JKAU: Eng. Sci., **Vol. 22** No.1, pp: 3-16 (2011 A.D. / 1432A.H.)
DOI: 10.4197 / Eng. 22-1.1

The Effect of 5 wt %Yettria-Stabilized Zirconia on Crystallized Glass-Ceramic System at Different Temperature

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Abstract. This work focuses on studying the effect of (5)wt% Yettria-stabilized Zirconia (ZrO_2 .Y_2O_3) addition on the crystallized glass – ceramic at different crystallization temperatures(*i.e.* 800, 900, 1000, 1100ºC) in the system (Na_2O – CaO – SiO_2 – P_2O_5), in order to get suitable materials that might have better physical, mechanical & biological properties that render them to be used safely to repair and reconstruct the diseased parts of living bodies. The results show an improvement in the mechanical properties due to the competition between the additions of the (ZrO_2 . Y_2O_3) and the crystallization temperature .The toughening phase (ZrO_2.Y_2O_3) works as a glass former and an intermediate that resulting in the formation of strong and tough glass-ceramic reinforced by the phases $ZrSiO_4$ and $CaSiO_3$. A radiological examination for one month of an implanted sample of a sintered glass-ceramic that contains (5)wt% of (ZrO_2.Y_2O_3) in a bone tibia of a local breed dog was done .The results revealed no sign of inflammatory at the site of the operation and no toxic substances were released, with a complete bone defect bridging.

Keywords: Bioceramic; Bioactive; glass; ceramic; Fracture toughness; Sintering.

1. Introduction

Of the mineral phase of bone. It consists of 70% limits, so that it will be responsible For the advancement of science and technology in the development of high-impact materials, ceramic products, especially those used in medical, veterinary, pharmaceutical and biological applications invented, and used in the construction of the living body in order to repair or replace the defective parts after cultivation in compensation for the damaged fabric [1].

In 1960, the used ceramic materials were mainly zirconia and alumina inside the body, in contaminate with the living tissue because it provides the biocompatibility as well as high mechanical strength[2].

Bonding to bone was first demonstrated for a certain compositional range of bioactive glasses which contained SiO_2, Na_2O, CaO, and P_2O_5. There are three keys which are considered a compositional feature to these glasses that distinguished them from traditional $Na_2O - CaO - SiO_2$ glasses[3]:

- Less than (60) mol. % SiO_2.
- High - Na_2O and high – CaO content.
- High – CaO / P_2O_5 ratio.

Then the glass was used to be an effective bio- active material, which has the ability to link and evaluate the backbone, and then produce a glass – ceramic that contains hydroxyapatite [Ca_{10} (PO_4) 6 (OH) $_2$] symbolized by (HA),and therefore speeds up the proportion of bone formation in the pores [4]. Therefore, ceramic materials have become a natural choice for the replacement of bones and teeth as well as other applications [5-7]. Apatite phase that is taking shape in the effective implantation vital to have the same chemical composition for the link surface interface [8-10]. Based on glass that used for implantation of silica(SiO_2) base and which may contain small amounts of crystalline phases, the development has begun the first of such kind of bio-glass windows when Hench suggested a vital installation.SiO_2 base consists of (6% P_2O_5, 24.5% Na_2O 24.5% CaO, 45%SiO_2) it is very effective in building bone, compared with hydroxyapatite [11]. As a result of the effective surface in response to these types, activities of such materials are considered as vital or active substances.

Produced glass ceramic contains OXY Fluorite apatite Ca_{10} (PO_4) 6 (OHF) $_2$, and wollstonite $CaSiO_3$ in the glass matrix of the (MgO - CaO - SiO_2), called glass- ceramic, and another ceramic has been developed called a vital bioferrait and contains apatite and flokofait Mg_3 ($AlSi_3O_{10}$) (F_2) [Na, K] used in medical applications [12].

There are also silicon rubbers. cellophane, and carbon [13-15], but the main disadvantage of these materials are being difficult to be used as a structural material and, difficult to set up or assembled to give useful synthetic materials [8]. Table 1 explains the stages of the interaction of the materials of certain activity with the living tissue.

