of supporting multiple hits. They proposed that a glass–ceramic plate as an impact face, combined with one or more glass layers and a backing layer of a high resistance to impact material gives a better performance than a system having only a glass–ceramic or a glass as the impact face. In one of the presented configurations, the residual glass phase lies on 2–80 vol.% while the crystalline phase lies on the 20–98 vol.%. In another configuration, the residual glass phase is present on a 2–50 vol.% rate, while the crystalline phase lies on the 50–98 vol.%. The crystalline phases were selected from the group of β -quartz, mullite ($3Al_2O_3 \cdot 2SiO_2$), spinel or combinations of them. According to them, a configuration that mixes glass and glass–ceramics performs better than an all-glass or an all-glass–ceramic armor. In another study [67], a protective system having 20–90 vol.% of crystalline phase (β -quartz and/or mullite) is proposed, which has a grain size from 10 to 40 nm and 2–80 vol.% of residual glass phase. The glass–ceramic shows a Knoop Hardness of 600. The crystallization cycle and glass composition prior to crystallization are not indicated.

Weinhold [68] proposed a multilayer transparent protection system having at least 3 layers of Robax[®] or Zerodur[®] (both LAS) glass–ceramics material or a layer of soda-lime or borosilicate glass between two glass–ceramic layers. Many examples of multilayer assembly are given in the patent. These examples were tested against 0.30 cal. manganese-molybdenum armor piercing ammunition (M2 AP). Each configuration had

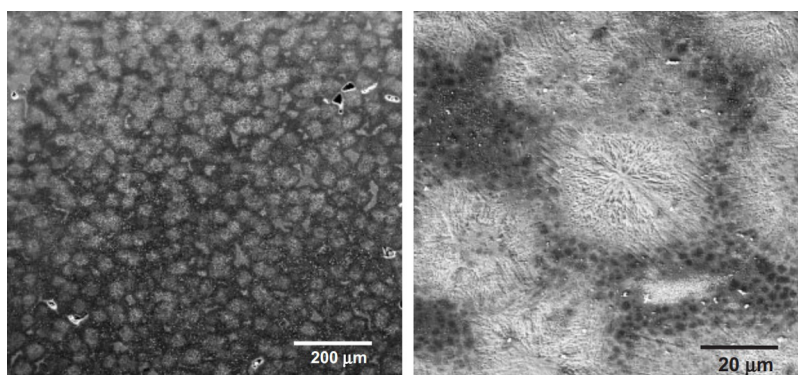


Fig. 8 – (a) Low and (b) high magnification SEM micrographs of the microstructure of a transparent glass–ceramic material having micron size crystals [11].

from 4 to 5 layers comprising glass, polymer and glass-ceramic material. Depending on the assembly, it blocked or not the incoming projectile, confirming the inherent difficulty of this type of research.

Comte and Wondraczek [69] projected a new glass-ceramic material of the LAS system. Several examples are presented in the text, all crystallized after 150 min or less in a temperature below 1000 °C. Nucleating agents, TiO₂, ZrO₂ and Sn₂O are applied to promote bulk nucleation. The combined amount lies on the interval of 3.1–4.3 wt%. This work [69] focuses on the development of the aforementioned glass-ceramic, and one of the possible applications is ballistic protection. No ballistic tests were conducted, nor the ballistic characteristics of the material were explored or explained.

Budd and Darrant [35] developed a TGC material to be used as ballistic protection. Their material is a lithium disilicate based material, with ZrO₂ as the major and P₂O₅ as the minor nucleating agent. Examples of composition with crystallization cycle are presented in the text. The advantage related to previous art, according to the authors, is its enhanced mechanical properties compared to related materials, which could make lighter armors to be used, e.g., in aircrafts. The authors presented ballistic tests conducted on 5 examples of glass-ceramics. The glass-ceramic materials had a performance from 12 to 18% higher when compared to soda-lime-silica glass.

