Synthesis and Explosive Consolidation of Titanium, Aluminium, Boron and Carbon Containing Powders

Mikheil Chikhradze 1,2,4, George Oniashvili 1, Nikoloz Chikhradze 2,4, Fernand D.S Marquis 3

1 F. Tavadze Institute of Metallurgy and Materials Science, 10 E. Mindelistr, Tbilisi 0111, Georgia
2 G. Tsulukidze Mining Institute, 7 E. Mindeli Str., Tbilisi 0186, Georgia
3 San Diego State University, 5500 Campanile Drive San Diego, CA 92182-8010, USA
4 Georgian Technical University, 75 Kostava Str., Tbilisi 0175, Georgia

Email address: m.chikhradze@gtu.ge

Abstract. The development of modern technologies in the field of materials science has increased the interest towards the bulk materials with improved physical, chemical and mechanical properties. Composites, fabricated in Ti-Al-B-C systems are characterized by unique physical and mechanical properties. They are attractive for aerospace, power engineering, machine and chemical applications. The technologies to fabricate ultrafine grained powder and bulk materials in Ti-Al-B-C system are described in the paper. It includes results of theoretical and experimental investigation for selection of powders composition and determination of thermodynamic conditions for bland preparation, as well as optimal technological parameters for mechanical alloying and adiabatic compaction. The crystalline coarse Ti, Al, C powders and amorphous B were used as precursors and blends with different compositions of Ti-Al, Ti-Al-C, Ti-B-C and Ti-Al-B were prepared. Preliminary determination/selection of blend compositions was made on the basis of phase diagrams. The powders were mixed according to the selected ratios of components to produce the blend. Blends were processed in “Fritsch” Planetary premium line ball mill for mechanical alloying, syntheses of new phases, amorphization and ultrafine powder production. The blends processing time was variable: 1 to 20 hours. The optimal technological regimes of nano blend preparation were determined experimentally. Ball milled nano blends were placed in metallic tube and loaded by shock waves for realization of consolidation in adiabatic regime. The structure and properties of the obtained ultrafine grained materials depending on the processing parameters are investigated and discussed. For consolidation of the mixture, explosive compaction technology is applied at room temperatures. The prepared mixtures were located in low carbon steel tube and blast energies were used for explosive consolidation compositions. The relationship of ball milling technological parameters and explosive consolidation conditions on the structure/properties of the obtained samples are described in the paper.

1. Introduction
Intermetallics, fabricated in Ti-Al-B-C system are characterized with unique physical and mechanical properties.
They have a high specific strength under tensile and compression conditions, good high temperature corrosion, oxidation and wear resistant properties [1, 2, 3].

Binary and ternary system phase diagrams offer the possibility to obtain composites with wide spectrum of phase composition, in crystalline and amorphous structures. Depending on the composition and structure, the synthesized intermetallics/composites exhibit different special properties. The high potential of the system for development of new structural/composite materials in different thermodynamic conditions is very attractive. The increased attention on the system is stipulated by development of nanomaterials, as nano/ultrafine-grained materials exhibit the unique complex of properties in comparison with coarse-grained materials [4,5,6]. It is expected that the ultrafine grained intermetallics obtained in Ti-Al-B-C system should be characterized with significantly improved physical and mechanical properties.

Practical implementation of nanomaterial’s novel properties depends on the improvement of synthesis methods to produce bulk nanocrystalline materials in large scale. Widespread application of nanocrystalline materials requires: i) low cost production of the industrial applicable quantity of nanopowder and ii) efficient technology of synthesis/consolidation of nanoparticles for obtaining bulk materials.

The laboratory methods of nanopowder preparation (condensation from vapor, electrodeposition, chemical, inert gas condensation and etc.) are mainly used for research, because of the high cost and low output capacity. Large volume fraction of atoms in the grain/particles boundaries and increased chemical activity of nanosized particles create additional problems for handling and consolidation.

