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Abstract. Diopside is a type of ceramics highly valued for its beauty and strength. The overall goal of this work is to utilize local raw materials within the following fractions: doloma obtained from mineral dolomite and SiO_2. The density of diopside samples without sintering is 1.87 g/cm^3. It is seen that sintering increases the density of the diopside samples sintered between 1150°C and 1300°C. It has been found that slightly lower tensile strength and micro hardness values in the range of 1 and 4.2 GPa were obtained. To improve the relative density of the sintered diopside and their mechanical properties, different amounts of Na_2CO_3 (0.5 and 1.0 mass%) have been added. The prepared diopside shows a micro hardness in the range of 5.7 GPa through 6 GPa for the samples containing all Na_2CO_3 additions at lower temperatures. A tensile strength of 100 MPa for 1 % of Na_2CO_3 addition was achieved.

Keywords: Diopside, Sintering, Na_2CO_3, Doloma, SiO_2, Mechanical properties

1 Introduction

Since the discovery of biologically active glass, Bioglass®, by Hench et al. in 1970 [1], a great deal of much research has been carried out to apply glasses and glass–ceramics as human tissue substitutes. Actually, various kinds of bioactive glasses and glass–ceramics have been developed for use as biomedical materials [2-4]. Particular ceramics have been used as materials for artificial bone preparation [5]. Having biological affinity, calcium phosphate based ceramics such as hydroxyapatite (HAp) and tricalcium phosphate are used as biomaterials. Nevertheless, due to their poor mechanical properties, in particular their low fracture toughness, they cannot be used under a heavy load and their application is limited [6]. Therefore, in order to avoid all these drawbacks mentioned above selecting another material called diopside is an option of great importance. Diopside with chemical formula ($CaMgSi_2O_6$) is well accepted by the human body. This material can be used as for artificial bone preparation [5, 7] because they form a real bond with the surrounding bone tissue when implanted.

Calcium silicate based biomaterials including bioglass are nowadays a hot topic of research for bone tissue repair applications [8]. Diopside ($CaMgSi_2O_6$) belongs to the

group of silicate biomaterials and they have the ability to release silicate ions at a given concentration which helps osteoblasts to grow and differentiate [9]. It has been reported that the diopside has ability to induce apatite formation in-vitro in simulated body fluid (SBF) and bone formation in vivo [10]. Furthermore, it has been confirmed that the diopside possesses good bioactivity and excellent bending strength, fracture toughness both in-vitro and in-vivo [11]. In that respect, presently bioactive ceramics such as HA and β –TCP lack adequate mechanical strength which limits their application in load bearing area. On the other hand, calcium silicate and bio glass have a relatively quick degradation rate. Based on these considerations, diopside could therefore be considered, to be potential biomaterial for artificial bone and tooth.
Nonami et al. found that diopside, belonging to the ternary CaO-MgO-SiO_2 system has a fairly high mechanical strength and a satisfactory biological affinity, this giving a good biocompatibility [11]. According to a series of reports on diopside, the sintered body of diopside forms an apatite layer on the surface in contact with SBF [12, 13], and combines with living bone tissues more rapidly than HA in animal experiments [11]. On the basis of these findings, diopside is expected to have an excellent potential as a biomaterial for artificial bone and dental root. Moreover, the weight loss of diopside in an aqueous solution of lactic acid and physiological salt solution was also less than that of HA [11].
Furthermore, there are many diopside preparation routes: from its SiO_2, MgO and CaO constituent oxides, sol-gel process [12, 13], and solid-state reaction method. Because of their potential costs and relatively complicated samples preparation, the first two routes are discarded. For example, when powders were synthesized by sol-gel process, many expensive and toxic chemicals (such as acids) are generally used. Consequently, an alternative process is proposed. This process consists of replacing more expensive materials by other raw materials which are less expensive (and non toxics) and which are abundantly available. Also, because of Algeria is one of the countries in the world that have abundantly available raw materials. Another important advantage is the substantial reduction in energy use by decreasing the sintering temperature from about 1300°C to about 1225°C, when the present work is mainly focused on the effect of Na_2CO_3 additions on lowering sintering temperatures and improving both the relative density and mechanical properties of diopside specimens. This voluntary Na_2CO_3 addition was selected in this work in order to ameliorate certain physic-chemical properties of the elaborated diopside based bio-ceramics. Actually, Na_2CO_3 oxide besides of its relatively lower melting point is generally well classified as a biomaterial [14].

