Thermal and Mechanical Properties of Borosilicate Glass to Kovar Alloys Joint

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ABSTRACT: *The aim of the current study was to find a reliable joint between Borosilicate glass and Kovar alloys. For this purpose, the Dilatometer test was applied to calculate the thermal expansion coefficient of glass and Kovar alloys, and the materials with lower differences in the thermal expansion coefficient were used to join the Kovar to glass. Due to the nonmetallic properties of glass, it is theoretically impossible to join glass to metal as it shows no wettability. Therefore, a material was applied as a sealer between Kovar and glass to solve this problem. The Kovar samples were oxidized in the N_2-H_2-H_2O atmosphere to control the chemical composition and also form an oxide layer that does not contain Fe_2O_3. The tensile strength of the produced joints was investigated at different times and temperatures. The results showed that the highest tensile strength was 16.63 MPa which was achieved at 10 min and 1000°C.*

KEYWORDS: *Kovar alloys; Borosilicate glass; Sealing methods; Thermal expansion coefficient; Mechanical properties.*

INTRODUCTION

Metal-glass joints are widely used in the electronic, medical, and military industries. The main problems in joining two different materials are the difference in physical properties such as melting point, Elastic module, and expansion coefficient, and the formation of intermetallic compounds [1-4]. Various methods have been proposed for joining metal to glass which include: Adhesive bonding, fusion welding, Brazing, Diffusion Bonding, Electrostatic Bonding, and soldering [6-8]. However, the application of the joints produced by these methods is limited and has major problems in the nuclear industry and solar cells as they have to endure high temperatures which affect the adhesion and mechanical properties of the joints [9-11].

Borosilicate glass tempered glass is a type of glass that contains boron trioxide. The commercial name of this material is Pyrex [12]. This type of glass possesses a low thermal expansion coefficient (from $2*10^{-6}$ to $3.3*10^{-6}$) and high thermal stability which reduces the risk of failure during heating and cooling [13]. It is chemically stable and does not react with the foodstuff [14]. The maximum temperature that this kind of glass can be used is about 500°C [15]. On the basis of their chemical composition, they begin to deform above 500°C [16]. The heat treatment temperature for annealing of Borosilicate glass is nearly between 600-650°C [17,18]. It is commonly used for the construction of reagent bottles and flasks as well as lighting, electronics, and cookware [19].

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Table 1: Chemical composition of Kovar alloy

C	Si	Mn	Ni	Cr	W	Co	Fe
0.01	0.098	0.23	29.92	0.029	0.033	16.75	52.60

Table 2: Chemical composition of borosilicate glass

SiO_2	B_2O_3	Na_2O	Al_2O_3	K_2O	P_2O_5	SO_3	Fe_2O_3
72.1	8.7	7.7	6.2	4	0.052	0.045	0.21

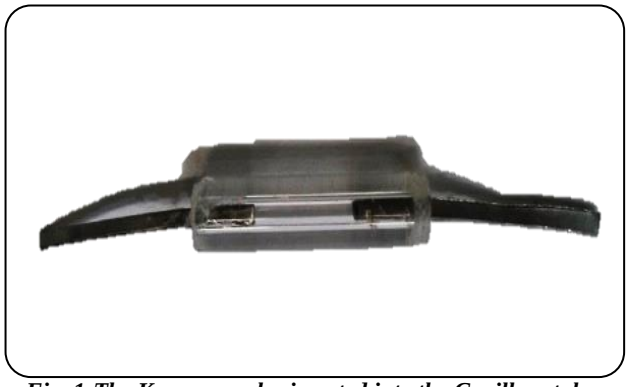

Fig. 1:The Kovar samples inserted into the Capillary tubes

The Kovar alloy (ASTM F-15) is an alloy consisting of Iron, Cobalt, and Nickel [20]. This alloy has a low thermal expansion coefficient and shows magnetic properties below curie temperature [21]. This material has a wide range of applications in the microelectronic industry [22]. It shows almost the same characteristics of thermal expansion as Borosilicate glass which makes it suitable for making a steady joint between these materials [23]. Kovar was invented to make a reliable glass-to-metal seal [24], which is required in electronic devices such as light bulbs, vacuum tubes, and in vacuum systems in chemistry.[25]

Luo et al studied the wetting and spreading behavior of borosilicate glass on the surface of Kovar alloy, and suggested three wetting stages: incubation period, reaction period, and equilibrium period [26]. *Kuo et al*. investigated the matching sealing of ASF series glass to pre-oxidized Kovar alloy under the protection of inert gas, and the sealing strength of ASF110 glass to Kovar alloy was about 3.9 MPa [27].

