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HIGH TEMPERATURE MATERIALS SYNTHESIS FOR DEFENCE APPLICATIONS: CURRENT STATUS AND FUTURE TRENDS

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Abstract: *When it comes to materials synthesis, conventional techniques usually require low to moderate temperatures in order to avoid extreme conditions that could possibly impose limitations during the process. This would imply that a barrier is set upon the variety of materials that can be synthesized resulting in severe penury for specific materials required for extreme conditions. Such extreme conditions are found for example when rocket or space shuttles attempt reentry into the Earth's atmosphere. There, due to friction, extremely high temperatures make their appearance and sometimes test the limits of the heatshields used to prevent structural damage and complete destruction of the vehicle. Unfortunately, significant accidents have been observed in the past with the most notable that of the Columbia Space Shuttle (STS – 107) that disintegrated on February 1st, 2003 upon reentry into the Earth's atmosphere. This accident was found to originate from a faulty ceramic tile used in the heat shield that triggered an uncontrollable chain reaction that resulted in the catastrophic failure of the heat shield. This accident, especially, acted as a catalyst in order to investigate new materials that would withstand extreme high temperatures and thus would require extremely high temperatures to synthesize. In this work we will present new synthesis techniques that are non – conventional and have been widely used in order to synthesize novel materials that span from oxide glasses, to Graphene and open up new paths and functionalities with great importance in Defense, Security and Aerospace applications.*

Keywords: *High Temperature, amorphous materials, ceramics, non-conventional synthesis, defense applications*

1. Introduction

For the most procedures requiring materials synthesis the first step is to choose a suitable phase diagram that describes the relationship of the composition versus temperature for various binary or ternary phase diagrams. It also shows the phases that will occur for a constant composition while temperature rises or for a constant temperature and/or pressure. Phase diagrams are essentially a road map that will provide information about the behavior of the material for various temperatures and compositions. This is especially important for amorphous materials and especially oxide glasses. Binary phase diagrams with many eutectic points can prove exceptional candidates for amorphization. This is because at the eutectic points the material transits from the liquid state to the solid state without having to exist in any other phase, namely liquid and solid in a binary mixture. Physiochemically this is also important for glasses because this means that the supercooled region for a glassy system is very small. Hence the basic principle for glass formation that dictates rapid cooling would also favor this kind of supercooling regions that will favourably transit the material from the melt to the glass.

Because high temperatures are not only difficult to achieve but also difficult to maintain, various new techniques have been proposed in order for fast melting and accuracy. The most important technique in this direction is the CO_2 laser melting, where a CO_2 laser operating in a continuous wave mode at 10.6 μm of wavelength is used in order to melt, extremely fast, various types of materials.

If we focus on glass synthesis, achieving high temperatures is a delicate process, where the initial batch is melted usually contained in special containers (such as alumina, or platinum) until complete melt of the batch occurs. Subsequently, the melt is poured on aluminum or steel plates and is rapidly cooled in order to achieve vitrification. This process though, although extremely popular and fundamental in terms of glass synthesis has some important limitations. The first and most important is that when very high melting temperatures are required, then there is a high possibility that the melt will start reacting with the crucible inside which is contained. That will cause severe contamination of the melt resulting in a glass with altered composition and obviously altered properties than the ones desired from the initial batch. This is also possible not only for Al_2O_3 crucibles but also Pt. This obstacle in glass synthesis was overcome by combining the CO_2 laser melting with aerodynamic levitation (ADL) and thus practically vitrifying the sample on an air cushion [1].

Glasses and amorphous materials in general have proved to be important materials when it comes to defense applications. Their use in vehicle armor especially for glass panels (windshields, etc.) have attracted much attention over the years as recent developments call for lighter, thinner and more durable materials in order to counteract the ever-evolving threats.

It is very important, in order to be able to explore new materials possessing new possible functionalities to be able to synthesize them with novel techniques, tackling the problems that were discussed above. This calls for in depth knowledge of their structural characteristics which can be linked with macroscopic properties such as mechanical strength, scratch resistant, antiballistic use and so on.

