Development of the Solder Glass Paste with TiO2 additive in glass – to – Metal Sealing process

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Abstract

Solder glass paste developing by adding Titanium dioxide (TiO_2) to the paste compilation, which used in metallic rods sealing with quartz tubes . This kind of sealing is used in a lot of industrial applications such as : the flash lamps that required special fabrication conditions , thermal probes and many others . The paste was used as intermediate substance between the quartz glass tube surface and the surface of the metallic Tungsten (W) rod . The sealing temperature range was (410 – 520 ºC) and the best result been in (470 ºC) . The grain size of (TiO_2) powder was (60 micron) . The samples were tested in a high vacuum system with controlled heating unite . many of the samples that passed successfully in different tests were used in practical system ; Xe flash lamp , Ion Argon laser and high sensitive thermal probes which insured their efficiency in operation process . The different conditions of sealing process were studied to get best results , such conditions ; samples cleaning before sealing , oxidation effects during sealing process and annealing of samples after sealing process . This research showed the effect of adding Titanium dioxide (TiO_2) to the glass solder paste which improve the mechanical and thermal properties . Good efficiency of the developed solder glass paste encourage to use it in many gas laser systems .

Key words: Solder glass , Glass to metal sealing , Titanium dioxide

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تطوير عجينة الصمغ الزجاجي باضافة ثنائي اوكسيد التيتانيوم اليها في عملية لحام زجاج – معدن

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الخلاصة

جرى تطوير عجينة اللحام باضافة ثنائي اوكسيد التيتانيوم (TiO_2) الى مكونات عجينة الصمغ الزجاجي المستخدمة في لحام الاقطاب المعدنية مع أسطوانات الكوارتز لتلائم تصنيع و أستخدامات العديد من التطبيقات الصناعية مثل المصباح الوميضي الذي يُصنع تحت ظروف التفريغ العالي والمتحسسات الحرارية وغيرها .

و أستخدمت الخلطة كوسط بيني بين السطح زجاج الكوارتز(Quart) و أقطاب التنكستن (w) في مدى درجات الحرارة كانت أفضلها في درجة الحرارة (450 ºC) . وكان الحجم الحبيبي لمسحوق ثنائي اوكسيد التيتانيوم (60 micron). وجرى فحص العينات المصنعة بمنظومة التفريغ العالي و التسخين الحراري أضافة الى تشغيل النماذج في منظومات عميلة أثبتت كفاءة اللحام و كفاءة خلط اللحام المطورة الجديدة. كما جرى دراسة ظروف اللحام المختلف للحصول على أفضل النتائج إلى جانب تأثير تنظيف و صقل العينات قبل اللحام و تأثير الأكسدة الحاصلة أثناء عملية اللحام أضافة إلى دراسة تأثير عملية التلدين على العينات بعد اللحام. واوضح البحث امكانية ودور ثنائي اوكسيد التيتانيوم على تحسين الخواص الميكانيكية والحرارية لعجينة اللحام تلك . أدى نجاح عجينة اللحام المطورة إلى أستخدامها في منظومات أخرى كمنظومات الليزر الغازية.

الكلمات المفتاحية: الصمغ الزجاجي ، لحام زجاج معدن ، ثنائي اوكسيد التيتانيوم

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Introduction

As with metallic solders, glass solders are glasses with a very low melting temperature that are used to join glass to ; other kinds of glasses , metals or ceramics with as little thermal impact as possible to the materials to be joined.

Glass – to- metal sealing can be achieved by several methods [1-4], using a liquid phase at some stage in the bonding process. Investigations of solid state bonding of glass –to-metal sealing and of intermetalic compound to glass have also been described . [5-6] . An earlier paper reported the thermal expansion study for glass –to – metal sealing [7]. Generally, soldering process carried on the temperature range (450 – 550 ºC) . Thermal expansion of soldering glasses determined by the components to be soldered. The solder glass powder (60 micron) or less, is mixed with methanol to an easy – to use suspension or paste. By using nitrocellulose dissolved in amyl acetates as a carrier, the powder will adhere, even after solution dries. TiO_2 improve the mechanical properties as well as lower the melting point of the paste. Bonding is achieved by the simultaneous application of heat and pressure, and results of bond strength measurements are given. The needing for glass-to-metal sealing appeared in Xenon Flash Lamps fabrication experiments, to place the electrodes of flash lamp for electrical discharge, glass – to – metal sealing was needed hardly.