Several conventional methods (hot isostatic pressing (HIP), spark plasma syntheses (SPS), mechanical alloying (MA), laser engineered net shaping (LE) and etc.) are known for obtaining bulk ultrafine grained/ nanostructured materials. One of the attractive methods from conventional methods is Self-propagating High-temperature Synthesis (SHS). Wide spectrum of materials is synthesized (Multilayer Functional Gradient Alloys, SIGMA type) on the basis of refractory compounds TiC, TiB₂, Cr₃C₂, TiNi by SHS Method.

The disadvantages of the above mentioned technologies may be divided in two parts. The first is connected to nanopowders preparation, which includes control of particle sizes, chemical instability, separation, storage and handling. The second is connected with fabrication of bulk nanostructured samples, including limitations in sizes and geometry of bulk material, energy consumption, necessity of complicated facility/equipment, difficulties in controlling grain sizes, coarsening of the structure under high temperatures for extended period of time and problems of integration of different technological regimes in one cycle (syntheses-cladding-welding).

On the basis of above described problems, the main objects of the investigations were:

a) Ball-milling technology (for obtaining amorphous and nanopowders, as a precursor for synthesis of bulk materials);

b) Shock-wave compaction technology (for fabrication of bulk nanostructured materials).

2. Experimental Procedures

For the selection of powder compositions and ultrafine powder preparation the following procedures were applied. Coarse Ti, Al, C and amorphous Boron powders were used as starting elements. Precursors were sorted by vibratory sieves by particle sizes: (-0.16; + 0.063) mm; (-0.315; + 0.16) mm; +0.315mm. Different initial compositions of Ti-Al-B-C system consisting of Ti/Al, 5Ti/5Al/20B and 3Ti/2Al/1C elemental molar ratios were prepared for experiments. Preliminary selection of blend compositions was made on the base of theoretical investigations. Phase equilibrium system was determined based on the Gibbs’s principle-minimization of total energy. High energy Planetary premium line ball mill (Figure 2) from company Fritsch was used for Mechanical Alloying (MA), amorphization and nanopowder production. The mill was equipped with Zirconium Oxide jars and balls. Ratio of ball to powder considering the mass was 10:1. The time of the processing was varied in range: 1h, 2h, 5h, 15h and 20h. Rotation speed of the jars was 500 rpm. X-ray investigations identified diffraction lines of elementary Al, Ti, B, C, titanium and aluminium oxides. During the MA, the synthesizes of Titanium aluminides in
Ti-Al-B system (TiAl, TiAl_3, Ti_3Al,) were confirmed, when the processing time exceeded 5 hours. The SEM investigations were carried out for the 3Ti/2Al/1C and 5Ti/5Al/20B blends. Micrograph of the nanoblend, obtained under MA in ball mill is shown in Figure 1. Tendency of amorphization and nanopowder formation is proportional to processing time and confirmed by structural investigations and particle’s size measurements.

![Figure 1](image1.png)

**Figure 1.** SEM micrograph of the Ti-Al-B nanoblend; Ball mill processing time of 5 hours

The nanopowder preparation requires permanent control and reliable protection from spark and strong mechanical interaction. The powder becomes too aggressive and reactive and the risk of self-combustion initiation is very high. The reaction may be self-induced during the long time milling. For that reason, the long-time technological regimes should be realized under special media for prevention from non-controlled combustion/reaction. The result of self-induced reaction during the ball milling is presented on Figure 2, where the wall of zirconium oxide jar is coated with quite thick layer of multiphase Ti-Al-B intermetallides.