2. The ADL technique

The ADL technique is based upon the simple principle of equalizing the weight of the levitated sample by the upward force of a stream of air. When these two opposite forces are equal to each other, then stable levitation can be achieved, and the sample is immobilized. After that, the CO_2 laser line irradiates the sample and gradually increases its temperature. The most notable in this technique is that amorphization of the sample takes place in “thin air” as there is no crucible or container that hosts the sample. Thus, this technique is also termed in the literature as “container-less CO_2 laser melting”. In Figure 1 all the different components for the ADL setup are shown.

The procedure involves the following steps:

i) The initial stoichiometric batch is mechanically mixed until a completely homogeneous batch is prepared.

ii) Small amounts of the initial batch are carefully placed on a water-cooled copper hearth in order to synthesize small polycrystalline beads.

iii) The CO_2 laser is turned on and its intensity is gradually increased. The material starts to melt and due to surface tension, a white polycrystalline sphere is synthesized upon shut down of the laser’s beam.

iv) The water-cooled copper hearth is substituted by a copper jet and the sample is levitated under Ar gas flow until stable levitation is achieved.

v) The CO_2 laser beam is turned on and its intensity is gradually increased until complete melt of the sample occurs. Then the laser is suddenly turned off and the melt is rapidly quenched thus yielding a glass bead, completely colorless and transparent. This is shown in Figures 2 and 3.

vi) The procedure is repeated again and again.

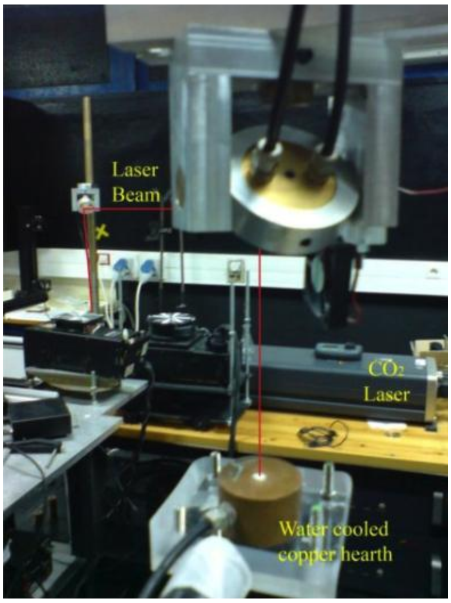

Figure 1. The ADL setup where all the various components are shown [2].

Figure 2. The copper jet with the spherical bead just before melting [2].

Figure 3. The glassy beads after synthesis under the ADL technique [2].

These glasses serve as ideal model candidates in order to elucidate their structural characteristics and thus try to find linkages between structure and properties in an effort to synthesize novel multifunctional materials with enhances properties. The glasses shown in Figure 3, are Yttrium Aluminate glasses in a compositional range 27 mol% $\leq x \leq$ 30 mol% with x denoting the Y_2O_3 content. In a recent study by our group [3] it was made possible to elucidate the coordination environment of Yttrium atoms by means of Nuclear Magnetic Resonance (NMR) spectroscopy and it was found that Yttrium atoms can occupy sites with 6 and 8-fold coordination polyhedra.

Rare earth aluminate glasses are very well known for their superior mechanical properties, high durability and strength which has made them ideal candidates for high durability screens and glass panels.

The CO_2 melting technique has also been used in order to grow 2D materials namely epitaxial Graphene after irradiation of a SiC ceramic wafer [4]. This has brought a revolution into Graphene growth with a fast and reliable method that can provide many functionalities in SiC wafers. This is extremely important in the aerospace industry where specific coatings on turbine blades can be substituted by SiC components which after irradiation can have an epitaxial Graphene layer which in turn can reduce the heat fingerprint of the jet turbines. This is very important in cases where the jets are stealth technology and/or the missions flown require minimal heat fingerprints.

