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العدد السادس عشر

دراسة تأثير إضافة اوكسيد النحاس الى الزركونيا

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المستخلص :

تم استخدام الزركونيا نوع (partial stabilized Zirconia: ZrO_2 plus 5.4wt% Y_2O_3) واستخدام بولي فينيل الكحول بنسبة 1% كمادة رابطة خلال عمليات ضغط وتشكيل النماذج. تم اختيار أفضل ضغط لكبس العينات يقابله أفضل كثافة رطبة وكان مقدارها $2.821g/cm^3$ مقابل ضغط مقداره 250bar ، وتم اعتماد هذا الضغط لكبس جميع النماذج المحضرة. تم تحضير نماذج من الزركونيا بإضافة نسب من اوكسيد النحاس مقدارها (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6,) ومن ثم إجراء المعاملة الحرارية عند درجة حرارة $1350^{\circ}C$ لمدة ساعتين بمعدل ارتفاع وانخفاض مقداره $5^{\circ}C/min$. تم حساب بعض الخواص الفيزيائية والميكانيكية كالكتافة ومقدار الانكماش الكلي والقطر وصلادة فيكرز ومتانة الانكسار البرازيلية والمسامية ونسبة امتصاص الماء. من خلال النتائج ظهر انخفاض بمقدار الكثافة والصلادة والمتانة مع زيادة نسب اوكسيد النحاس، وظهر هناك زيادة في قطر النماذج مع زيادة نسبة اوكسيد النحاس.

الكلمات المفتاحية: الزركونيا ، الطور السائل ، صهر المواد .
مجلة العلوم الأساسية

Study the Effect of Adding Copper Oxide to Zirconia

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**Abstract:**

Zirconia (partial stabilized Zirconia: ZrO_2 plus 5.4 wt% Y_2O_3) and 1% polyvinyl alcohol were used as a binder during modeling and compression processes. The best pressure for compressing the samples was chosen corresponding to the best wet density 2.821 g/cm³ against a pressure of 250 bar, and this pressure was approved for compressing all the prepared samples. Samples of Zirconia were prepared by adding percentages of copper oxide of 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1 after that conducting a heat treatment at a temperature 1350°C for two hours at a rate of rise and fall its value is 5°C/min. Some physical and mechanical properties such as density, total shrinkage amount, diameter, Vickers hardness, Brazilian fracture strength, porosity and water absorption were calculated. Through the results, a decrease in the density, hardness, and Brazilian fracture strength appeared with the increase in the percentage of copper oxide, and there was an increase in the diameter of the samples with the increase in the percentage of copper oxide.

Keywords: Zirconia, liquid phase, refractory materials .

1-Introduction:

1-1 Zirconia: Zirconia ZrO_2 was discovered by the German chemist M. H. Klaproth in 1789, and the name zirconium is derived from the Arabic word Zargon, which means golden color. Zirconia is present in nature at a rate of (96.5-98.5) % and in an impure form [1,2].

Zirconia has good mechanical properties such as high toughness, high chemical resistance, chemically inert, high hardness, and high melting point, so it entered many industries, including dental and bone industries as biological applications and in the refractory industry, where it is added to improve its properties [3]. Zirconia changes crystal structures with increasing temperature and returns with a reverse transformation when lowering the temperature. It has three crystal systems, which are the monoclinic system, the tetragonal system, and the cubic system as shown in Fig. (1) [3-5].

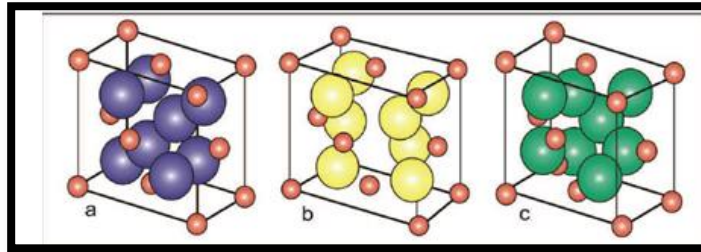


Fig. (1): Crystal structures of ZrO_2 : (a) Monoclinic, (b) tetragonal and (c) Cubic [2]