![Figure 2](image2.png)

**Figure 2.** Result of self-induced reaction in ball mill jar.

Next important stage of the research was the selection of efficient/rational technology for fabrication of bulk composites. This work proposes explosive consolidation (EC) of nanopowders for fabrication of bulk samples as an alternative of conventional compaction technologies.
The motivation was preliminary works, showing that explosive consolidation of metal-ceramic compositions is not only feasible but can produce materials near theoretical densities [7, 8, 9, 10]. It was clear that preliminary ball milling (for fragmentation, mechanical alloying and critical reduction of particles sizes) should significantly increase the sintering ability of the blend and improve the compacting process and mechanical alloying of selected powder compositions. The major advantages of EC for bulk nanomaterials production are the realization of high pressure, short processing time and super high cooling rate (adiabatic cooling). The shock wave loading of high exothermic reactants allows to generate in situ process of shock wave induced synthesis + EC. Technology doesn’t require additional energy from outside sources. High cooling rate is guaranteed, as the dynamic compression is accompanied with adiabatic cooling and as a result preserves the amorphous structure.

The EC experiments were performed at the underground explosive chamber. The base has developed infrastructure (Chamber, Storage, Security service) and is equipped for investigation of explosive and blasting technologies. The chamber is connected with cable system to observation station, which is equipped by sensors and high speed video camera for registration and observation detonation and shock wave parameters. For shock wave generation (explosive compaction), the industrial explosives were used in the experiments. The major energetic characteristics of explosives are presented in table 1.

### Table 1. Energetic characteristics of explosive materials

| Explosives                  | Energy of explosion, $E_w$, kJ/kg | Gravimetric density, $\rho$, gr/cm$^3$ | Pressure on St.3, $P \times 10^9$ N/m$^2$ | Gas volume of explosion, $V$, l/kg | Speed of a detonation, $D$, km/c |
|-----------------------------|-----------------------------------|----------------------------------------|------------------------------------------|----------------------------------|---------------------------------|
| NH$_4$NO$_3$                | 1439                              | 1.0                                    | 1.5                                      | 980                             | 1.8-2.0                         |
| ANFO (AN)                   | 3815                              | 0.8                                    | 4.5                                      | 980-990                         | 2.8                             |
| 79%NH$_4$NO$_3$+21%C$_6$H$_2$(NO$_2$)$_3$CH$_3$ | 4300                              | 0.8-1.0                                | 10                                       | 895                            | 3.6-4.2                         |
| 60%AN+40%, III19/7          | 2920                              | 0.98                                   | 3                                        | 948-976                         | 5.2                             |
| C$_3$H$_6$O$_6$N$_6$        | 5439                              | 1.1-1.82                               | 20                                       | 950                            | 8.6                             |

Consolidation of the samples was performed in two stages. The powder blend was charged in low carbon steel tube container and in the first stage the pre-densification of the mixtures was performed under static press loading (intensity of loading $P=500-1000$ kg/cm$^2$). Cylindrical container/tube was closed at both sides. A cardboard box was filled with the powdered explosive and placed around the cylindrical powder container. The experiments were performed at room temperature. The shock wave pressure (loading intensity) was varied in range 3-20 GPa. In set conditions the explosive was detonated by an electrical detonator.

### 3. Results and Discussions

Fabrication of bulk nanocomposites from nanopowders requires selection of the compaction technological parameters. The three main factors that must be considered for optimization of shock wave compaction regime are: 1. Selection of explosive, mass and geometry; 2. Selection and determination of powder container parameters; 3. Powder related parameters: composition, charging density, particle sizes and their distribution. Selection of container’s material for each particular cases needs the detailed investigations as well. For selection of container parameters, cylindrical axis symmetric experimental set up was used according to preliminary calculations.

The optimal shock wave loading pressure was varied between (7-10) GPa. In this condition, the configuration of loading/unloading waves in powder and container allows to initiate the syntheses in the reaction mixture, simultaneously consolidate it and fix the phase composition under adiabatic cooling. If shock wave pressure and developed energy exceed the strength limits of the container, the effects are
destructive (Figure 3b). In particular cases, the tangential stresses developed on the border of metal/container (Fe/Cu) and blend/intermetallic provide the welding/joining of the metallic surfaces with nanostructured intermetallic and as a result the Functional Gradient Materials (FGM) are obtained. The welding zone represents metal matrix, reinforced by nanoparticles and synthesized intermetallicides. As a result, the distribution of the hardness and other properties from metal layer to nanocomposite layer changes smoothly.