Gallo et al. [70] have a patent request where they studied different glass compositions of the MAS system. They obtained TGC and opaque glass-ceramics. After single-stage heat treatments conducted in the range of 950–1050 °C for 80 min, the crystalline phases present on the opaque glass-ceramic were sapphirine (7MgO·9Al₂O₃·3SiO₂), rutile (TiO₂), quartz (SiO₂) and spinel (MgO·Al₂O₃). TGC were obtained after double-stage heat treatments. Nucleation heat treatment was conducted in the range of 650–780 °C, during periods ranging from 10 min to 5 days followed by a growth heat treatment in the range of 800–1000 °C, during 1–3 h, leading to sapphirine and spinel as crystalline phases. Reported Vickers hardness for TGC and opaque glass-ceramics was 10 GPa. The advantages of this configuration, according to the authors, is that a polycrystalline, transparent material obtained via nanocrystals presents a higher hardness than parent glass and is less complex to be manufactured when compared to single-crystal ceramics, such as spinel and sapphire, commonly used as add-on armor.

Cunha et al. [11] published the only paper known to us dealing with a new formulation of large grain, highly crystalline glass-ceramic, which could perhaps be used as ballistic protection. The authors developed a translucent Na_{4+2x}Ca_{4-x}Si₆O₁₈ soda-lime-silica glass-ceramic, with micron-size crystals and 96% of crystallinity. The key feature for translucency of their highly crystalline glass-ceramic is

Table 5 – Compositional ranges of oxides (in weight%) of different glass-ceramics, compiled from the patents referenced in the bibliography (for those which the compositional range is presented), and the highlighted (^a) oxides used as nucleating agents. LAS, lithium-aluminum-silicate; LS2, lithium disilicate; AE, alkaline-earth-aluminum-silicate; MAS, magnesium-aluminum-silicate.

Oxides	LAS/LS2	AE	MAS
SiO ₂	55–71	35–50	30–65
Al ₂ O ₃	2–8/15–25	30–45	10–30
MgO	0–2		2.0–9.8 and 13–30
Li ₂ O	0.1–15.5		
^a TiO ₂	0–5		6.5–8.5
^a ZrO ₂	0–5		0.1–2.9
^a SnO ₂	0–1.2		
^a P ₂ O ₅	0–3		
Nb ₂ O ₅	0–0.6		
ZnO	0–4		
Na ₂ O	0–1.5	0.1–22	
K ₂ O	0–1.3	0.1–26	8–20
Fe ₂ O ₃	0–0.2		
As ₂ O ₃	0–1.5		
BaO	0–3		
B ₂ O ₃	0–2		1.0–2.5
CeO ₂	0–0.4		
SrO	0–2		
Sb ₂ O ₃	0–1.5		1.1–7.0
V ₂ O ₃	0.01–0.06		
∑ TiO ₂ + ZrO ₂	0.5–4.3		6.6–11.4
∑ TiO ₂ + ZrO ₂ + SnO ₂	3.1–6		
∑ TiO ₂ + ZrO ₂ + SnO ₂ + HfO ₂	0.5–10	6–10	6–10
∑ TiO ₂ + SnO ₂	0–1.7		
∑ Na ₂ O + K ₂ O	0–1.5		
∑ Gd ₂ O ₃ + La ₂ O ₃ + Ta ₂ O ₅ + Y ₂ O ₃	0–4		
∑ Nd ₂ O ₃ + Er ₂ O ₃	0–0.08		
∑ MgO + ZnO			5–20
∑ CaO + SrO + BaO	0–4		

Table 6 – Vickers hardness, Young's Modulus and fracture toughness of selected ceramic materials and from the most common glass–ceramic systems used for ballistic protection.

Material	Vickers hardness (GPa)	Young's Modulus (GPa)	K _{IC} (MPa m ^{1/2})
SiC	23 [71]	410 [72]	5.50 [73]
B ₄ C	36 [74]	445 [74]	2.50–5.00 [75]
Si ₃ N ₄	14 [71]	300 [76]	6.00 [73]
BN	74 [77]	675 [74]	2.60 [74]
Spinel	14.1 [25]	273 [25]	1.95 [25]
Sapphire (mono-Al ₂ O ₃)	17.4 [25]	435 [25]	2.14 [25]
Poly-Al ₂ O ₃	14.8–20 [25]	380 [25]	3.60 [25]
AlON	13.5 [78]	323 [79]	2.00 [79]
MAS-GC	>7.55 [80]	>90 [81]	2.50 [80]
LAS-GC	5.4 [82]	85 [83]	
LS2-GC	6.3 [35]	80–88 [84]	1.7–2.4 [35]

that the refractive index of the residual glass matrix matched that of the average of the crystal phase. The crystal size ranged from 5 to 30 μm , as shown in Fig. 8. Translucency was also assured by the absence of pores, which is an alleged advantage of glass–ceramics over sintered ceramic materials. The advantage of the proposed material is that, with higher degree of crystallinity, higher mechanical properties can be achieved, since for most compositions, the crystallized version has higher mechanical properties such as Vickers hardness and Young's Modulus, when compared to the glass with similar composition.