The present research covers the manufacture of bioactive- glass - ceramic in the system (Na_2O-CaO-SiO_2-P_2O_5) using the process of sintering to prepare the products for medical implantation which are more appropriate and may have better physical, mechanical and biological characteristics when compared with the glass –ceramic that crystallizes from the cast bulk glass.

Table 1. Reaction stages of bioactive implant.

Stage	***Reaction***
1	Rapid exchange of Na^+ or K^+ with H^+ or H_3O^+ from solution: $Si\text{-}O\text{-}Na^+ + H^+ + OH^- \rightarrow Si\text{-}OH^+ + Na^+\ (solution) + OH^-$ This stage is usually controlled by diffusion and exhibits a $t^{-1/2}$ dependence.
2	Loss of soluble silica in the form of $Si(OH)_4$ to the solution, resulting from breaking of Si-O-Si bonds and formation of Si-OH (solution) at the glass solution interface: $Si\text{-}O\text{-}Si + H2O \rightarrow Si\text{-}OH + OH\text{-}Si$ This stage is usually controlled by interfacial reaction and exhibits a t^{10} dependence.
3	Condensation and repolymerization of a SiO_2 –rich layer on the surface depleted in alkalis and alkaline – earth cations: $O\text{–}Si\text{-}OH + HO\text{–}Si\text{-}O \rightarrow O\text{–}Si\text{-}O\text{–}Si\text{-}O + H_2O$
4	Migration of Ca^{2+} and PO_4^{3-} groups to the surface through the SiO_2- rich layer forming a CaO-P_2O_5- rich film on top of the SiO_2- rich layer, followed by growth of the amorphous CaO-P_2O_5 rich film by incorporation of soluble calcium and phosphates from solution.
5	Crystallization of the amorphous CaO-P_2O_5 film by incorporation of OH^-, CO_3^{2-}, or F^- anions from solution to form a mixed hydroxyl, carbonate, fluorapatite layer.

The maximum fracture toughness for the sintered glass powder compact in this study was achieved due to surface roughness, crack tilting and twisting during propagation, caused by thermal expansion mismatch and elastic modulus mismatch stresses which play an important role in toughening the formed glass-ceramic, *i.e.*, Termed (toughening by crack deflection). It's believed that $ZrO_2.Y_2O_3$ addition will act as a handicap to crack propagation and increase the internal strength [16] .

The crystallization of glass to form glass - ceramic results in the formation of voids, which coalesce to form large pore. The voids

accumulate periodically like tree rings, and become a structural defect that degrades the mechanical properties of the glass - ceramics. For that we had suggest the idea of using the sintering process with $ZrO_2.Y_20_3$ addition to improve the engineering. Characteristics of the (Na_2O – CaO – SiO_2 P_2O_5) system.

Table 2. Present Uses of Bioceramics [1].

Orthopedic load – bearing applications Al_2O_3 ,Stabilized zirconia , PE – HA composite
Coatings for chemical bonding*(orthopedic, dental, and maxillofacial prosthetics)*
Dental implants Al_2O_3 , HA , Bioactive glass – ceramics
Alveolar ridge augmentations Al_2O_3 , HA , HA- autogenously bone composite , HA- PLA composite , Bioactive glasses
Otolaryngological Al_2O_3 , HA , Bioactive glasses , Bioactive glass – ceramics
Artificial tendon and ligament PLA – carbon – fiber composite
Artificial heart valves Paralytic carbon coating
Coatings for tissue I ngrowth (cardiovascular, orthopedic, dental, and maxillofacial prosthetics) , Al_2O_3
Temporary bone space fillers TCP , Calcium and phosphate salts
Periodontal pocket obliteration HA , HA- PLA composite , TCP , Calcium and phosphate salts , Bioactive glasses
Maxillofacial reconstruction Al_2O_3 , HA , HA – PLA composite , Bioactive glasses
Percutaneous access devices Bioactive glass – ceramics , Bioactive glasses , HA
Orthopedic fixation devices PLA – carbon fibers , PLA – calcium phosphate – bases glass fibers
Spinal surgery Bioactive glass – ceramic , HA

2. Experimental Part

Table 3 presents the chemical composition of glass powder, in the system (Na_2O-CaO-SiO_2-P_2O_5) that is used in this study as a raw material for the preparation of sintered samples and sizing of Glass powders to (< 53) microns were done. The physical characteristics of the powder are listed in Table 4.