Tensile as well as the vacuum – thermal testing system were used to check the bounding strength and the chemical reaction had take place. Investigations on the mechanism of the contract growth are also discussed . This glass Solder bond is much stronger than epoxy and is not susceptible to degradation from humidity. The expansion coefficient of glass Solder and silica fiber match because both are glass. As a result, minimum stress is applied to the fiber at the bonding point. Not only does the glass Solder bonding technique provide a bond

The flash tubes utilize a quartz tube construction wherein the pulse discharge is contained within a narrow, thick- wall bore , end cap construction, readily adaptable to efficient liquid cooling. The flash tubes are of low impedance , and are , capable of with standing extremely high current densities [8].

that is stronger than an epoxy bond and impervious to moisture, but it is also fast and inexpensive for use in a practical, fused coupler manufacturing process, Specific mechanical tests, including vibration, impact, and sample retention were performed to evaluate the strength of the bonds between the glass solder, quartz and the Tungsten . For the sample retention tests, tensile forces were applied to the sample leads by attaching weights of known mass. The present paper concerns the solid state bonding of metal to glasses.

Materials and Instrumentation

Experimental Details

Materials and Instrumentation

The metal used was (Tungsten W). The glass was pure quartz tubes. Table (1) shows the physical properties of the material used in experimental sealing . Bonding experiments were carried out on specimens and tested by a vacuum and thermal testing system as indicated in fig. (1).

Table (1) Physical properties of material used in glass- to – metal sealing experiments [8]

Material	Density (g m/cm^3)	Thermal conductivity (°c /nm)	Linear thermal expansion X10^{-6} (c^{-1})	Average modules of Elasticized (E Gpa)	Electrical resistively (P) (Ohm.mm)
Quartz	2.65	0.012	85	310 GPa	10^{12}
Tungsten (w)	19.25	39.08	4.6	22	10^{-4}

Sealing paste that used in pervious work for glass –to- metal sealing may different [9]. Metals with the borosilicate and quartz) had developed to be a suitable paste for the present work ; sealing tungsten (W) poles with the quartz tube in Xe- flash lamp fabrication , with a consideration of the properties of the two materials, especially the high melting point and the crystal structure for both. The new developed sealing paste composition , that used in this work was :- SiO_2 45% , Al_2O_3 20% , PbO 17.8% , Na_2O 10% MnO 7% , Ag_2O 2.2% , NiO 1.8% , CoO 1.2% , CuO 0.8% and TiO_2 4.2% . Phosphoric acid (H_3Po_4) , methanol and amyl acetate as a carrier .

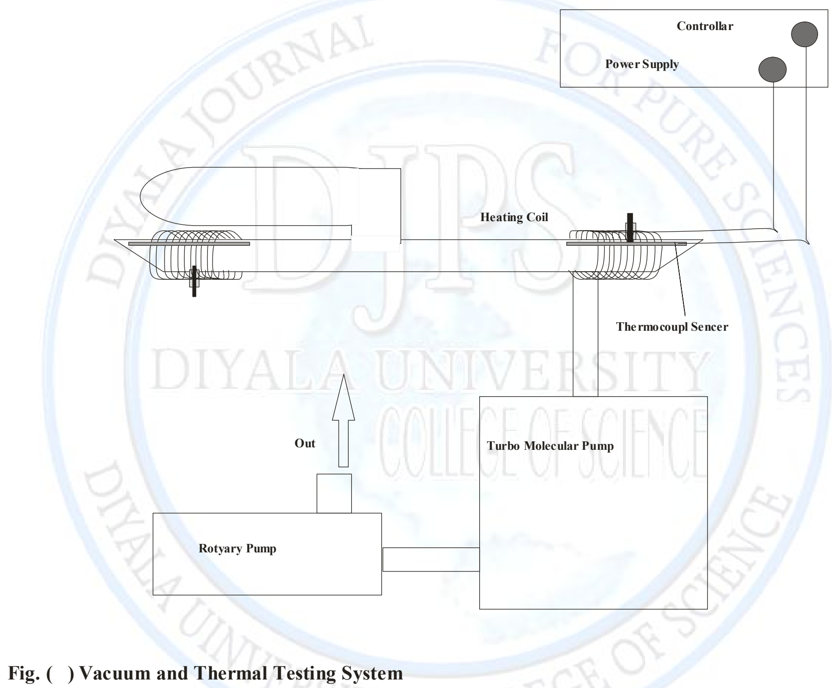

Fig. (1) Vacuum and thermal Testing system for bounding samples

Cleaning and Procedure of the Specimens:

