Graphene-SiC Nanocomposites for New Body Armour Systems

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ABSTRACT

Graphene is undoubtedly the most researched nanomaterial because of its unique properties allow the preparation of nanocomposites (nanotechnology-based composites) for many industrial applications: optoelectronics, bioengineering, supercomputing, multifunctional composites, energy, sensing, etc. In addition, it is possible to combine graphene with other nanomaterials to achieve very specific properties in the resulting nanocomposite. Body armour systems need to be improved for defeating new threats of fourth generation warfare and terrorism, however, in the application of these nanocomposites to increase the dynamic strength against supersonic impacts, experimental data are practically non-existent. In this work, the ballistic characterization of a series of polyester resin laminated plates reinforced with fiberglass woven fabric and doped with pristine few-layer graphene (0.25%-1.00% w/w) or loaded with silicon carbide (SiC) ceramic nanoparticles (25%-75% w/w) was carried out. The ballistic limit (V_0) of these plates was determined with 7.62x51 FMJ ammunition, in accordance with the NATO STANAG 2920 standard. After the analysis of all the obtained results and previous ones, a new series of optimized specimens was manufactured, using the same polymer matrix but nanoreinforced with both graphene and SiC nanoparticles and using a military grade para-aramid fabric as reinforcing fibers. The ballistic limit (V_0) of these plates was determined using both 7.62x51 FMJ and 5.56x45 SS109 ammunitions. The results showed improvements in V_0 parameter regarding to the unmodified laminated plates of 11.1% and 22.6%, respectively. These results show that nanocomposites based on graphene and nanoceramics can provide solutions of interest in the design and development of disruptive materials for a new generation of body armour systems, providing better levels of protection and lightness to the NATO soldiers.

1.0 INTRODUCTION AND AIM

Current conflicts and those that will develop in the near future can be adequately framed in the concept of Fourth Generation Warfare (4GW), originally enunciated by William S. Lind, and that reached special repercussion from 2005 and during the worst years of the Iraqi insurgency [1]. Today, other nomenclatures such as asymmetric or hybrid warfare are also used to refer to this new reality. The nucleus of this phenomenon is not a military evolution but a political, social and moral revolution: a crisis of state legitimacy. Throughout the world, citizens of different countries are transferring their primary loyalty from the state to other entities: ethnic groups, religions, gangs, ideologies and “causes”. This type of conflicts is characterized by the fact that, although tactical, operational and strategic levels still exist, all of them can occur in a very limited space-time, since operations take place fundamentally both in urban environments and in close combat conditions, which can change very quickly.

A body armour or Soldier Passive Protection System (SPPS) is an individual protective equipment, whose functions are to prevent the penetration of projectiles from firearms, fragments of shrapnel or knives into the body, to absorb the energy of impact and to reduce the caused trauma. Conventional body armour systems are relatively flexible and light, because they are made of synthetic fibre fabrics arranged in successive layers, but only offer protection against the impact of projectiles from handguns with deformable core, shotgun pellets and small fragments such as of hand grenades. Protection against high speed rifle projectiles, larger shrapnel or very sharp objects requires the use of rigid plates that normally overlap a conventional vest, but they have the great disadvantage of being thick, heavy and uncomfortable, so its use significantly limits the mobility of the wearer.

Analysis of the data referring to the number of casualties suffered by the multinational coalition troops deployed in "Enduring Freedom", "Iraqi Freedom", "New Dawn", "Inherent Resolve" and "Freedom's Sentinel" operations (percentages, causes, anatomical location, etc.), shows similar patterns to all large-scale conflicts since the World War II (inclusive) except for three fundamental changes. In the first place, the percentage of casualties caused by some type of explosive mechanism (IEDs, artillery, hand grenades, etc.) is 84%, in opposition to 13% caused by firearms; this is the most marked differentiation seen to date. Secondly, there has been a substantial change in the location of the wounds, resulting in a notable increase both in the number of casualties caused by head-neck and limb injuries and in the number of wounds per combatant resulting in casualties [2-6]. Finally, there is a new threat that was not contemplated in previous statistics because of its incidence on the total was irrelevant, but now it is approaching 3% and it is increasingly significant: traffic accidents in the Area of Operations (AO).