3. Future trends

Because high temperature instrumentation can provide very important data regarding the physicochemical properties of materials, recently, a new expansion of the ADL and CO_2 laser melting was introduced in order to acquire high temperature thermodynamic data. It was termed “drop and catch” calorimeter which was used in order to acquire basic thermodynamic data at very high temperatures, namely, above 1500 ^{0}C [5]. The setup is practically the same, except from the aerodynamic nozzle which now consists of a nozzle that has the ability to split, thus allowing the levitated sample to drop under its own weight. As the sample falls, it is splatted by two copper thermocouples recording a heat signal that is attributed to various properties such as heat of fusion. Figure 4 shows the split nozzle component. This high temperature thermochemistry opens a huge door into understanding more about the thermochemical and thermophysical properties of high temperature materials. Most data originating from this kind of materials are practically unknown because temperatures at this level (above 1500 ^{0}C) could not be reached with conventional methods and of course, as stated above, at this level of temperature everything reacts with everything. This means that no container could be used in order to accept any kind of material without risking reacting with its container. This path has just started to provide results and many more data are expected to be produced with this DnC calorimetry technique.

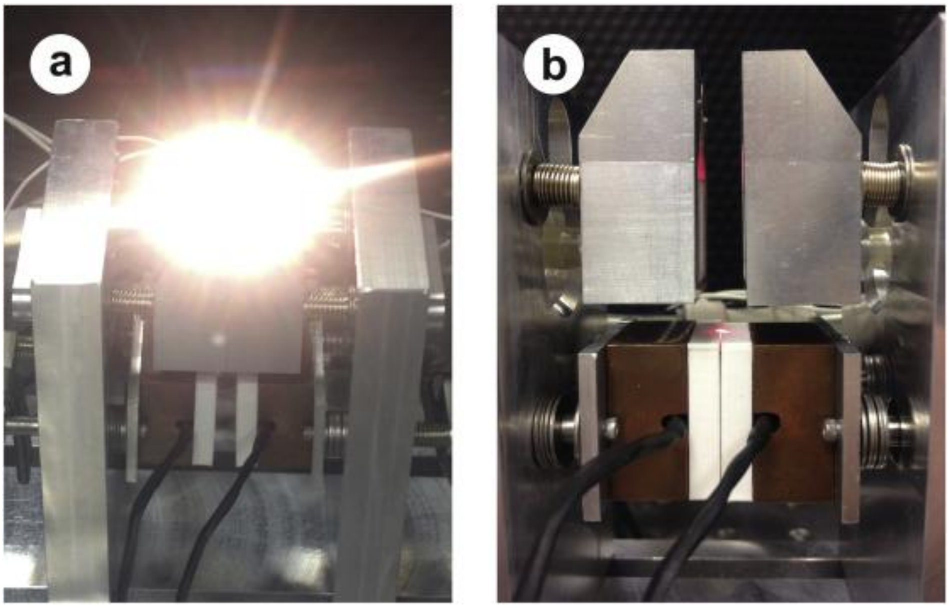

Figure 4. Split nozzle component a) the sample is levitated and melted by the laser b) the nozzle has split and the thermocouples below have splatted it between the two copper ends [5].

4. Conclusions

We presented the novel technique for synthesis of high temperature materials which combines ADL with CO_2 laser melting in order to synthesize a series of novel amorphous materials and 2D materials which cannot be synthesized by any other way due to extremely high temperature required for synthesis. These novel materials have never been systematically investigated in the past which opens up new and unexplored pathways in the variety of possible applications they have in Defense and Aerospace. This technique combined with other novel techniques such as the DnC calorimetry provide the ability to explore new materials with new functionalities as they can withstand extremely high temperatures around and above 1500 ^{0}C.

It is directly evident that new data acquired from these techniques can provide new ceramic and amorphous materials, lightweight, durable, impact and heat resistant that will make them ideal candidates for defense applications and protective gear for personnel and equipment.

We should also keep in mind that these techniques are also very quick in terms of synthesis. Very little time is required in order to melt these materials, of the order of just a few seconds. This implies that materials synthesis can be achieved in large numbers in contrast with large ovens that require a lot of time, sometimes several hours, in order to reach high temperatures and melt similar materials.

We are literally on the verge of a new era in materials synthesis where conventional techniques will be substituted by non-conventional synthesis techniques that will be characterized by precision, quickness and effectiveness. The defense and aerospace ecosystem will surely benefit from them in a future that changes dramatically fast.

5. Acknowledgments

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