To avoid the excessive presentation of tables, only the glass–ceramic system studied in each patent will be discussed. Thus, Table 5 presents compositions compiled from the patents, separated by glass systems: lithium-aluminum-silicate (LAS) and lithium disilicate (LS2); alkaline-earth-aluminum-silicate (AE) and magnesium-aluminum-silicate (MAS). Table 6 presents the Vickers hardness, E and fracture toughness for the most common ceramic materials used as ballistic protection, as well as for glass–ceramics of the MAS, LS2 and LAS system for comparison.

From the compositional range of proposed TGC, research efforts have focused on silicate systems, and all of them use nucleating agents to promote internal crystallization. It is frustrating to observe that ballistic tests have not been reported, except for very few glass–ceramics, mainly from the Li₂O–SiO₂ system. Therefore, there is a window of opportunity in this regard. Glass–ceramics can be used as good replacements of transparent ceramics. Although, sometimes, they present less attractive mechanical properties, such as lower hardness and E, it has been shown that a proper combination of properties can lead to a material with optimized performance. Their relatively low cost is another advantage of glass–ceramics, as transparent ceramic materials are mainly single-crystal plates, which are not only very expensive, but also difficult to produce.

5. Conclusions and perspectives

As we have shown in this review, which includes all papers and patents known to the authors on TGC for ballistic protection, only a very limited number of reports have been published so far. It is obvious that companies working in this field do not

publish, and even do not file patents, on their best materials. They prefer to keep them as industrial secrets.

The search for better performance, as shown by the few available patents, has been concentrated on different configurations of protective systems using well-known materials, rather than on the research and development of new glass–ceramics. For this specific reason, a wide range of possibilities can be foreseen for researching glass–ceramics. We believe three main topics could be further investigated: (i) a more in-depth understanding of the major properties required for armor materials and their influence on the performance of the whole assembly, and (ii) a search for new better performing glass–ceramic than the current known materials; (iii) computer simulations of glass–ceramic behavior guided by actual ballistic tests.

Concerning the first item, ballistic impacts are extremely fast, localized events, with high-energy transfer, making them complicated to propose a general methodology to predict the ballistic performance of a material. There is still fertile ground to be covered on this subject before a good model to predict (in all cases and for all range of properties) the ballistic performance of a material. Therefore, computer simulations might be the key technique here.

Glass–ceramics indeed present interesting combinations of properties that make them suitable to be used as ballistic protection. Their relative low density when compared to polycrystalline ceramics, would make it possible to assemble lighter protection systems. They could perhaps be a suitable replacement for transparent ceramics, such as sapphire and spinel. Although glass–ceramics combine good mechanical properties with high processability and relatively lower densities than transparent oxide ceramics, they have been barely researched. Lithium-disilicates and magnesium-aluminum-silicates have been the preferred systems. We believe many other types of glass–ceramics present useful, relevant characteristics for transparent armors and warrant further research.

Funding information

Fundação de Amparo à Pesquisa do Estado de São Paulo, Grant/Award Number: 2013/07793-6, 2014/03004-0; Center for Research, Technology and Education in Vitreous

Materials, Grant/Award Number: 2013/07793-6; Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – (CAPES) Brazil – Finance Code 001.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

The authors would like to thank Professor Celso Jorge Villas Boas, for his constructive criticism of the manuscript. The authors thank the São Paulo State Research Foundation (FAPESP) for the funding (grant # 2013/07793-6 (CEPID/CeRTEV), and also the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – (CAPES) Brazil – Finance Code 001. LSG acknowledges FAPESP for the funding grants, numbers 2013/00457-0 and 2014/03004-0.

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