At room temperature, the system is monoclinic and stable, and when the temperature rises to $1170\text{ }^\circ\text{C}$, it turns into a tetragonal system, then it turns into a cubic system with an increase in temperature at $2370\text{ }^\circ\text{C}$ [3,4]. Fig. (2) Transformations of the crystal structures of Zirconia with temperature [3]. When the temperature is lowered, the reverse transformation takes place, and this phenomenon increases the durability, as well as an increase in size by 4% [5]. These transformations affect the thermal stability of the product. To get rid of these transformations, stabilizers are added to the Zirconia, which are oxides that stop the transformation when the temperature is lowered, such as Y_2O_3 , MgO and CaO . There are two types of stabilized Zirconia [6]:

- Partially stabilized Zirconia PSZ: It is done by adding oxides that are stabilized at a rate of less than 8mol.%
- Stabilized Zirconia (SZ): It is done by adding oxides that are stabilized at a rate greater than 8mol.% .

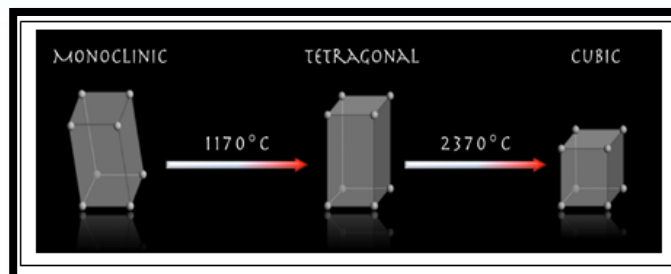


Fig.(2): Transformations of the crystal structures of ZrO_2 with temperature [3]

1-2 Copper oxide: It is one of the chemical compounds of copper. There are two types of oxides, copper oxide CuO and copper oxide Cu_2O [7]. It is



considered an important semiconductor because it has good physical properties. Copper oxide dissolves in acids but does not dissolve in bases or water. Its density is 6.4g/cm³. And its melting point 1235°C and can be obtained from the oxidation of copper, abundantly available, non-toxic and low-cost of production [7-10]. Copper monoxide CuO differs from copper dioxide Cu₂O in color, crystalline structure, optical properties, etc., where CuO is black while Cu₂O is dark red when Cu₂O is exposed to air and temperatures up to 350°C can turn into CuO, and at high temperatures, it is possible for the reverse transformation to occur, i.e. CuO turns into Cu₂O [11,12]. The crystal structure of copper oxide is illustrated in Table (1), while Fig.(3) shows the crystal structure of copper oxide.

Table (1) shows the crystal structure of copper oxide [13]

Phase	Cu ₂ O	CuO
Crystal Structure	Cubic	Monoclinic
Crystal Lattice	a=b=c=4.27Å	a = 4.6837 Å b = 3.4226 Å c = 5.1288 Å ∠ = 99.54°
Shortest Distance		
dCu-O	1.84 Å	1.95 Å
dO-O	3.68 Å	2.62 Å
dCu-Cu	3.02 Å	2.90 Å

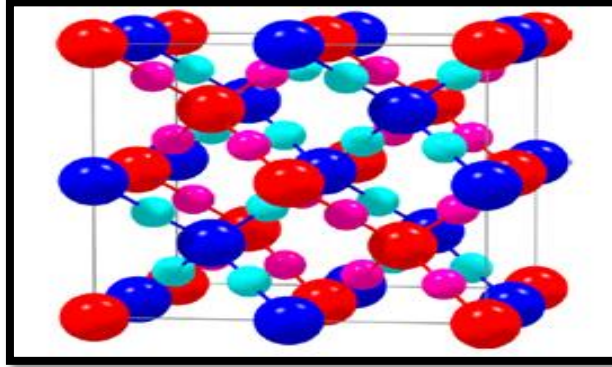


Fig.(3): shows the crystal structure of Cu_2O [13].

2- The Experimental Part:

2-1 Materials used:

Zirconium oxide type partial stabilized Zirconia: ZrO_2 plus 5.4wt% Y_2O_3 from (Zirconia Sales –GU185SS-U.K.), with particle size was $0.39 \mu\text{m}$.