2 Materials and methods

2.1 Preparation of specimens

The diopside was prepared by weighing out the specified quantities of a pure SiO_2 and doloma (CaO.MgO) powders. The doloma (CaO.MgO) has been obtained from dolomite after calcination at 950°C for 4 h. The purity of the added doloma is about

99.6 mass%. It contains, mainly, 0.27 mass% Fe_2O_3, 0.07 mass% Al_2O_3 and 0.02 mass% Na_2O as impurities. As reported by Ming et al. [15], this raw material may be classified as a high-purity calcium and Magnesium oxides (CaO.MgO ≥ 99.0%).

Doloma was mixed with 55.5 mass% SiO_2. Afterwards, the mixtures were ball milled in aqueous media for 4 h, dried and calcined at 700°C, during 2 h. Two sintering processes were applied; the first route is usually used to produce the diopside, even thought it leads to a low density; it is called process 1[16]. The second route is the proposed process used in this study. Egg white amounts (10 mass%) have been added into the above powders before mixing and compacting at 120 MPa. After drying at 80°C [16], the samples were sintered in the range of temperature 900-1300°C for 2 h.

Then, Na_2CO_3 was added in the range of 0.5-1.0 mass%. Afterwards, the powder was uniaxially compacted at 112 MPa into disks of 13 mm in diameter (according to the second process). The green compacts were, subsequently, fired at different temperatures ranging between 1100°C and 1275°C for 2 h. The bulk density was obtained by using water displacement or Archimedes method. The proposed process is more detailed elsewhere [17].

2.2 Characterizations

The tensile strength testing of specimens was obtained using a diametral compression test (FORM TEST SEIDNER D 79-40) (Germany). One of the fundamental aspects of this test is the relatively small proportion of the specimen volume which reaches the peak stress at fracture.

In its simplest form, a right circular cylindrical specimen is compressed diametrally between two flat platens. A biaxial stress state is produced within the test specimen and, on the assumption of ideal line loading; the vertical plane is subjected to a uniform horizontal tensile strength of magnitude

$$\sigma_t = 2P/\pi dt \tag{1}$$

where σ_t (MPa) is the maximum tensile stress, P(N) is the applied load at fracture, d(mm) is the specimen diameter and t(mm) is the specimen thickness.

The correspondence between measured tensile strength (σ_t) value and its equivalent 3 point flexural (bending) strength (σ_f) is given by the following equation:

$$\sigma_f \text{ (MPa)} = 2.7\ \sigma_t \text{ (MPa)} \tag{2}$$

This equation was also confirmed by ref. [18, 19]. It should be noticed that this deduced flexural strength is needed for comparison since it is generally used by the major investigators.

Hardness is an important mechanical property for the application of various materials. A general definition of hardness is the mechanical resistance of a solid object to permanent change1. Various experimental methods for determining hardness are available, e.g., Vickers, Brinell, Rockwell, and Knoop. The principle of these methods is to measure indentation hardness, i.e., a harder material is indented to a sample at a selected load with the size of the indented hole being related to the hardness of the material. From an industrial point of view, it is desirable to predict the hardness of a new material before manufacturing. If prediction is feasible, it could furthermore contribute to the development of new superhard materials.

In this study Vickers hardness values were measured with a micro-hardness testing machines (Leitez Wetzlar 6844) (Germany). Phase compositions of prepared samples were identified by X-ray diffraction (XRD) (BRUKER, D8 ADVANCE) (Karlsruhe, Germany) with a CuKα radiation ($\lambda = 0.154$ nm) and a Ni filter, working voltage 40 kV, and working current 30 mA.

3 Results and Discussion

3.1 Sintering of Samples

It should be noticed that there are many diopside preparation (synthesis) routes: from its SiO_2 and CaO constituent oxides, sol–gel process and the present process in question. Because of their potential costs and relatively complicated samples preparation, the first two routes are discarded.

For example, when powders were synthesized by sol–gel process many expensive and toxic chemicals (such as acids) are generally used. Consequently, an alternative process is proposed. This process consists of replacing these more expensive starting materials by others less expensive (and non toxics) and activated CaO powders. It has been found that, using the two proposed processes described before; the density of diopside samples sintered at 1300°C for 2 h is less than 82% of the theoretical density, using the first process. In contrast to this, about 96% of theoretical density is achieved according to the second (present) process, under the same conditions and without any addition. That is why this process has been selected or applied in this study.

Selected X-ray spectra of diopside samples (without additions), sintered at different temperatures (800° -1300°C), are shown in Fig. 1a.

This figure shows that diopside crystallization is improved when the sintering temperature is increased, where the more intense peaks of monoclinic diopside are visible.