In view of the above, there is a tendency for current SPPSs to become inadequate to the combatant new needs. Protection/weight, mobility and adaptability are increasingly determining aspects. Examples of this new reality are the future American SPS (Soldier Protection System) or the Russian Ratnik-3 (Figure 1-1) [7, 8].

Figure 1-1: Soldier Protection System (SPS) under development by the United States Army (a) and Ratnik-3 under development by the Russian Army (b) [7,8].

Since its discovery in 2004 by Geim and Novoselov [9], graphene has aroused a growing interest in various technological sectors and even more so in the defence sector. Structurally, graphene is a monoatomic thickness sheet formed by carbon atoms with sp^2 hybridization, linked together and constituting a hexagonal crystalline lattice, whose length of the C-C bond is 1.42 Å [10]. Although, in addition to graphene, there are other nanomaterials that have already been proposed for their application in the field of nanocomposites [11], recently this is the nanomaterial that is generating most interest. This is because, although graphene stands out above all for the properties that postulate it to be the material par excellence in electronics and computing of the future, it also has surprising mechanical properties [12].

Late 2014, a joint team of researchers from Rice University and the Massachusetts Institute of Technology published a study on the mechanical properties of graphene against high velocity impacts of SiO_2 microspheres [13]. However, to date, the only published study on the capabilities of graphene nanocomposites in terms of ballistic protection on a macroscopic scale has been carried out in Spain [14].

To analyse the feasibility of developing new materials based on graphene and nanoceramics for its possible application in new generation SPPSs, our research team has carried out this study on the influence that the addition of graphene and SiC nanoparticles into a composite material has on its properties as a protection against ballistic impacts of both sniper and assault rifle ammunitions. This paper presents the results obtained using a series of nanocomposites prepared from a polyester resin reinforced with fiberglass and para-aramids and doped with pristine few-layer graphene (≤7 layers) and SiC nanoparticles.

2.0 MATERIALS AND METHODS

Pristine few-layer graphene was synthesized in our laboratory and characterized by X-Ray Fluorescence (XRF) spectroscopy (BRUKER S4 PIONEER, multires-He_{36}), Raman spectroscopy (Jovin-Ivon LabRam, SiO_2/Si, 532 nm) and high-resolution transmission electron microscopy or HR-TEM (JEOL JEM-2100, 200 kV) as described in previous works [14,15].

The materials used to manufacture the nanocomposites were the previously produced graphene, an orthophthalic unsaturated polyester resin (Recapoli 955 INF DCPD), SiC pseudo-spherical nanoparticles (Minerals Water, ~50 nm), a bi-directional E-glass fibre fabric (plain, 0º/90º, 600 $g \cdot m^{-2}$) and a para-aramid fibre fabric for military use (plain, 0º/90º, 200 $g \cdot m^{-2}$).

Preparation of doped matrices of nanocomposite was carried out in a similar way to that described in our patent with some modifications [16], using separately four different graphene doping ratios (0.25%, 0.50%, 0.75% and 1.00%) and three percentages of nano-SiC load (25%, 50% and 75%) by weight (w/w). The production of the laminated plates was carried out using a combined technique of hand lay-up and vacuum assisted moulding under pressure at room temperature. Based on the results obtained, a similar procedure was followed for the manufacture of combined polyester resin specimens reinforced with para-aramids and doped with graphene and nanoceramics. Once the curing processes were finished, the specimens were machined in 250 mm x 250 mm x 5 mm square plates, as shown in Figures 2-1 and 2-2.

Characterisation of the ballistic limit (V_0) of all the specimens was carried out in collaboration with military snipers from *Tercio de Levante* of the Spanish Marine Corps, in accordance with the guidelines established in the NATO STANAG 2920 standard [17], using a system developed for this purpose and installed in the shooting range of this unit. V_0 parameter is defined as the maximum velocity for which the probability of perforation of a given projectile is 0%. It is the best parameter for the characterisation of the ballistic protection of a material against high velocity rifle ammunitions. An Accuracy International AW 07 11664 precision rifle with 7.62x51 mm FMJ ammunition and a Heckler & Koch HK G36 E assault rifle with 5.56x45 SS109 ammunition were used as weapons for the tests. The Spanish Navy ammunitions workshop located at the Algameca Naval Station provided several series of cartridges with modified propellant loads (100%, 90%, 80%, 70%, 60% and 50%) for the experiments, to obtain the ballistic behaviour curves of the materials tested in a wide range of impact velocities.