Copper oxide (Cu_2O) supplied by the English company (BDH).

Polyvinyl alcohol - PVA from Chinese polyvinyl alcohol (PVA)-1600 company (www.e-chem.com.cn), PVA was used as a binder.

2-2 Experimental Procedure:

The Zirconia samples were prepared by adding the binder at 1% for the purpose of pressing the samples at different pressures with a steel mold of diameter 10mm to choose the best green density against the preferred pressure. Through the results, the appropriate pressure 250 bar was chosen for pressing the work samples.

The Zirconia samples were prepared by adding percentages of copper oxide of 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1. The samples forming with a pressure of 250 bar and then conducting a heat treatment at a temperature of 1350°C for two hours, the rate of rise and fall in temperature $5^\circ\text{C}/\text{min}$. Some physical and mechanical properties such as density, total shrinkage, diameter, Vickers hardness and Brazilian fracture strength were calculated. Through the results a decrease in the density, hardness, and Brazilian fracture strength and an increase in the diameter of the samples appeared with the increase in the proportions of copper oxide.



2-3 Results and Discussion:

In order to verify the materials used, X-ray diffraction was examined. Fig. (4) represents the X-ray spectrum of zirconium oxide, which includes Zirconia phase 100%, while fig.(5) represents the X-ray spectrum of copper oxide, which includes Cu_2O and CuO . The CuO phase appeared as a result of the transformation of Cu_2O into CuO due to storage conditions and exposure to air.

Fig.(6) represents the change of wet density with different pressures in order to choose the best pressure for compressing the samples, and the pressure 250bar was chosen.

Diameter change with copper oxide percentages are shown in fig. (7) and through the figure it appears that the largest amount of diameter shrinkage is at pure zirconium and with the increase in copper oxide percentages we notice an increase in the diameter of the samples from the pure sample. Whereas fig.(8) shows the change of volume contraction (volume shrinkage) with copper oxide percentages, and it appears that there is a decrease in volume contraction with copper oxide percentages.

Figures (9-11) represent density, Vickers hardness, and Brazilian strength, respectively. While figures (12,13 and) represent the percentage of porosity and the percentage of water absorption, respectively, and the figures show that it is not possible to calculate the porosity and the percentage of water absorption accurately, because the surface pores are almost closed due to the melting of copper oxide and its exit on the surfaces of the models in the form of a glass layer that prevents the penetration of water into within forms.

The process of decreasing the density and increasing the diameter with the increase in the proportions of copper may be caused by the creation of voids (pores) in the samples as a result of the melting of copper oxide and its departure from the inside of the samples to the outside, but when calculating the porosity by Archimedes' method, we could not calculate the ratios of voids or porosity because the samples do not absorb water (or the water cannot penetrate the surface of the samples to enter the inside of the samples) and this phenomenon can have useful applications in thermal insulation of



furnace linings and any other thermal insulation applications because under normal conditions no moisture is formed inside the samples.