Although studies have been done on joining Borosilicate glass and Kovar alloys, there are few details on the tensile strength of the joint. The objective of this study is to make a reliable joint between Borosilicate glass and Kovar alloys and investigate the effects of different parameters on the tensile strength of the product.

EXPERIMENTAL SECTION

Samples preparation

The Kovar alloy (ASTM F-15) (Merck) and Borosilicate glass (SCHOTT) were used as the starting materials to make the samples. The chemical composition of these materials is shown in Tables 1 and 2.

In this work, three types of Borosilicate glass by three different companies were provided to choose the one that agreed more with the coefficient thermal expansion of the Kovar alloy (China, Iran, and Germany).

The Kovar alloy samples were in the shape of a square (2×20mm) with 1mm thickness and the Borosilicate glass samples were Capillary tubes with a length of 50mm. The Kovar samples were inserted into the Capillary tubes from both sides (4 mm from both sides). The prepared sample is shown in Fig.1. As the quality of the surface affects the joint strength [12], the surface of the alloys was polished carefully and washed 40 seconds in C_3H_6O (Merck, 99.99) and 25 seconds in the bath of Hydrochloric acid 10% (Sigma-Aldrich).

Oxidation of the Kovar samples

The Kovar samples were oxidized in the N_2-H_2-H_2O atmosphere to control the chemical composition and also form an oxide layer that does not contain Fe_2O_3. According to previous studies, Oxidizing in the N_2-H_2-H_2O atmosphere results in a joint with higher strength and quality [23]. In the process of joining metal to glass, oxidation and forming an oxide layer are the main steps [23]. Five different temperatures were used to oxidize the alloy and all the samples were kept 1 hour in each temperature. For oxidizing the Kovar surface, two capsules were applied. The first one contained N_2 (97%) + H_2 (3%), and the second was filled with pure N_2 (99.99%). In this step, a moisturizing gas system was needed. This system releases the gas in the form of tiny bubbles from under a distilled water pool and collects the moistened gas on the surface of the pool. In order to control the temperature and measure the moisture level, an instrument (standard-instruments-st-618-anemometer) was used. To evacuate the distilled water from the dissolved gas, N_2 gas was inbreathed through the water, and at the same time, the sample was at the cold place of the furnace (The Schaefer Group, Inc). Then the sample was moved slowly with a speed of 4cm/min to the center of the furnace and the flow of N_2 was replaced by N_2 (97%) + H_2 (3%)

Table 3: The condition of the samples in the furnace

Sample	Processing time	temperature
1	4min	940°C
2	4min	970°C
3	4min	1000°C
4	4min	1030°C
5	4min	1060°C
6	10min	1000°C
7	10min	1000°C
8	10min	1000°C
9	10mn	1000°C

Table 4:Results of dilatometry experiment for borosilicate glass

Sample : Borosilicate Glass (l0=47.40mm)	
Temperature (°C)	Thermal Expansion Coefficient (1/°C)
RT-100	8.1547×10^{-6}
RT-200	6.3424×10^{-6}
RT-300	5.5093×10^{-6}
RT-400	5.0717×10^{-6}
RT-500	4.6935×10^{-6}

to start the oxidation process. After one hour, the flow of gases was stopped, and in order to prevent further oxidation, dry N_2 was used in the atmosphere of the furnace [8,9]. It should be mentioned that the mass of the samples before and after the oxidation process was measured carefully.

Joining process

After preparing the samples, a dilatometry experiment (CNHangzhou Yueke Instrument Co) was used to determine the thermal expansion coefficient of Kovar and Borosilicate glass. The thermal expansion matching between two different materials is a critical parameter.

Before starting the joining process, N_2 with a flow of 240 Lit/h was inbreathed in the furnace for 15 min to evacuate the furnace and also prevent the entrance of O_2 which could lead to further oxidation. The prepared samples were moved slowly (2 cm/h) to the furnace. The main parameters in this study were the temperature and keeping time in the furnace. The condition of the samples in the furnace is shown in Table 3. In order to keep the joining parts from any possible damage, an insulator was used as the samples were coming out of the furnace.