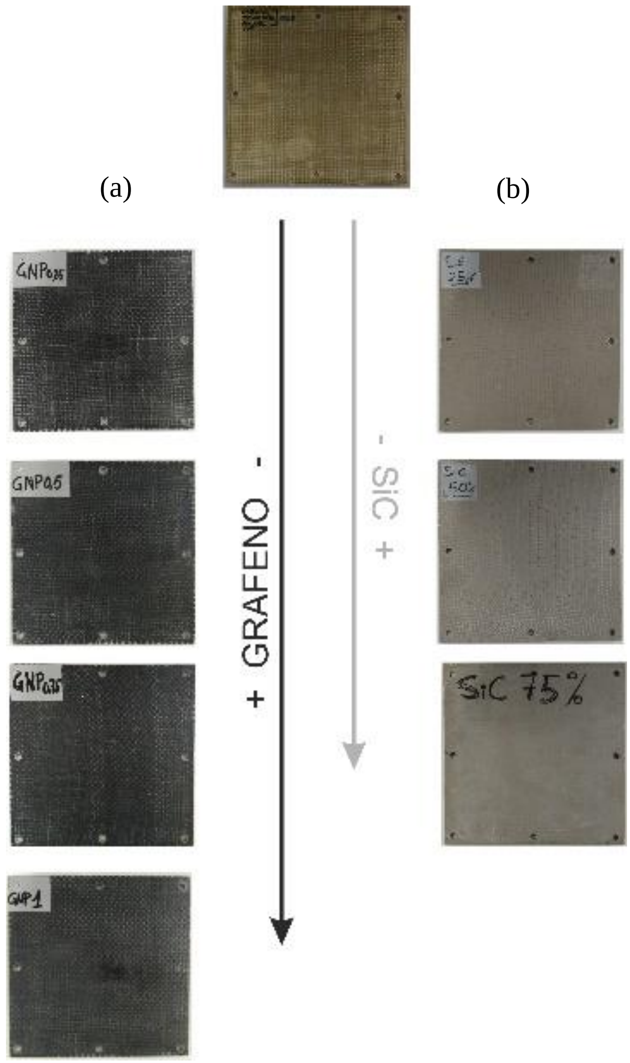

Figure 2-1: Fiberglass reinforced polyester specimens without doping (top), graphene doped (a) and nano-SiC loaded (b).

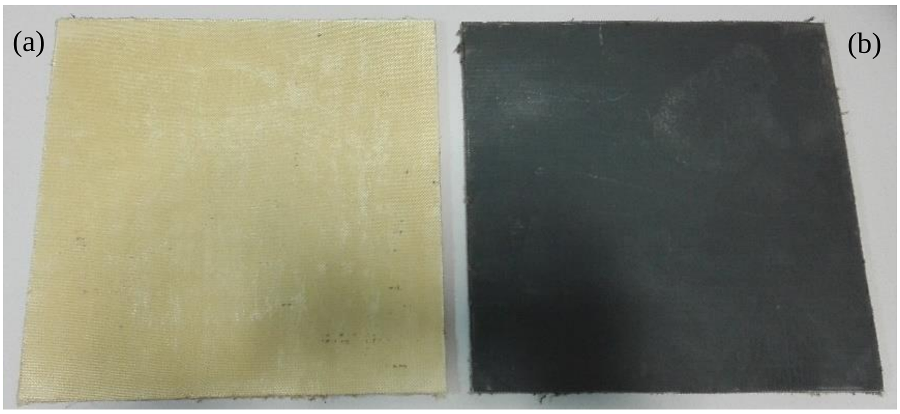

Figure 2-2: Specimens manufactured of polyester resin reinforced with para-aramids without modification (a) and doped with graphene and nano-SiC loaded (b).

3.0 RESULTS AND DISCUSSION

XRF elemental analysis showed a carbon purity in the sample of 99.3%. Figure 3-1 shows Raman spectrum of the obtained graphene with its fundamental characterization peaks and parameters together with HR-TEM micrographs, which demonstrate that the synthesized nanomaterial is certainly pristine few-layer graphene (FLG) in accordance with scientific bibliography [18-22].