3.2 Effect of Na_2CO_3 additions on sintering of compacts

The effect of Na_2CO_3 additions on diopside nucleation and crystallization is shown in Fig. 1b. Selected XRD spectra of samples containing different amounts of Na_2CO_3, sintered 740°C are shown in figure 1b. This figure shows that diopside crystallization first begun in samples containing 0.5 and 1.0 mass% of Na_2CO_3, by the appearance of the more intense peaks of monoclinic diopside. By contrast, the crystallization of diopside for samples containing lower percentages (0.5 mass% Na_2CO_3) is delayed. Therefore, it can be said that Na_2CO_3 additions (for concentrations higher than 0.5 mass% Na_2CO_3) promote diopside crystallization process at a relatively lower temperature (740°C).

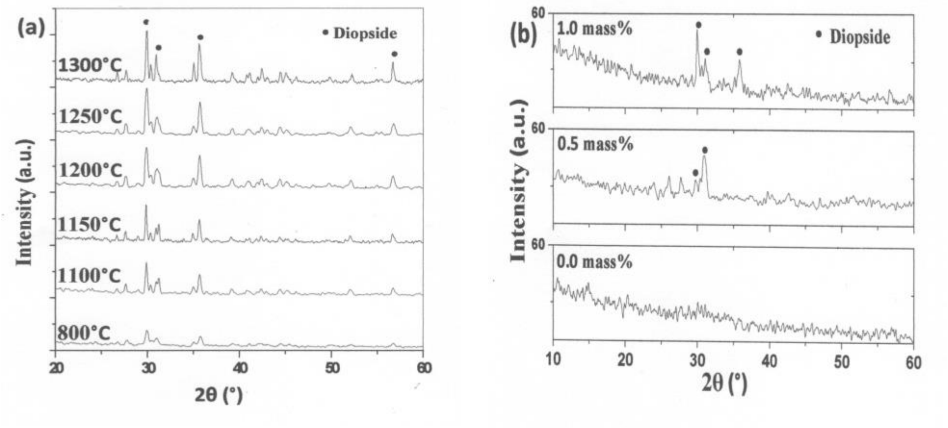

Fig. 1. (a) XRD spectra of diopside samples (without additions) sintered at different temperatures for 2 h. and (b) XRD spectra of specimens, containing different percentages of Na_2CO_3 (mass%), calcined at 740°C for 2 h.

The green density of diopside samples was 1.87 g/cm^3. It is seen that sintering increases the density of the diopside samples sintered at a temperature ranged between 1100° and 1300°C, while a decrease in relative density is occurred between 1300 and 1325°C. To improve both the relative density and mechanical properties of the sintered diopside samples, different amounts of Na_2CO_3 (0.5 - 1.0 mass%) have been added. It has been found that the sintering temperature is lowered by about 75°C when Na_2CO_3 was added. In fact, the sintering temperature of samples without additions was decreased from 1300 to 1225°C for samples with Na_2CO_3 addition.

An enhancement in relative density of diopside samples was obtained when different amounts of Na_2CO_3 have been added. In fact, a relative density higher than 93% of theoretical is reached, for diopside samples containing, only, 1.0 mass% Na_2CO_3 and sintered at 1225°C for 2 h (Fig. 2a). This value is much higher than that of diopside samples (83%) without Na_2CO_3 additions. The effect of both sintering temperature and Na_2CO_3 additions on the bulk density of compacts is illustrated in fig. 2a. It puts in evidence the presence of three main stages. The first one (from

1100° to 1225°C) is characterised by a sharp increase in relative density with increasing sintering temperature, for all prepared samples. In the intermediate stage (from 1225° to 1250°C), the relative density levelled at constant values for all samples, apart from diopside samples without additions, sintered at 1250°C. Finally, a slight decrease in relative density is obtained, in the third stage (from 1250° to 1300°C). The relative density of diopside samples, can reach 98.1% of theoretical density for diopside samples containing 1 mass% Na_2CO_3 and sintered at 1250°C for 2 h (Fig. 2a). This value is much higher than that measured for diopside samples (86.2%) without Na_2CO_3 addition.

The high rate of sintering during the first stage for samples containing 0.5 and 1 mass% Na_2CO_3 confirms the significant effect of this addition on the liquid phase formation. Therefore, the liquid phase sintering mechanism is evident. Even though several mechanisms may be distinguished, by which the liquid phase contributes to its sintering. Additionally, the presence of the liquid phase may lead to the re-arrangement of atoms and becoming consequently more mobilized. The presence of the liquid phase may also encourage small particles to move through it towards the concavity regions of larger granules or particles in order to promote grain growth and therefore greater densification of the material.