Tensile strength measurement

A universal testing (Zwick/Roell Z020) machine of 20kN maximum load cell capacity was applied to determine the tensile strength of the joined parts, A tensile test was done according to ASTM E8. For all the samples, the jaw speed of the machine was fixed at 1 mm/min, and for each temperature and timekeeping, the average results of three samples were reported.

RESULTS AND DISCUSSION

Dilatometry experiment

The results of the dilatometry test for Borosilicate glass in five different temperatures are given in the Table. 4. It can be seen that the thermal expansion coefficient has an inverse relation with temperature because as the temperature increases, the glass tends to soften gradually and its expansion takes a tridimensional nature and refuses to expand in the direction of the dilatometer. Fig. 2 demonstrates the thermal expansion coefficient curve of Kovar and Borosilicate glass as a function of temperature for the three different manufacturers. It can be concluded that sample 1 has the best overlap with Kovar alloy so the rest of the experiment was done by Borosilicate glass sample 1 (Iran).

Oxidation process

The mass of the samples before and after the oxidation process is given in the table. 5. It can be considered that the difference between m_i (initial mass) and m_f (the mass after oxidation) increases at higher temperatures which can be attributed to the activation of the diffusion processes that are extremely dependent on temperature. For instance, O_2 diffusion from the oxide layer forms intergranular oxides in the alloy grainboundary [26,27]. The $\Delta m/A$ (surface area) versus temperature curve is plotted in Fig. 5.

Tensile strength

The results of the tensile testing for the samples oxidized at five different temperatures (for 4min) are shown in Fig. 4. The diagrams show that up to 1000°C the fracture force increases and it begins to decrease in higher temperatures. In temperatures below 1000°C the diffusion rate is not enough to form a chemical bonding, As the oxidation temperature increases, the bonding between the Kovar alloy and glass gets stronger, and at higher temperatures, because of the enhancement of the diffusion process, it decreases again [20,24]. In 1000°C the maximum fore is 231.17N which is 14.76MPa. For the rest

Table 5:The difference between initial and final mass of the samples during the oxidation process

Oxidation Temperature	Oxidation Time	Initial mass(m_i)	Final mass(m_f)	$\Delta m=m_f-m_i$	$\Delta m/A$
550°C	1min	2.1101g	2.1110g	0.9g	0.1020g/m^2
630°C	1min	2.2205g	2.2225g	2.0g	0.2247 g/m^2
800°C	1min	2.5214g	2.5236g	2.2g	0.2471 g/m^2
900°C	1min	2.4511g	2.4544g	3.3g	0.3707 g/m^2
1000°C	1min	2.9651g	2.9698g	4.7g	0.5280 g/m^2