Table 3. Chemical Composition of Bioactive Glass Powder.

Sample. No	SiO_2 %	CaO %	Na_2O %	P_2O_5 %
bioactive glass	47.68	33.6	8.6	9.8

Table 4. the Physical Properties of the Bioactive Glass powder.

Data	Characteristics
20.831gm/cm^3	Theoretical density
2.61 gm/cm^3	Real density
0.860 gm/cm^3	Apparent density
Fragmented	Particle density
12551.27 gm/cm^2	Surface area
(1160-0.16) microns	Particle size

Table 5 presents the chemical composition of the zirconia powder used in this study. A binder of 2% (Poly - Vinyl Alcohol) (PVA) was added to the glass powder, as well as 1% of calcium fluoride (CaF_2), to contribute to the formation of a Hydroxyapatite,

Table 5. Chemical Composition of (ZrO_2 .Y_2O_3) Powder.

Oxides	Wt. %
ZrO_2 + HFO_2	93.8
Y_2O_3	5.4
SiO_2	0.11
TiO_2	0.12
Al_2O_3	0.25
Fe_2O_3	0.003
Na_2O	0.02
CaO	0.05

Which is essential to tissue formation more rapidly than the glass alone, and increases the layer compounds and their resistance.

Mixing ratios were established by weight of the base bioglass system (Na_2O - CaO - SiO_2 - P_2O_5) with the ratios by weight of zirconia powder partially stabilized yettria of (5) wt%, with 1wt% calcium fluoride .A 250 ml of distilled water was added to binder of 2% PVA in order to completely ensure the dissolution of the binder. The process was accomplished at a slightly high temperature, and time of mixing was 15 minutes, using a laboratory mixer.

After mixing, the slurry was filtered and dried at a temperature of 85°C for two hours and then the powder was re-milled and sized to less than (53) microns. Ratios have been identified and specific weight of glass -ceramic of (3) grams of each sample ,each batch sample was mixed for 2 hours on the base of wet mixing, by adding 1.5% ethanol.

Pressing process was accomplished by using a stainless steel mould (X121) with a diameter of (16.9) mm. Samples were prepared at pressure of (175) MPa of a piston capacity of (12) tons. The process of sintering was completed in an electrical programmable furnace at different temperatures (800, 900, 1000, 1100) ° C The rate of heating and cooling was (5) ° C / min.

2.1 Evaluation

X-ray diffraction test was used to determine the generated phases in the resulting sintered samples. The diffraction angle ranges between (10 - 60) °. Vickers method was used to measure the hardness of the sintered samples at loading force of (5) N [17-18]. To evaluate fracture toughness, indentation by Vickers was used at which the crack length was measured at a load higher than (10kg), and K_{IC} was calculated using equation (1) [18-19].

Where K_{Ic}: the strength of the fracture ($MPa.m^{1/2}$).

P: applied load (kg).

$$K_{Ic} = 0.079\left(\frac{P}{a^{3/2}}\right)\log\left(4.5\ \frac{a}{c}\right) \quad for\ 0.6 \le \frac{c}{a} \le 4.5$$

A: radius of the indent (mm).

L: length of the crack (mm).

C: (a + L) (mm).

2.2 Sample Implantation

One of the prepared samples was implanted in a dog model of A local breed dogs of an age (1.5) year and weight of (15) kg.

Clinical tests were conducted before commencing the experiment to ensure that the model used is free of disease, and it was injected with a dose of the anti-external and internal Ivermection drug of (1) mil for each (kg) of body weight.

The practical steps of the surgical operation include giving the half dose of the combination of Ketamine hydrochloride of (15) mg \ kg ketamine and (5) mg \ kg Zailazen injection (IM), Surgical region was prepared beginning from the Stifle joint to the end of the list, and then giving the second half of the dose till reaching the stage of surgical anesthesia. After determining the location and direction of tibia, (9 × 15 mm in the third part of the leg) construction work of surgeons was done. Tendons were isolated from the opened area under the skin, the exposed bone was removed using electrical drill, and the gap sample was filled by the prepared system (Na_2O – CaO- SiO_2 - P_2O_5) which is reinforced by (5) wt % ($ZrO_2.Y_2O_3$).