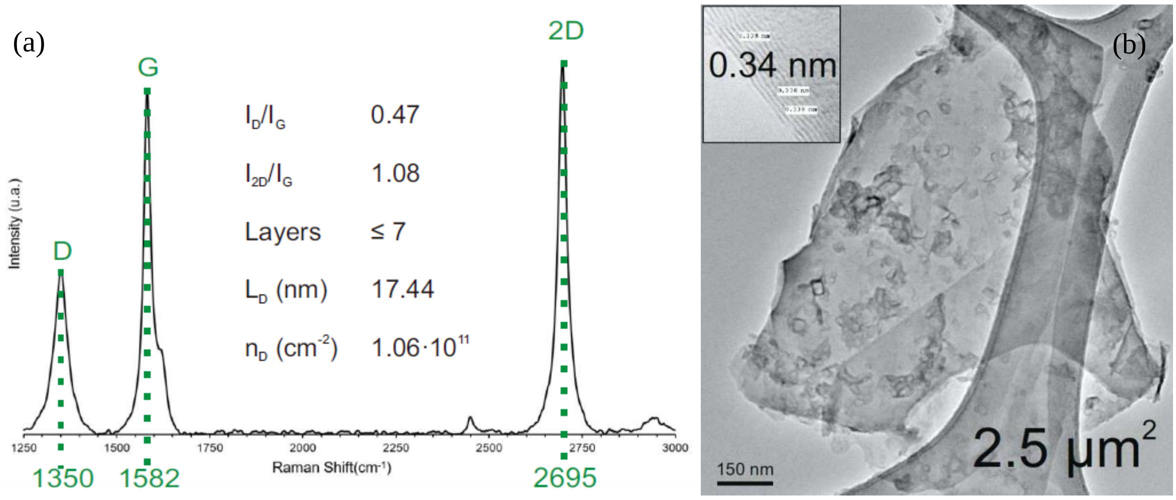

Figure 3-1: Raman spectrum of the obtained graphene with the position of the peaks of interest (D, G and 2D) and its most relevant parameters (a). HR-TEM images of FLG with its average area, distance between crystalline planes and the low number of layers (b).

Experimental data of strike velocities (V_s) and exit velocities (V_e) of the projectiles obtained in ballistic characterization tests (7.62x51 FMJ) allowed to determine the experimental values of the ballistic limit (V_0) for all fiberglass reinforced polyester plates (Figures 3-2 and 3-3).

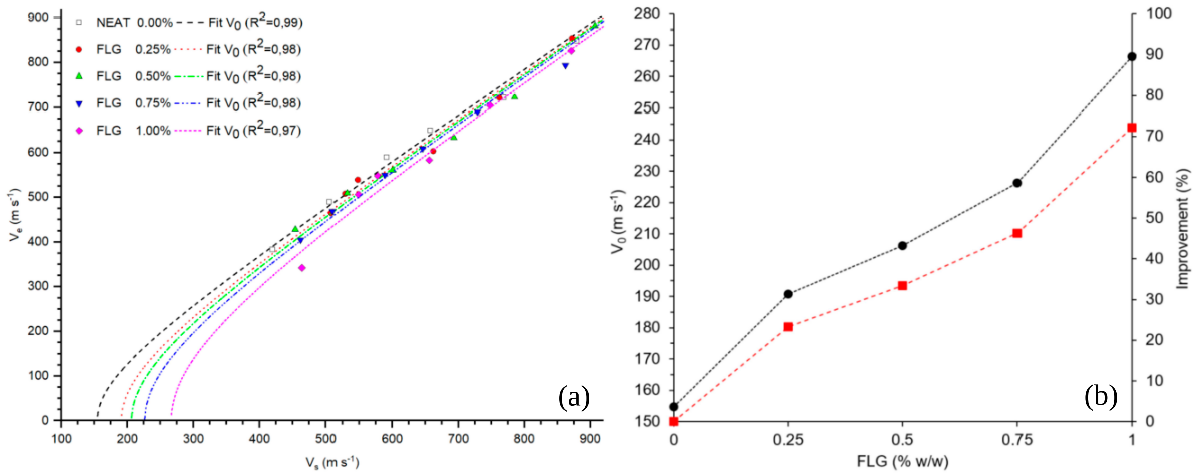

Figure 3-2: V_s versus V_e of the unmodified plate (NEAT) and the different FLG doped specimens tested with their V_0 parameter fitting curves (a). Experimental results obtained for V_0 parameter in terms of absolute values (black) and relative improvement (red) versus FLG doping ratio (b).