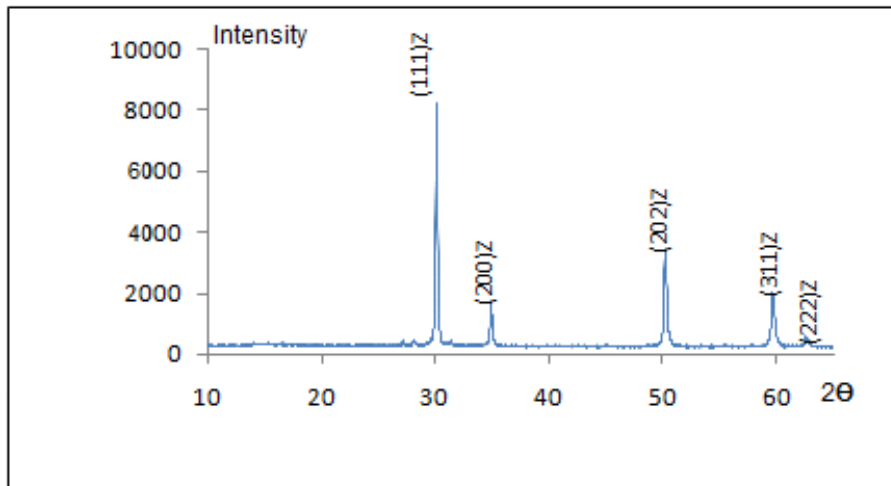


Fig.(4) Shows the XRD diagram of ZrO_2

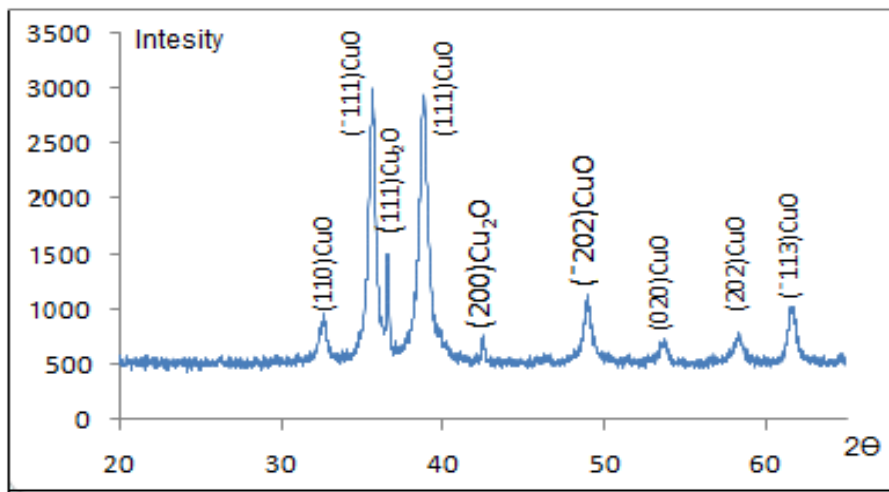


Fig.(5) Shows the XRD diagram of Cu_2O

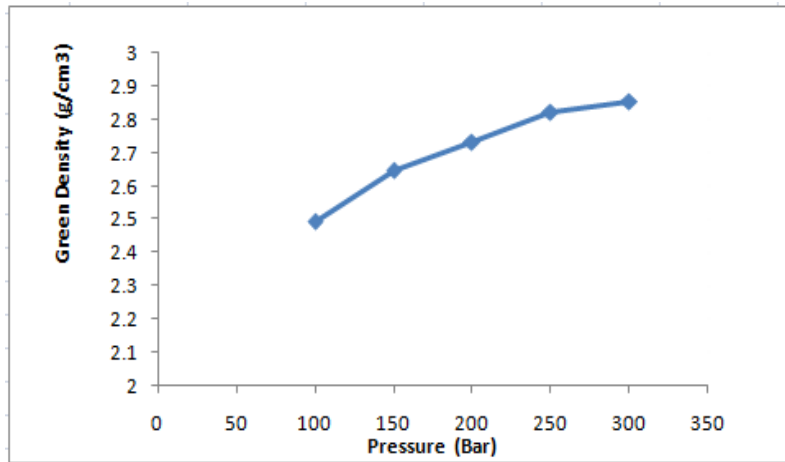


Fig.(6) Shows the change of wet density with pressure

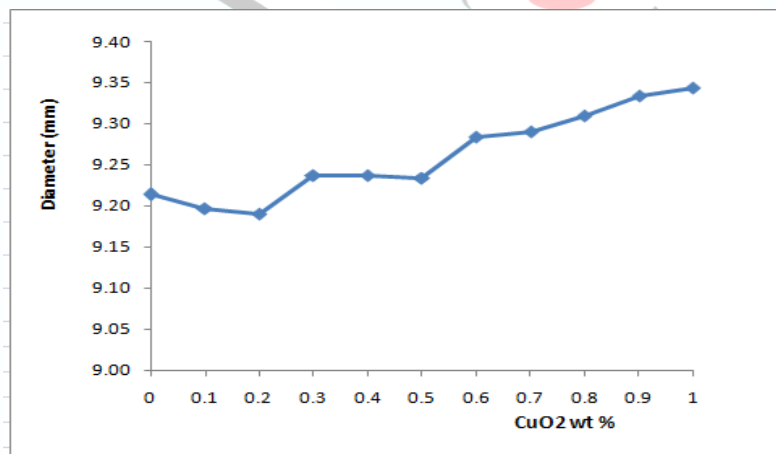


Fig.(7) Shows the change of diameter with the percentage of Cu₂O

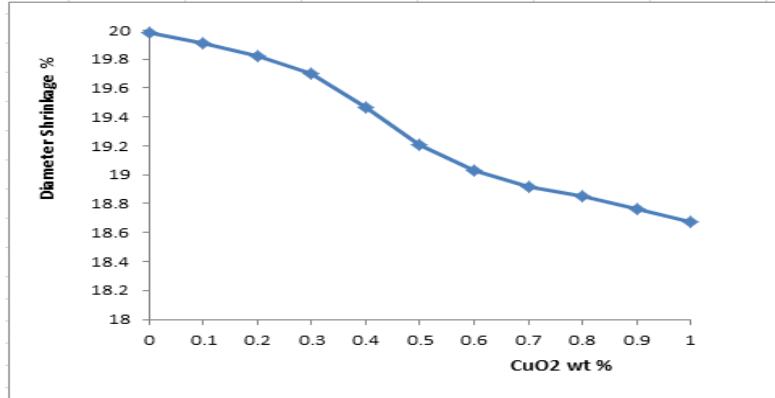


Fig.(8) Shows the volume shrinkage changes with the percentage of Cu₂O

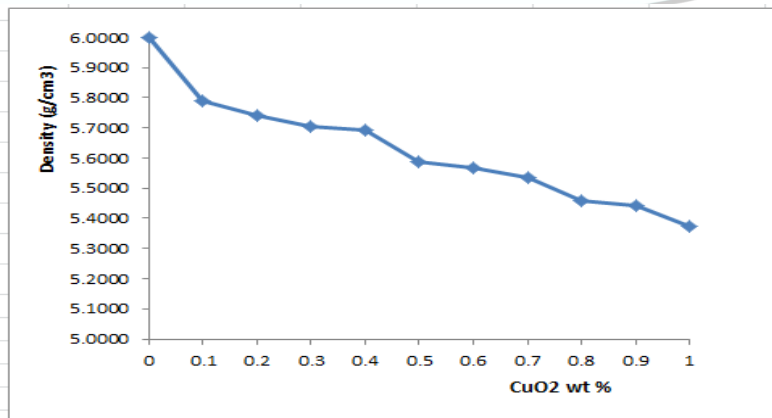