The tubes and face were ground flat with (10 mm) diamond grain, the quartz glass tubes were cleaned in heated (40%) nitric acid (HNO_3) for (5 min), rinsed in water and fired in air at (530ºk) for (10min) , then cooled gradually and were kept in vacuum dictation[9] .

The metals with oxides that are unstable in hydrogen below the melting point of the metals, were heated for (5 min) in dry hydrogen at (400º k) below their melting point. After cooling to room temperature all the metallic specimens cleaned by rubbing with tungsten wool and degreasing in benzene, heated again in dry hydrogen at (300 ºC) in a furnace. The strength of the seals was dependent on the material cleaning and polishing . Metals and the alloy had been lapped flat with (10.0 and 5.0 Mm) diamond paste . samples were divided into two groups. One group received a final polish with (5Mm) the other were polished with (10Mm) . The glass sample surface had been polished to an optical finish with an optical tissues wetted by 30% HF –10% HCl at (65ºC) by standard methods[10].

Results and Discussion

Glass –to- Metal Sealing Process

The parts to be bounded were stacked and heated to about (0.9Tm) (Tm is the melting point of the metals in ºk) in a hydrogen shielded tube furnace . Pressure was then applied and maintained for a certain time. The parts were allowed to cool after pressure was removed. The optimal bonding conditions of temperature , pressure and time were determined experimentally.

Typical curves for the bounded area are given in fig.(2) sealing time as a function of sealing temperature, fig (3) Viscosity as a function of the temperature of solder glass , fig (4) linear thermal expansion as a function of temperature , fig (5) thermal expansion for the different samples that used (borosilicate , quartz and the solder glass) as a function of temperature, fig (6) sealing temperature as a function of breaking strength and fig (7) deformation percentage as a function of breaking strength and fig (8) breaking strength of the sealing as a function of plastic deformation. There is a minimum pressure for a complete bonding. Initial bonding occurs at much lower temperature than (0.9 Tm), as can be seen in Fig.(6). The optimum bonding also given is table (3).

Table (2) conditions for bonding Glass-to- metals

Materials	Temp.(ºk)	Pressure (N/m^2)	Time (sec)	Bounding strength (n/m^2)
w-quartz	740	$3 * 10^4$	120	$6.5 * 10^7$

Sealing process and Testing

A lot of experiments had carried on to check several things; the sealing strength, cleaning and polishing effect on sealing, sealing temperature, nature and properties of the interface during and after the sealing process , contact growth and the mechanism of sealing . All of the samples in the study were able to support tensile loads in excess of 5kgf (49N) without failure of the glass solder bonds.

Couplers packaged using the GlasSolder® technique have proven to be quite robust when tested for both vibration and impact. The vibration tests were conducted over the frequency range of 10Hz to 55Hz, in accordance with the test conditions specified in Telcordia GR-1209. During the impact tests conducted from a height of 1.8 meters, each coupler was dropped eight times along each of three mutually perpendicular axes. In both cases of vibration and impact, the average change in insertion loss following the tests was only ~0.1dB.

Qualification Tests.

Table (3) Breaking Strength of the sealing bond in tensile test

Plastic Deformation %	Breaking Strength (N / m^2)		Breaking Strength (N / m^2)	
	Borosilicate glass		Quartz glass	
	With TiO_2	Without TiO_2	With TiO_2	Without TiO_2
10	2.1	0.4	1.4	0.9
20	3.6	1.9	2.6	2.1
30	4.2	2.2	4.2	3.8
40	5.0	2.8	6.1	5.4
50	5.6	2.9	7.9	6.2
60	5.8	2.2	8.9	6.9
70	Fail	Fail	8.3	7.8

Temperature (T) = 25 ºC   Pressure (P) = 1 atm

A number of couplers were built for qualification testing in accordance with the test criteria specified in Telcordia GR-1209. Three different groups of couplers were assembled. Results obtained for the temperature cycle test indicated smaller changes and greater consistency using the bonding technique.