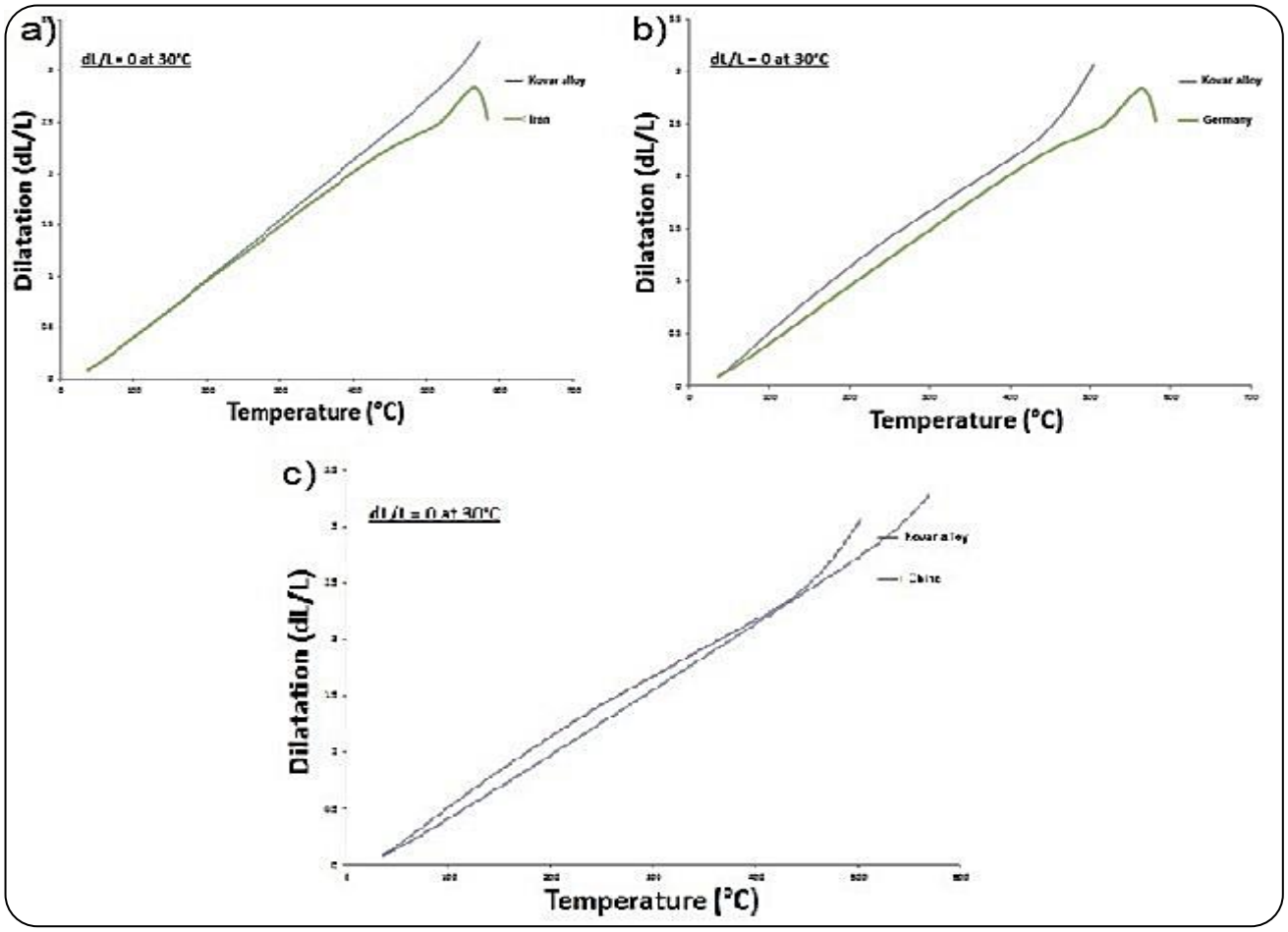

Fig. 2: The thermal expansion coefficient curve of Kovar and borosilicate glass as a function of temperature: a)Iran, b) Germany, c)China

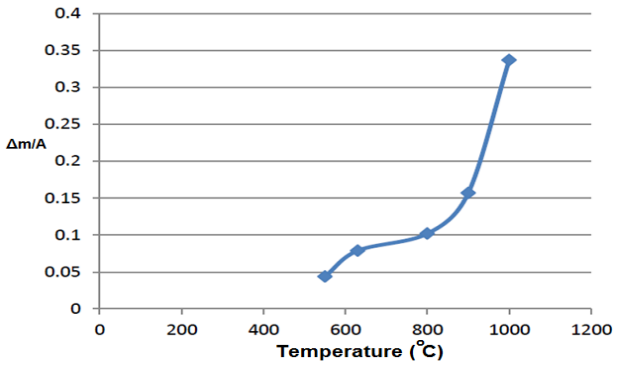

Fig. 3:The Δm/A versus temperature

of the samples, 1000°C was selected as the optimum temperature and they were kept for 6, 10, 14, and 20 min in the furnace to choose the timekeeping with the highest value of tensile strength.

Diagram 5 shows the samples kept at four different times. The maximum force was obtained for the sample oxidized for 10min which was 266.08 N and 16.63MPa.

The glass consists of ionic bonds and covalent bonds, these strong bonds make a stable and brittle material, but the metal consists of the electron cloud. As a result, there is a low wettability between glass and metal [28]. The main