After the end of the operation, the released muscles were drove back to their normal township levels, and the type of skin was closed by using a simple surgical silk threads. Then, the model was given a systemic antibiotic of penicillin for (5) days, and streptomycin injections in the muscle. The sutures were taken (7) days after the operation, and the cases were followed up with radiology. The surgery was accomplished at the Department of Surgery, College of Veterinary Medicine- University of Baghdad – Iraq.

3. Results and Discussion

X-ray diffraction patterns, as shown in Fig. 1, were the basis for determining the phases of bone reconstruction, which are the working

Phases to provide a sense of effective chemical bonds with defected bone. Calcium phosphate phase $Ca_2P_2O_7$ appeared at almost all X-ray diffraction patterns of sintered samples. The other major phase observed is the Wolastonite $CaSiO_3$. Which is the phase of glass-reinforced ceramics system? Also other phases were noticed at increasing temperature, (*i.e.* Ca_3 $(PO_4)_2$), as well as (sodium hydrogen phosphate Na_2HPO_4 , zirconia silicate $ZrSiO_4$, phosphate zirconia ZrP_2O_7, and zirconia ZrO_2 as non-interactive).

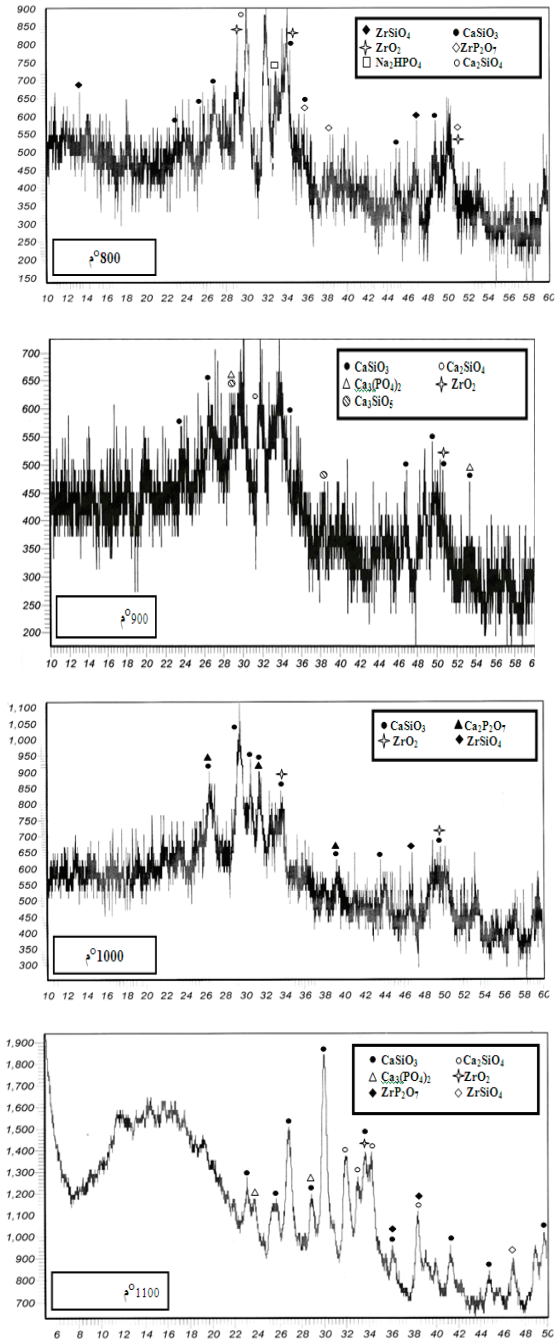

Fig. 1. X-ray diffraction patterns of a system (Na_2O-CaO-SiO_2-P_2O_5) of (5) wt% (ZrO_2.Y_2O_3) at crystallization temperatures (800, 900, 1000 1100) °C.

The reason for the emergence of the first phase of calcium phosphate is due to the shape which is perpendicular to the surface. The rate of growth at the surface is faster than on the inner side, as well as the number of surfaces being relatively numerous and the distance between the grains and the process of calcium phosphate $Ca_2P_2O_7$ is relatively short compared with the inside[1]. It should be pointed out that the overlap between the main phase and the resulting calcium silicate, gives the body its strength and high durability.