Table (3) show the Breaking Strength and plastic deformation of the sealing bond in tensile test.

Specimens Cleaning Effect

The following demonstrates to what extent surface roughness affects the properties of the seal. The rough surface was obtain by lapping with (10µm) diamond paste , and omitting any polishing. In each case the surface roughness was measured . Scaling temp. (470 ºC) with Annealing in N_2

Table (4) Failures in sealing due to the roughness

Surface Roughness (microns)	Failures in glass %
2	0
5	0
10	0
15	0
17	0
20	3
25	8
30	10
35	14
40	20
45	20
50	20
60	20

Contact Growth

The contact growth was considered in the study of seal regions for the glass – to-metal sealing . A mechanism other than pronounced metal deformation must operate to develop contact between the metal and glass over the entire available surface. This phenomenon of pt-quartz bonds.

The contact surface increases with heating time until the lamellae merge into each other. This cannot be due to deformation since the actual deformation is too small. A possible explanation for the contact growth may be found in the surface diffusion of the glass atoms into metal surface [11 – 13] and metal atom in the glass surface. Simultaneous vacancy diffusion enables the pores to be closed . Migration of metal atom into the quartz surface contribute to the growth of the contact surface diffusion, however , can change the pore shape, but not the size.

However, the contact area increase with temperature[14- 16], the pores at the interface disappear. This can be explained only if vacancy diffusion occurs. Owing to the difference in diffusion characteristics, the Fe-Ni-Co alloy needs a longer time to close pores than the tungsten (w). Fig (7) shown that tungsten (w) can be bounded to the quartz in (0.5 sec), assuming that the pores are not > 1mm.

Surface roughness is important. If the rough glass surface is pressel on metal, the asperities penetrate the oxide larger and make close contact with the metal. The surface pores are then also filled by plastic flow of the metal, which occurs at compressive stresses lower than those required to comes shearing strain in the metal at a smooth interface.

Annealing Effect

The investigatal whether seals could be heated to temperatures in excess of the sealing temperature without a deleterrions effect on the seal strength. The following experiments was preformatted a lot of seals, subdivided into three groups which received the following treatments:-

Group (A) annealing in N_2 wilt slow cooling rate 3ºC/1h

Group (B) annealing in air with cooling 10ºC/1h

Group (C) no treatment

Heat treatment –annealing were performed in an oxidizing and protective environment because it was thought that conceivably the respective gaves might diffuse into the region of the seal and react with the oxide. Visual examination as well as , microscopic examinations of the heat treated seals showed a little effect on the group (B) samples, that mean that the seal region with the oxygen during the annealing processes. While the group (C) samples showed a clear failing in Vacuum- Thermal testing system as well as in tensite testes.

Thermal Expansion of some Sealant Compositions

The geometry of the seal in important in case of the big different in thermal expansion of two pecion , because the difference in thermal expansion cause thermal stresses .

To avoid stress concentration in the seal must be control two important factors; the temperature and time during and after the sealing process.

The thermal expansion characteristics change both with the temperature and the seal position as well as the time. Change interface of composition during sealing process lead to change the thermal expansion.

Conclusions

The results of the calculations for applied to oxygen – active metals, obtained from measurements , of the total deformation , that results show that:

1 -the strain is fairly high for oxygen martial. Nevertheless, plastic deformation on a microscopic scale will occur in the first stage of the bond formation between the quartz and Tungsten (w) , because the initial contact surface is only a small part of the available surface .

2 - The strength of w –quartz seals can be higher than the bulk strength of the metal itself. Vacuum- tight bonding of glass –to- metal was reproducible by the He leak rate tests at room temperature and above within the range of (300 ºk- 700ºk).

3 – TiO_2 addition , improve the mechanical properties of the sealing bond which get a higher strength than that without TiO_2 .