Ballistic limit of graphene doped specimens rises with the increase of the FLG doping ratio, reaching a maximum value of 266.4 m·s^{-1} for laminate doped at 1% by weight. This increase represents a relative improvement of 72.2% compared to undoped laminated plate. These results are in accordance with previous ones obtained by our research group and they suggest that low graphene doping ratios are able to improve the transmission of stresses inside the material and the propagation velocity of the shock wave, which are the most important phenomena in order to understand the behaviour of these nanocomposites. Therefore, the improvements in the V_0 parameter unequivocally support the viability of the development of new graphene-based nanocomposites with better ballistic protection using low doping ratios, due to the high capacity of graphene as a very effective reinforcing agent at nano-scale.

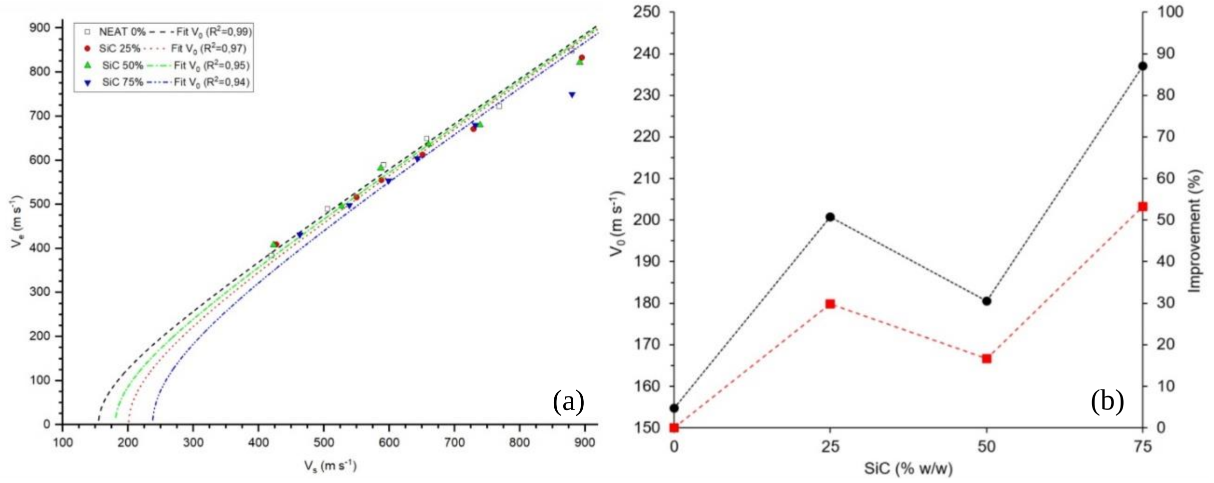

Figure 3-3: V_s versus V_e of the unmodified plate (NEAT) and the different nano-SiC loaded specimens tested with their V_0 parameter fitting curves (a). Experimental results obtained for V_0 parameter in terms of absolute values (black) and relative improvement (red) versus nano-SiC load (b).

Nano-SiC loaded specimens have higher ballistic limits than unloaded specimen in all cases, reaching a maximum V_0 of 237 m·s^{-1} for laminate loaded at 75% by weight, which represents a relative improvement of 53.2% with respect to the unmodified plate. However, in this case it can be observed that the enhancements in V_0 parameter do not follow a completely predictable behaviour, since the improvement obtained for the 50% load is the lowest one. This apparently chaotic behaviour is not so at all, but is due to the fact that the responsible mechanism for the upgrade in the ballistic properties of the nanocomposite is a noticeable hardening of the material, caused by the high loads of SiC nanoparticles. In our research team we refer to this phenomenon as “nanoceramization". At lower loads (25%) the material begins to harden but its behaviour continues to be ruled mainly by its polymeric components while at higher loads (75%), SiC nanoparticles become the most influential component in material properties, so the nanocomposite hardens enormously and behaves almost as a monolithic ceramic. In the intermediate load zone (50%), both mechanisms compete with each other, causing an antagonism which is responsible for obtaining the lowest improvement in the V_0 parameter.