The results of the hardness tests by Vickers technique are shown in Fig. 2, and the fracture toughness tests by measuring the length of the indent resulting from Vickers (K_{IC}) used for ceramic materials are shown in Fig. 3 At temperatures of 800° C and up to 1000° C with the existence of zirconia, the hardness and the toughness have decreased with increasing temperature.

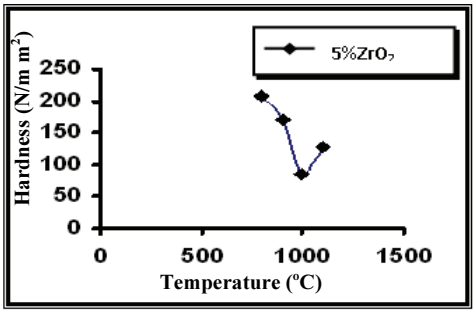

Fig. 2. Effect of Crystallization Temperature in the Hardness of (5) wt %($ZrO_2.Y_2O_3$).

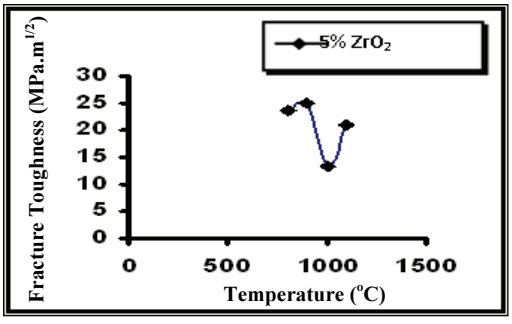

Fig. 3. Effect of Crystallization Temperature in the Fracture Toughness of (5) wt% ($ZrO_2.Y_2O_3$).

As temperature increased, crystal grew with the possibility of increasing the number of cracks, particularly near the grain boundaries, The difference in thermal expansion of phases and the weakness of the reinforced phases $CaSiO_3$ and $CaSiO_4$ increased too. At higher temperature of 1100°C an increase in the values of hardness and fracture toughness which is related to the zirconia added to the composition, was recorded. This increase supports the formation of secondary reinforced phases represented by $ZrSiO_4$ and leads to greater adherence of the bioactive glass- ceramics.

3.1 Biological Evaluation

Examination of X-ray diffraction patterns revealed, as shown in Fig. 1 and Table 6, the appearance of the phases of basic Bone-builder, *i.e*., $Ca_2P_2O_7$ and Wallastonine as a reinforcement phase which has bioactivity, somewhat less. These phases have bioactivity which tends to help in the process of bone recovery in agreement with the findings of Grympas [20]. Speed healing of bone is attributed to the nature of the chemical composition of these phases that are similar to the chemical structure of natural bone mineral that helps into offsetting the loss of bone. As for the biological effectiveness of the models derived from the X-rays radiograph shown in Fig. 4 (a), there is a bone gap filled with prepared sample having dimensions of (10 × 15) mm. At the end of the second week, bone tissue formation and the implant appeared to be of dimensions (15 × 8) mm, as shown in Fig. 4 (b), as a result of the process of absorption of the implanted material.

Table 6. x -ray diffraction phases revealed by addition of (5) wt %($ZrO_2.Y_2O_3$).

Temperatures[^oC]			
800	**900**	**1000**	**1100**
$CaSiO_3$	$CaSiO_3$	$CaSiO_3$	$CaSiO_3$
Ca_2SiO_4	$Ca_2P_2O_7$	ZrO_2	Ca_2SiO_4
		$Ca_2P_2O_7$	
$ZrSiO_4$	Ca_2SiO_4		
ZrO_2	$Ca_3(PO_4)_2$	$ZrSiO_4$	
Na_2HPO_4			

At the end of the fourth week, the defective bone cavity was almost closed without the appearance of any inflammatory or signs of rejection of tissue around the implantation area. The size of the form is invariably almost (14.5 × 8) mm, with a wavy surface because of absorption process. The matter of implanted sample and transformation of the dark appearance of the implant, due to absorption, with clear channel began to show the bone marrow, as shown in Fig. 4 (c).