Fig.(9) Shows the density changes with the percentage of Cu₂O

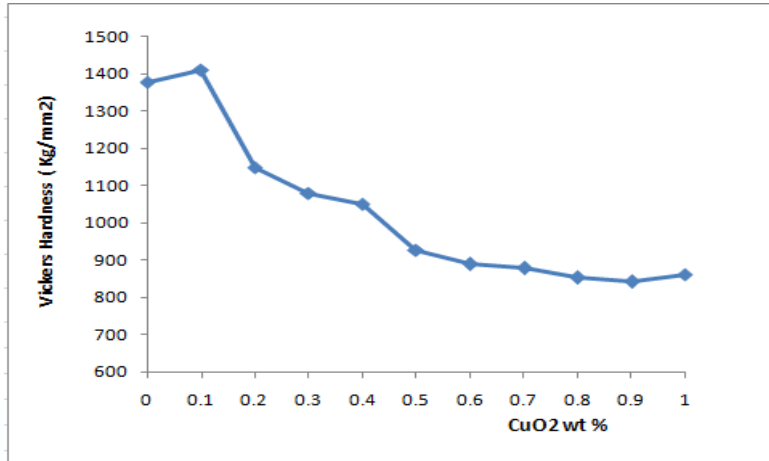


Fig.(10) Shows the change in Vickers hardness with the percentage of Cu₂O

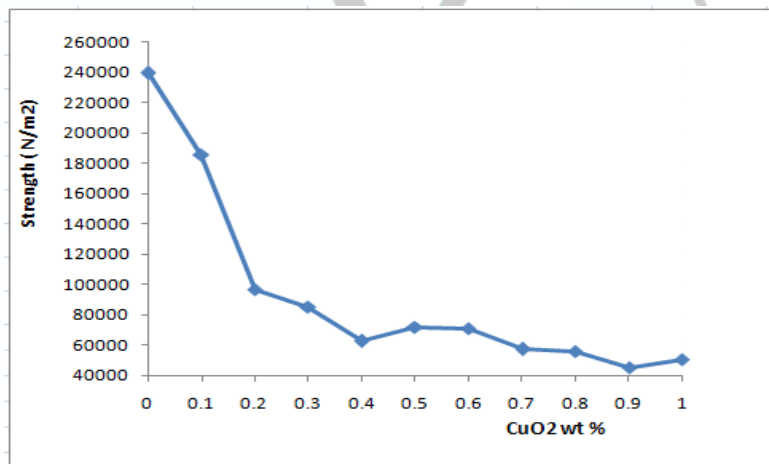


Fig.(11) Shows the Brazilian strength changes with the percentage of Cu_2O

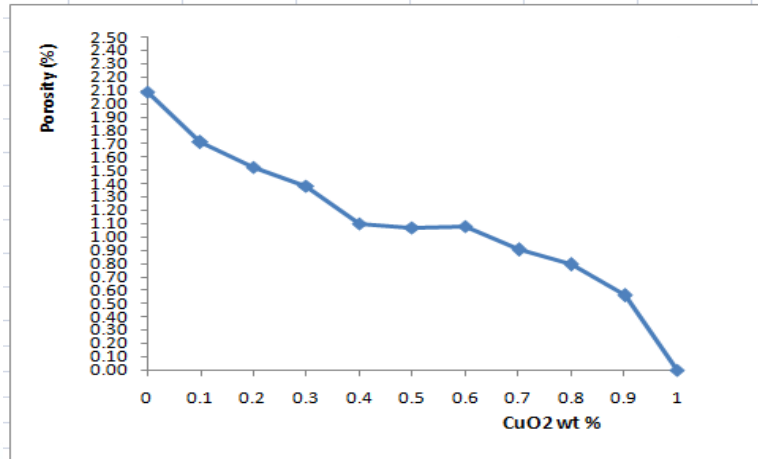


Fig.(12) Shows the porosity changes with the percentage of Cu_2O

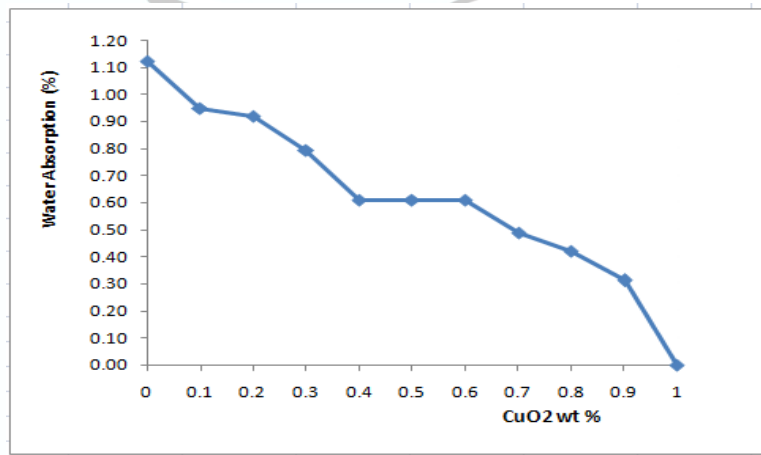


Fig. (13) Shows the water absorption with the percentage of Cu_2O

3- Conclusion:

After heat treatment of the samples, it was found that the largest shrinkage in diameter is the pure sample, while the other samples increase in diameter with an increase in the percentage of copper oxide, which leaves pores, while the surface of the samples may have formed a glass layer of copper oxide, and that water or moisture does not penetrate into the included samples. Copper oxide is very useful in thermal insulation applications.

4- References:



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