**Figure 3.** Photograph of samples: (a) obtained in optimal technological regime; b) Destroyed sample; P=20GPa; A ≥ Ep + Ecom

Following bulk compacts were recovered in different shapes and prepared for investigations. The density of specimens was determined (cut from different part of samples) by the Archimedean method. The microstructure was studied by SEM (Figure 4).

**Figure 4.** SEM micrographs of bulk TiAl Band composites obtained by shock wave consolidation: P=10 GPa

4. Conclusions
The investigations, which were carried out to study the mechanisms of preparation/synthesis of blends for obtaining bulk materials by using explosive consolidation technology and the results of number of experiments enables to conclude the following:

- For preliminary selection of explosives and configuration, computer modelling was used. The calculated results were validated experimentally.
- Regimes for the synthesis of nanocomposites in Ti-Al-B-C composition were elaborated;
- Rational EC technology was selected for fabrication of bulk materials by blast induced syntheses.

Acknowledgement
The work is supported by Sh. Rustaveli National Science Foundation (Grant #YS15_2.2.10_84).
References

[1] R. Mania, M. Dabrowski et al. Some application of TiAl-Micropowders Produced by Self-Propagating High Temperature syntheses, *International Journal of Self-Propagating High-Temperature Synthesis*, 2003 vol. 12 no. 3 s. 159–164

[2] E. A. Levashov, B. R. Senatulin et al, Peculiarities of the Functionally Graded Targets in Combustion Wave of the SHS-System with Working Layer Ti-Si-B, Ti-Si-C, Ti-B-N, Ti-Al-B, Ti-C, Book of Abstracts. IV Int. Symposium on SHS, Technion, Haifa, Israel, Feb. 17-21, 2002, p. 35

[3] A.N.Pityulin, A.E.Sytschev, A.S.Rogachev, A.G.Merzhanov. One-Stage Production of Functionally Graded Materials of the Metal-Hard Alloy Type by SHS Compaction. *Proceedings of 3 rd Int. Simp. on FGM*, Lausanne, Switzerland, pp. 101-108 (1995).

[4] N. Das, G. K. Dey et all, On Amorphization and Nanocomposite Formation in Al-Ni-Ti System by Mechanical Alloying, *Pramana Journal of Physics, Indian Academy of Sciences*, Vol. 65, No. 5, November 2005, pp. 831-840

[5] J. Hebeisen, P. Tylus, D. Zick, D. K. Mukhopadhyay, K. Brand, C. Suryanarayana, F. H. Froes, “Hot Isostatic Pressing of Nanostructured γ-TiAl Powders”, *Metals and Materials*, Vol. 2. No. 2 (1996) pp. 71-74

[6] C. Suryanarayana, T. Klassen, E. Ivanov, “Syntheses of Nanocomposites and Amorphous Alloys by Mechanical Alloying”, J. Materials Science, (2011) 46.6301-6315

[7] R. Prummer, Explosive Working of Porous Materials, Springer-Verlag Berlin Heldelberg, New York, 1987

[8] N. N. Thadhani, Shock-Induced Chemical reactions in Exotermic Intermetallic-Forming Powder Mixture Systems, *Proceeding of ICCES’05*, 1-10 December, 2005, India, p. 394

[9] N. Chikhradze, K. Staudhammer, F. Marquis, M. Chikhradze, Explosive Compaction of Me-Boron Containing Composite Powders, *Proceeding of Powder Metallurgy World Congress & Exhibition, PM2005*, Prague, Czech Republic, V.3, pp. 163-173, 2005

[10] N. Chikhradze, C. Politis, H. Henein, Formation of Ultrafine Grained Bulk Si and Si-Ge Alloys by Shock Wave Compaction Technology, *Proceeding of PM2010 World Congress – Nanotechnology*, v. 1, pp. 321-326