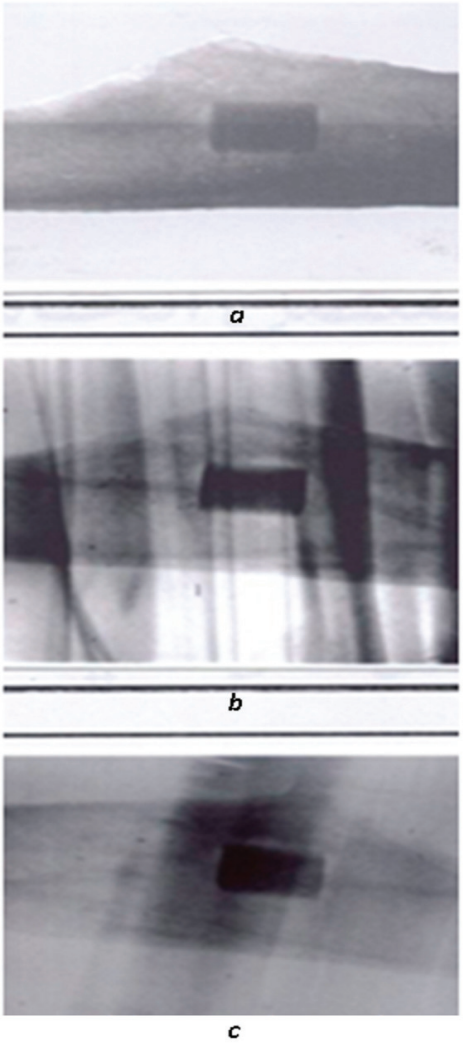

Fig. 4. Radiograph X- ray pictures of the Implanted sample in a Tibia: A-after operation. B-after Two weeks. C- after fourth weeks.

4. Conclusions

a - Temperature of crystallization (800 & 1100) are favorites to reach high hardness and fracture toughness when (5) wt% of ($ZrO_2.Y_2O_3$) is added.

b - Adding (5)wt% of ($ZrO_2.Y_2O_3$) phases which consist of Ca. root such as the strong phases of bioactivity $CaSiO_3$ and $Ca_2P_2O_7$, helps and accelerates the healing process of the bone.

c - Implantation of sintered glass ceramic containing (5)wt%($ZrO_2.Y_2O_3$) in the Tibia bone of a dog, for one month did not show any signs of infection at the implantation site and nontoxic substance release with a building bridge of the defected bone.

5. References

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تأثير إضافة ٥٪ من الزركونيا المثبتة جزئيا باليانريا على تبلور الزجاج–السيراميكي عند درجات حرارة مختلفة

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المستخلص. يركز هذا العمل على دراسة تأثير إضافة الزركونيا المثبتة جزئياً باليانريا وبمدى (5)٪ على تبلور الزجاج – السيراميكي عند درجات حرارة تبلور مختلفة (٨٠٠ – ٩٠٠ – ١٠٠٠ – ١١٠٠)°م في نظام $[Na_2O - CaO - SiO_2 -] P_2O_5$ بهدف الحصول على مادة ملائمة، التي يمكن أن تمتلك خواص ميكانيكية وكيميائية أفضل تؤهلها للاستخدام بشكل امن لإصلاح وتجديد الأجزاء المتضررة للأنسجة الصلدة في ألأجسام الحية.

بينت نتائج الدراسة تحسن في بعض الخواص الميكانيكية مثل الصلادة ومتانة الكسر، ويعود ذلك إلى نسبة الاضافة للزركونيا المثبتة بـــاليانريا و مع تزايد درجة حرارة التبلور. والذى ينتج عن تشكيل زجاج – سيراميكي قوي ومتين مقوى بطور ($ZrSiO_4$) بالاضافة الى ($CaSiO_3$). لقد بين الفحص الشعاعي للنموذج المزروع والمتمثل بـــالزجاج السيراميكي الملبد والحاوي على ٥٪ ($ZrO_2.Y_2O_3$) . في عظم لقصبة كلب لثلاثة اشهر. و المتابعة المستمرة الى عدم حدوث علامات لـــ التهابات في منطقة الزرع وعدم تحرر مواد سامة مع حدوث بناء لجسر عظمي كامل للعيب الذي أُحدث في عظم القصبة لنموذج من انسال الكلاب المحلية.

الكلمات المفتاحية: السيراميك الحيوي، المواد الحيوية، الزجاج – السيراميكي، ومتانة الكسر، التلبيد.