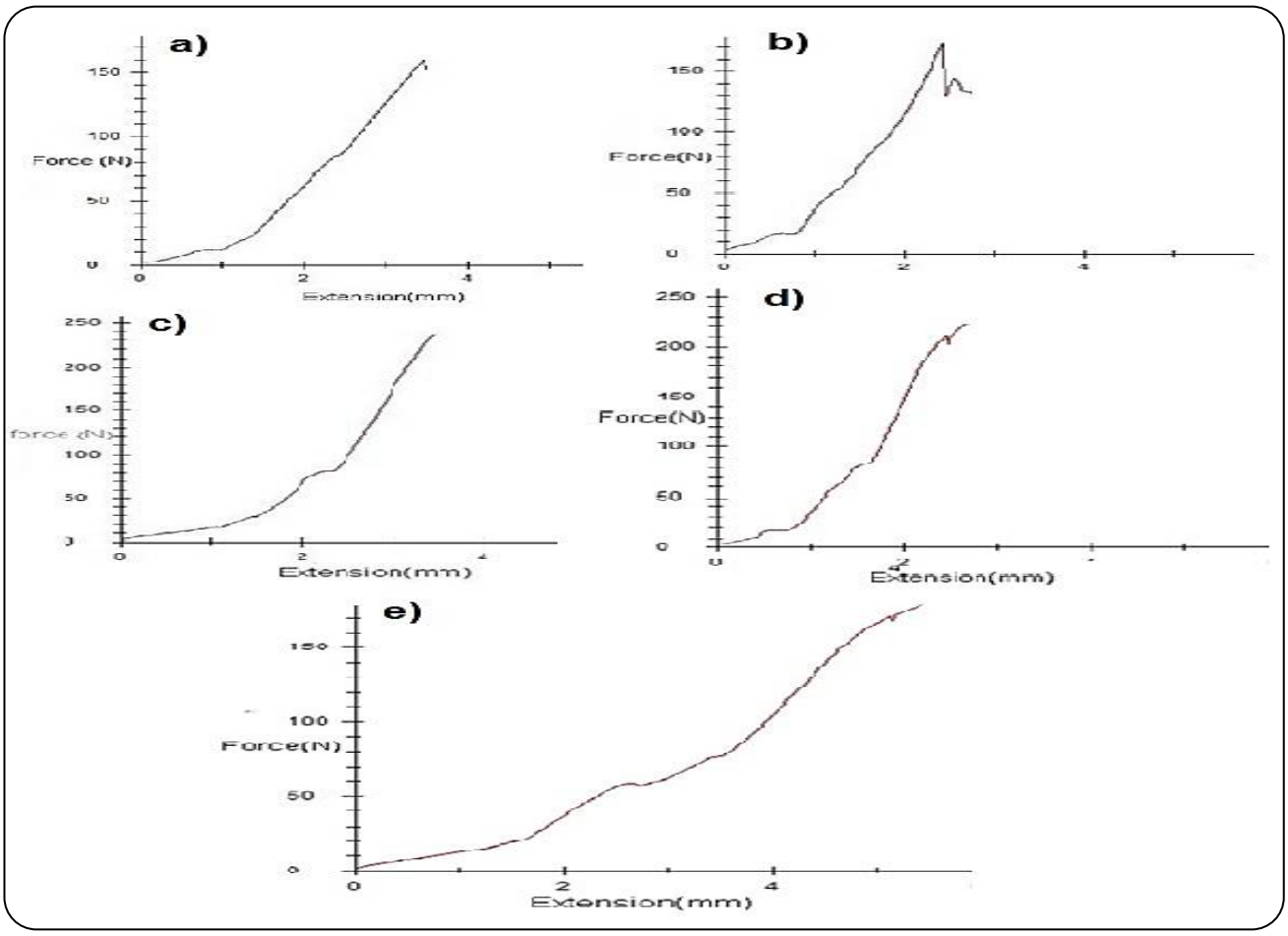

Fig. 4: The Force-strain curve for the sample oxidized 4 min at: a)940°C, b) 970°C, c) 1000°C d)1030°C, f) 1060°C

factors in joining Kovar alloy to Borosilicate glass are chemical and mechanical bondings. Chemical bonds form due to the dissolving of metal oxides in SiO_2. Moreover, the diffusion of Fe from metal to glass forms a chemical bond, too. During the joining process, Glass is in contact with the oxide layers of FeO and Fe_2O_4. The oxide layers of the alloy dissolve in the glass and the following reactions happen [23]:

$2Fe_3O_4 + 3SiO_2 = 3Fe_2SiO_4 + O_2$

$2FeO + SiO_2 = Fe_2SiO_4$

The main factors in forming the mechanical bonds are: a) surface roughness, b) diffusion of the glass in metal through the intergranular oxides [29]. The more the surface roughness, the more the mechanical bonding strength as a rough surface provides additional mechanical interlocking at the interface. [29,30].