However, the semi-stability observed in the second stage may be due to the fact that sintering reached its final stage, where the formed pores were closed, and the increase in temperature cannot increase further the sintering rate. Moreover, during the third stage the sintering temperature of diopside ceramics is lowered by the addition of 0.5 and 1.0 mass% Na_2CO_3. Because of its lower melting temperature, Na_2CO_3 may promote sintering of diopside. By contrast, the addition of 0.5 and 1 mass% Na_2CO_3 decrease the rate of sintering (during the third stage). This decrease may be due to the formation of an excessive liquid phase. In fact, the increase in sintering temperature may encourage excessive formation of the liquid phase which inhibits sintering in its turn. In addition, higher sintering temperatures may lead to the exit of some gases (like oxygen) involved in the chemical composition of raw materials. So, this is may be the main factor controlling this decrease in sintering rate. However, one can attribute this decrease to diopside decomposition. This interpretation may also be discarded because of its stability, in all sintered samples at the last stage.

3.3 Effect of Na_2CO_3 additions on mechanical properties of sintered diopside samples

Fig. 2b shows Vickers micro-hardness values of sintered samples. As would be expected, there is a significant increase in Vickers micro-hardness with the increase in sintering temperature (from 1150 to 1250°C) of samples containing 0.5 and 1 mass% Na_2CO_3. Micro-hardness value of about 6.0 GPa is obtained for samples with 1 mass% Na_2CO_3 at a relatively lower sintering temperature (about 1250°C), but the micro-hardness of samples without addition sintered at 1300°C is 4.7 GPa. When sintering temperature becomes higher than 1250°C, a remarkable decrease in micro-hardness for samples containing 0.5 and 1 mass% Na_2CO_3 is observed. By contrast, there is a continuous increase in Vickers micro-hardness for samples without additions. Consequently, its best hardness value was moderate (4.7 GPa) compared to human dental enamel (4 GPa) [19] and therefore is more suited for dental restoration purpose. This value (6.0 ± 0.4 GPa) is also significantly much higher than that reported by Zhang et al. [21] (5.4 MPa) of diopside-HA cmposite.

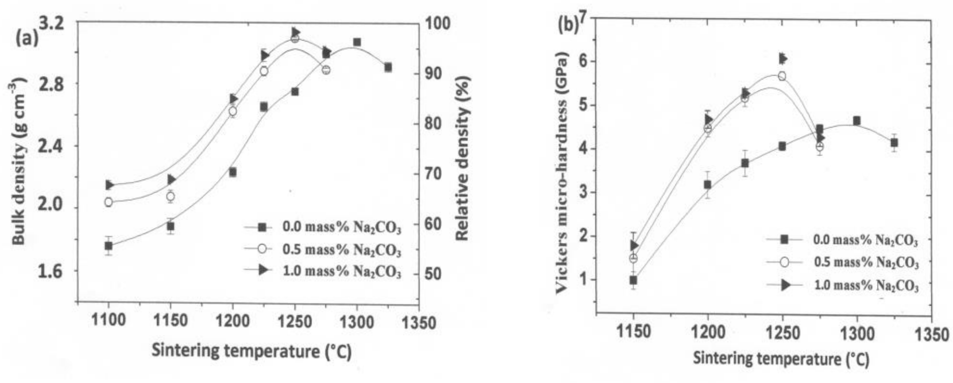

Fig. 2. (a) Effect of Na_2CO_3 additions on sinterability of diopside samples sintered at different temperatures for 2 h. and (b) Vickers micro-hardness as a function of sintering temperature for specimens containing different mass% Na_2CO_3.