4 – Thermal properties and thermal shock resistance of the bounded region has been better with TiO_2 addition than that without TiO_2 .

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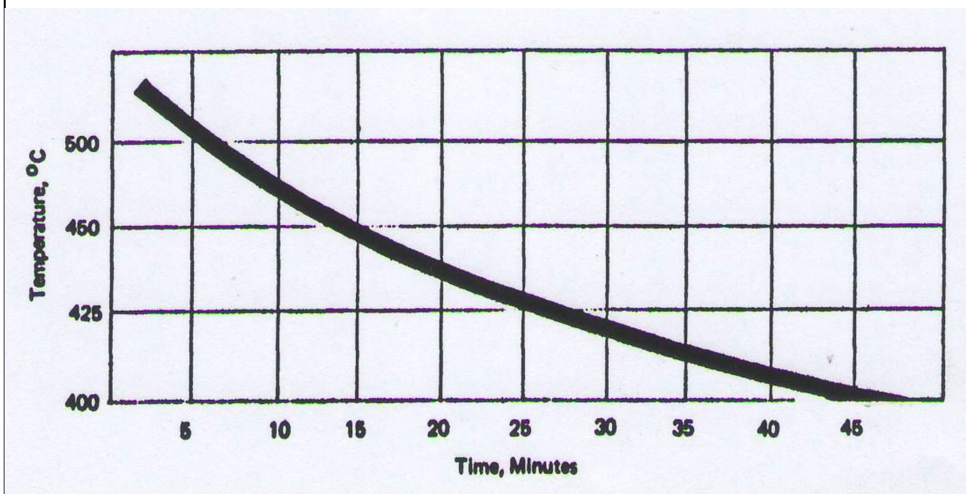

Fig. (2) Sealing time vs temperature of solder glass

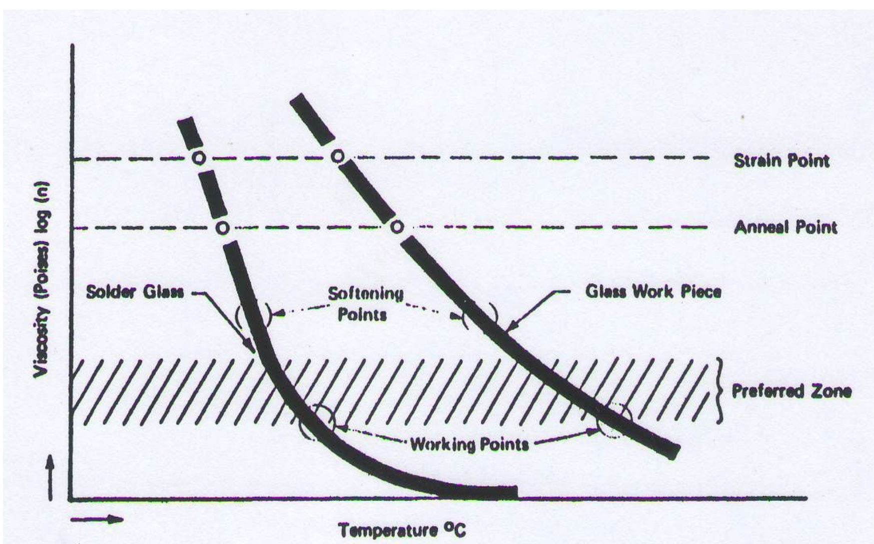

Fig. (3) Viscosity – temperature relationship of solder glass

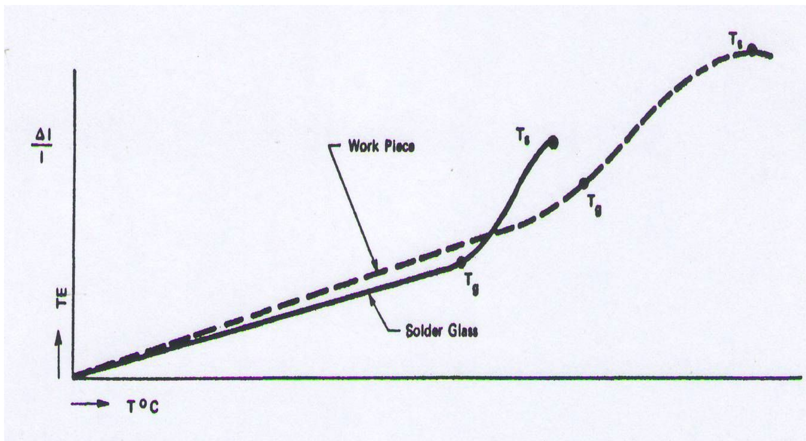

Fig. (4) Preferred relationship of thermal expansion curve of solder glass and work piece .