In temperatures below 1000°C, chemical bondins don't form completely because the diffusion of Fe needs enough activation energy. In temperatures above 1000°C, Although, the driving force for diffusion is enough, the deformation of the joint happens and leads to the decreases in the maximum fracture force. The reasons for the decrease in tensile strength for the samples kept more than 10 min in the furnace are almost the same. In the lower times, the diffusion is incomplete as this process is a function of time and temperature. However, as the time increases from 10 min, the diffusion of Fe atoms is fast which reduces the energy of chemical bondings.

CONCLUSIONS

In this study, Kovar alloys were successfully joined to Borosilicate glass and the effects of oxidation temperature and processing time in the furnace on the tensile strength of the joint were investigated. The Borosilicate glass used in this work was chosen carefully which agreed more with the coefficient thermal expansion of the Kovar alloy. The experimental results obtained in this study show

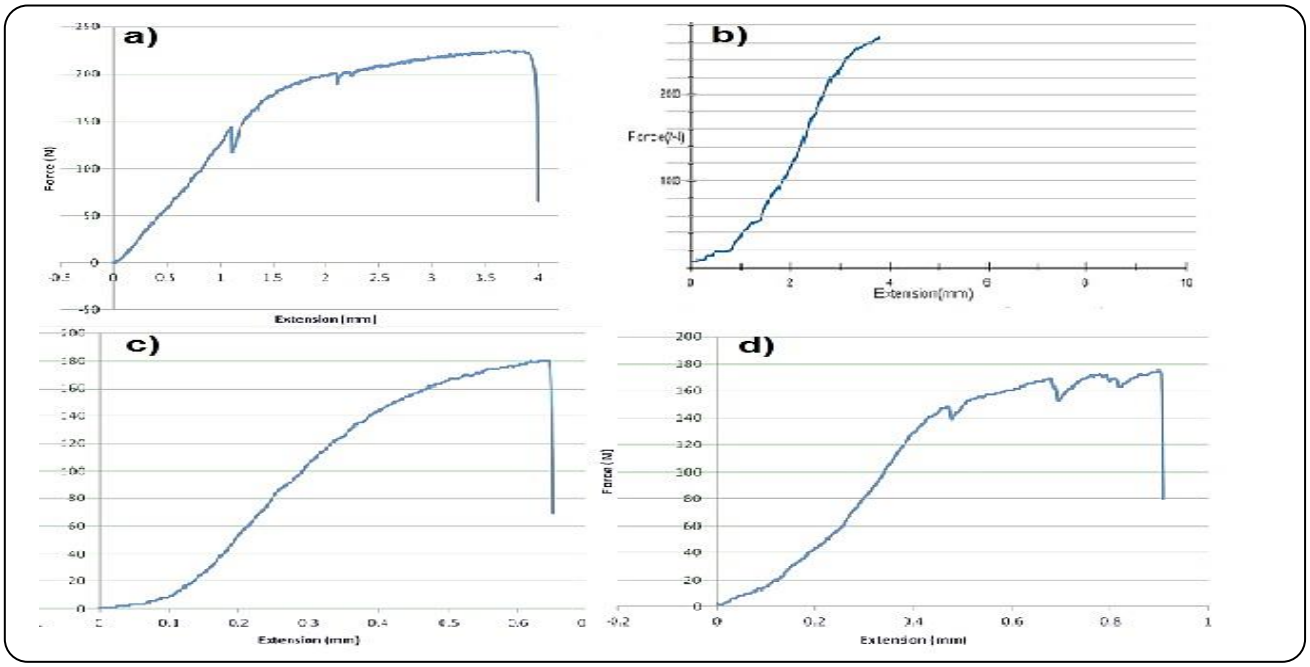

Fig.9: The Force-strain curve for the sample oxidized at 1000°C for: a) 6min, b)10min, c)14min, d)16min

that the optimum temperature and processing time for making a reliable joint between Kovar alloy and glass were 1000°C and 10 min, respectively. At 1000°C and 10 min, the highest value of the fracture strength was 16.63 MPa. The results showed that up to 1000°C the fracture force increases and it begins to decrease in higher temperatures. In temperatures below 1000°C, chemical bondings don't form completely and in temperatures above 1000°C, Although, the driving force for diffusion is enough, the deformation of the joint happens and leads to the decreases in the maximum fracture force. The processing time of the samples in the furnace was also a critical factor that affected the fracture force. As the time increases from 10 min, the diffusion of Fe atoms is fast which reduces the energy of chemical bondings.

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