Bending strength values of sintered diopside samples are shown in Fig. 3a. It was observed that a higher three point bending strength (264 ± 6 MPa) was also obtained for samples containing 1 mass% Na_2CO_3 and sintered at 1250°C for 2 h. By contrast, for samples sintered at 1275°C the bending strength decreased by the increase in Na_2CO_3 additions. For example, the bending strength decreased from 192 MPa for samples containing 0.5 mass% Na_2CO_3additions to about 160 MPa for samples containing 1 mass% Na_2CO_3. This decrease in bending strength values of samples containing 0.5 and 1 mass% Na_2CO_3 and sintered at 1275°C for 2 h is also accompanied with the decrease in Vickers microhardness of these samples. It can be said that these results underline the beneficial effect of Na_2CO_3 additions on bending strength and Vickers micro-hardness values of diopside samples. Indeed, the bending strength value of diopside samples was doubled when 0.5 and 1.0 mass% Na_2CO_3 has been added, for samples sintered at 1200°C under the same sintering conditions. For example, the bending strength increased from 140 MPa for samples without additions to about 163 MPa for samples containing 0.5 mass% Na_2CO_3. However, Vickers micro-hardness is also doubled but for samples containing only 1 mass% Na_2CO_3. A careful exam of Figs. 2a, 2b and 3a show that both Vickers micro-hardness and bending strength values of sintered diopside samples are, as would be expected, closely related to their relative densities. One can compare the obtained three point bending strength values using the present process with those reported by other studies carried out on diopside-based ceramics and particular materials. For example, the maximum bending strength (264 ± 6 MPa), in this study was obtained for $CaMgSi_2O_6$ ceramics containing 1 mass% of Na_2CO_3, sintered at 1250°C for 2 h, using the present process. It should be noticed that this higher strength is in a good agreement with the microstructure shown in Fig. 3b as reported by Ref. [18]. In fact, the cleavage incidence is clearly noticeable on this microstructure of fracture surface. In fact the dominant mode of fracture is trans granular. Obviously, this bending strength value is extremely higher than those reported by other works carried out on HA-based ceramics. For example, Nayak et al. [22] have found that the addition of 2 mass% ZrO_2 into HA increased its bending strength from about 35 to 70 MPa. Moreover, a bending strength of 300 ± 20 MPa was obtained for yttria-stabilized zirconia ceramics + 5 mass% of bioglass samples sintered at 1200°C [23], while nearly the same bending strength value (264 ± 6 MPa) was also measured for $CaMgSi_2O_6$ ceramics containing 1 mass% Na_2CO_3, sintered at 1250°C for 2 h, using the present process.

This result shows clearly the importance of the obtained value of bending strength when is compared (within the error bars) to one of the most resistant ceramics (corundum-based refractories). In fact, these interesting bending strength values are of great importance for many bioceramics applications.

A previous study showed that the bending strength may be controlled by many factors [24]. A general correlation seems to exist between densification, microstructural changes (average grain size, grain-size distribution and total porosity) and bending strength in sintered compacts as follows:

1. Densification and grain size are the dominant factors controlling strength, since most of the total pores were inter granular, e.g. the substantial increase in strengths of samples corresponded to a parallel increase in density which means a decrease in porosity ratio.

2. Consistently, the relatively higher strengths were occasioned by high relative densities and grain-size factors. This means that densification enhances bending strength whereas pore coalescence acts oppositely on it, in the presence of liquid phase.

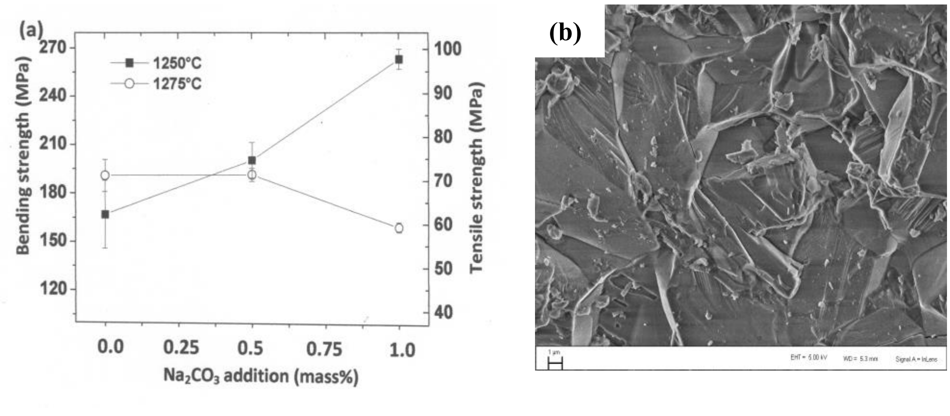

Fig. 3. (a) Tensile strength as function of Na_2CO_3 percentages (mass%) for samples sintered at 1250 and 1275°C for 2 h. and (b) SEM micrographs of diopside samples (without additions) sintered at 1300°C for 2 h.

4 Conclusions

It can be concluded that the relative density of diopside samples is closely related to both sintering temperatures and Na_2CO_3 addition. By addition of Na_2CO_3, sintering temperature was lowered by about 50°C (from 1300 to 1250°C). A relative density higher than 97% of the theoretical was reached for samples sintered, only, at 1250°C and containing 0.5 mass% Na_2CO_3. Micro-hardness value of about 6.0 GPa was obtained for samples with 1.0 mass% Na_2CO_3. An excellent three point bending strength value (264 ± 6 MPa) of samples containing 1.0 mass% Na_2CO_3 was achieved.

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