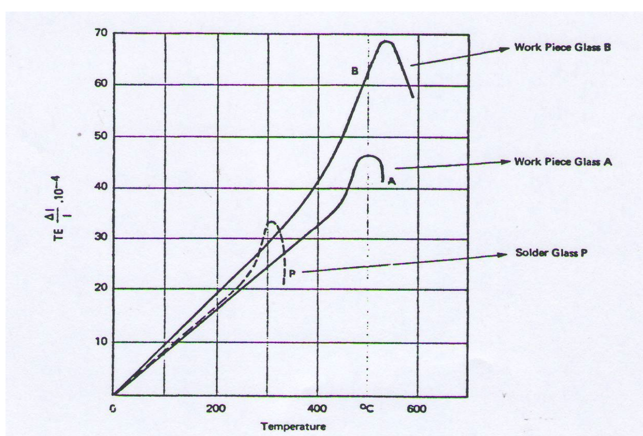

Fig. (5) Thermal expansion of solder glass , borosilicate glass and quartz

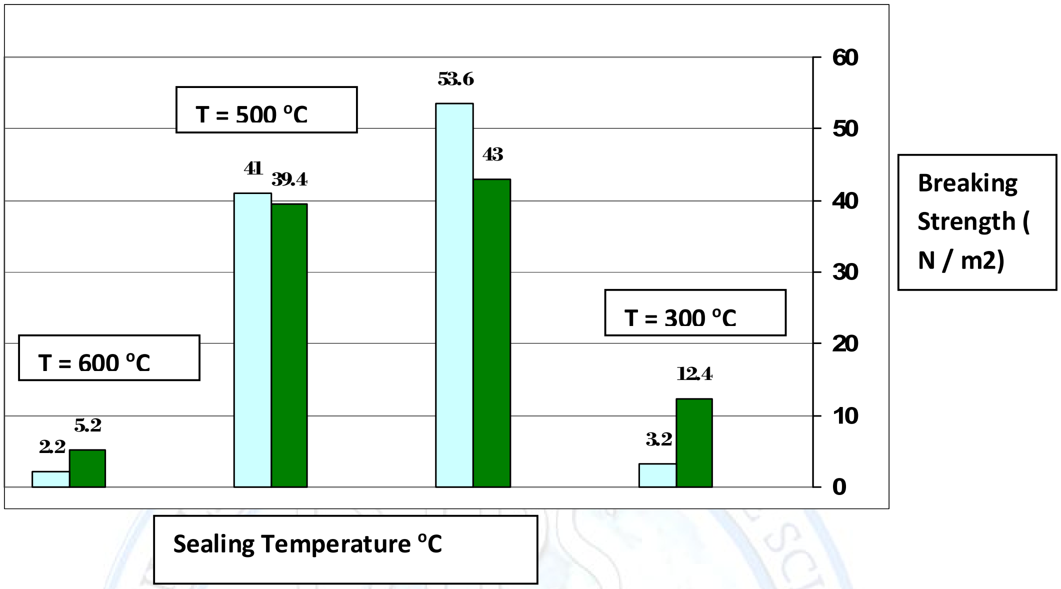

Fig. (6) Breaking Strength of the Sealing region as a function of the Plastic Deformation for the usage metals