Taking into consideration the obtained results with both nanomaterials separately, a new series of plates manufactured using both nanoreinforcening agents simultaneously was tested. Experimental data of the strike velocities (V_s) and exit velocities (V_e) of the projectiles, obtained in the ballistic characterization tests (7.62x51 FMJ and 5.56x45 SS109) allowed to determine the experimental values of the ballistic limit (V_0) for the polyester resin plates reinforced with para-aramids woven fabric, doped with pristine few-layer graphene and loaded with SiC nanoparticles together, as shown in Figures 3-4.

Ballistic limit of para-aramid reinforced polyester specimens doped with graphene and loaded with nano-SiC increases compared to undoped laminate, reaching maximum values and relative improvements with respect to undoped specimens of 160.8 m·s^{-1} (+11.1%) for 7.62x51 FMJ ammunition and 205.3 m·s^{-1} (+22.6%) for 5.56x45 SS109 ammunition.

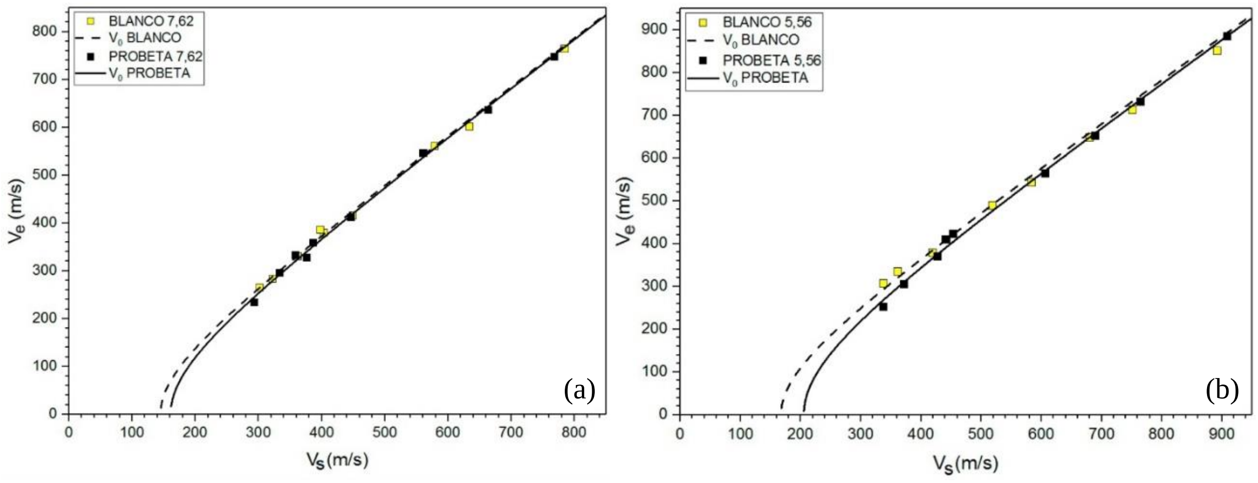

Figure 3-4: V_s versus V_e of the laminated plates tested with their V_0 parameter fitting curves for 7.62x51 FMJ ammunition (V_0=160.8 m·s^{-1}, R^2=0.98). Right: idem for 5.56x45 SS109 ammunition (V_0=205.3 m·s^{-1}, R^2=0.97). Yellow points (*BLANCO*) correspond to the unmodified specimens while black ones correspond to the modified specimens (*PROBETA*).

4.0 CONCLUSIONS

This work describes the obtained results by our research team in the study on the ability of graphene and SiC nanoceramics to improve the ballistic limit of a conventional composite material, consisting of a thermoset polyester resin matrix reinforced with fiberglass or para-aramids, doped with pristine few-layer graphene and loaded with SiC nanoparticles.

Ballistic characterization of nano-reinforced specimens shows improvements in V_0 parameter compared to undoped ones of 11.1% and 22.6% using 7.62x51 FMJ and 5.56x45 SS109 ammunition, respectively and in accordance with NATO STANAG 2920 standard protocols.

The obtained results show the viability of the development of new nanocomposites based on the combination of graphene and ceramic nanomaterials with improved ballistic protection properties, which allow the design and manufacture of a new generation of more efficient soldier passive protection systems. This technology will mean a notable increase in the operational capabilities and security of the units of the NATO soldiers.

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