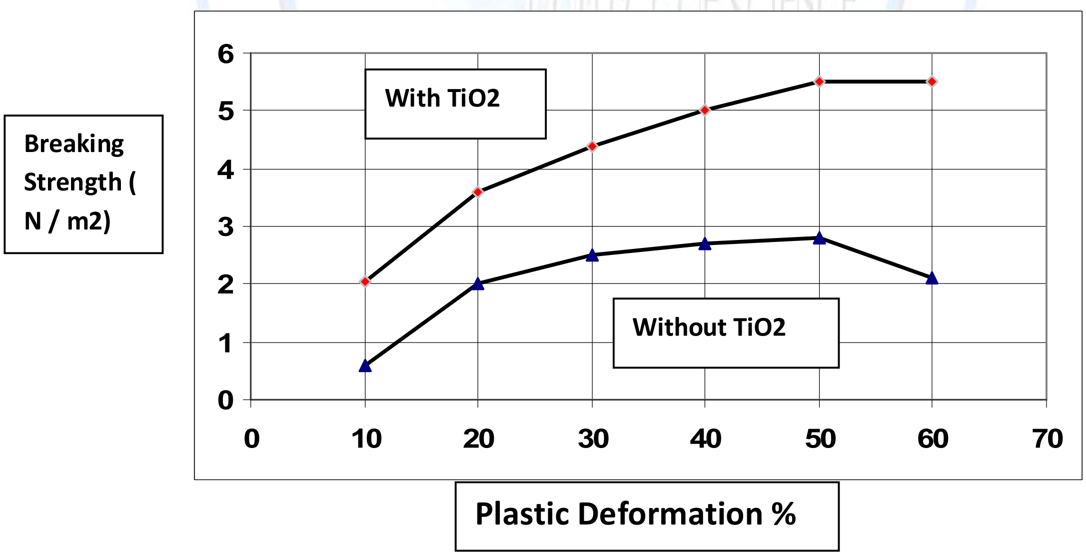

Fig. (7) Breaking Strength of the Sealing region as a function of the Plastic Deformation for the usage metals (borosilicate glass)

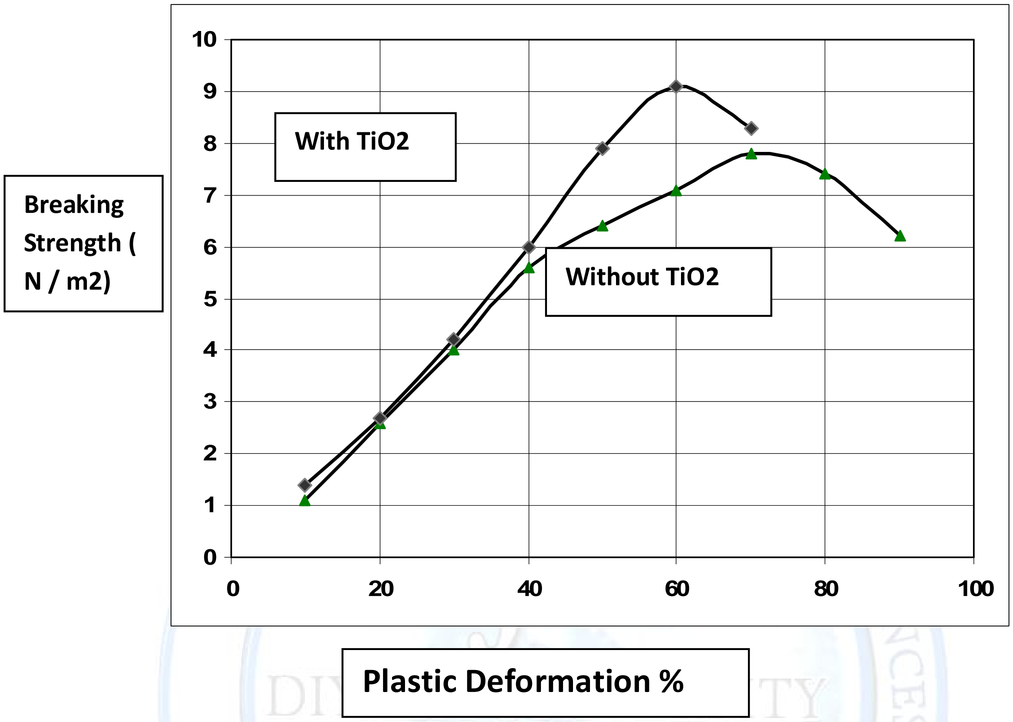

Fig. (8) Breaking Strength of the Sealing region as a function of the Plastic Deformation for the usage metals (quartz glass)