LOW TEMPERATURE TRANSIENT LIQUID PHASE BONDING OF COPPER

By

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Abstract

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This thesis describes a Pb-free solder alternative that is capable of fluxless bonding. The main advantage of this process is that it offers the benefits of low fabrication temperature (125°C) while producing a joint capable of withstanding low stresses at very high service temperatures (300°C+). The ternary alloy system of Bi-In-Sn was investigated in the bonding of copper substrates. All bonds were made at 125°C with 25psi of fixturing pressure. Primary solidification was observed in as little as 15 minutes. The mechanical properties of the joints were shear tested both at room temperature and at 100°C to simulate a conventional service environment. With sufficient dwell time (~250h), joints would not fail in shear even at stresses that caused significant substrate deformation. Scanning electron microscopy was used to examine the joints and the evolution of the diffusion process.

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Introduction

Soldering processes are used ubiquitously in the electronics industry to create joints with excellent thermal and electric conductivity. The eutectic alloy of Lead-Tin (Sn63-Pb37) has been used extensively because of its low melting/bonding temperature (183°C), its excellent solderability, and the mechanical characteristics of its joints. However, many recent regulations are prohibiting the use of lead in consumer electronics because of environmental problems with its disposal. One of the main difficulties with the "lead-free" solders is that they require a bonding temperature that is typically twenty to forty degrees higher than the Lead-Tin solder.

This increase in bonding temperature creates two problems. First, electronic assemblies many times contain heat sensitive components. If these components are damaged during the high temperature bonding process, entire assemblies will often be scrapped. Second, since the component materials within the electronics packaging have different coefficients of thermal expansion, the bonding temperature has a direct correlation with the post-bonding residual stresses. These stresses adversely affect the long-term reliability of the joints.

A reduction in soldering temperature from 220°C to 120°C would reduce thermal stresses by a factor of two at room temperature (20°C); however, solders that have such a low melting point lack the necessary creep resistance within the range of normal operating temperatures (60 to 80°C).

Low temperature transient liquid phase diffusion bonding (LTTLP) offers the possibility of bonding at low temperatures, solidifying isothermally by outward diffusion of one or more of the liquid components, and homogenizing to give mechanical properties nearly equal to that of the base material and a remelting temperature that is significantly higher than the bonding temperature. A decade ago Roman¹ and Hou² demonstrated the fesability of LTTLP soldering using commercially available In-Sn-Ga-Bi alloys. Their joints required aggressive fluxing. In addition, the lowest temperature solder alloys contained Pb and Cd, which are undesirable for environmental reasons.

The goal of this project was to develop a fluxless, Pb-free soldering process for electronic interconnects with a significant reduction in resultant thermal residual stresses (see figure 1), while maintaining creep and thermal fatigue strength. Such a process will both increase joint reliability and enable more widespread use of heat sensitive components.

This thesis had the specific goal of developing a LTTLP process that would have a bonding temperature of $\leq 125^{\circ}C$, a diffusion dwell time of $\leq 2hr$, and a remelting temperature of $\geq 200^{\circ}C$.



Figure 1- Finite element simulations of residual thermal stresses at room temperature for different bonding methods and their corresponding bonding temperatures

Background: TLP

Diffusion based bonding has been used for more than two thousand years, the earliest documented cases being in the civilization of the Etruscans³. The earliest modern research into the topic was published in an article from 1959⁴ that described some fundamental concepts of what was later termed "Transient Liquid Phase" bonding by Duvall et al⁵. There have since been authors who interchangeably use phrases such as Diffusion Brazing (DFB)⁶, transient insert liquid-metal diffusion (TILM) bonding⁷, Solid Liquid Interdiffusion (SLID) bonding, and TLP bonding. All of these bonding techniques refer to a diffusion driven process by which a liquid interlayer in the joint changes composition (either by liquid components diffusing away from the joint or solid components diffusing into the liquid region) and undergoes isothermal solidification.

Figure 2 outlines the fundamental process involved in the bonding for a two component system. The diagram shows a binary system composed of elements A and B. The fixture includes solid substrates, "A", with a thin interlayer composed of element "A" plus a melting point depressant, "B". In step a, the fixture is heated to a temperature slightly above the eutectic melting point. As the liquid begins to dissolve some of the substrate, the joint widens to a maximum thickness as the joint composition shifts to that of the liquidus (C₁) and the substrate composition reaches that of the solidus (C_s) . At these conditions, equilibrium is established and substrate dissolution ceases. Since the dissolution requires only short range diffusion, the activation energy for dissolution is typically lower than that required for interstitial diffusion⁸ and much lower than that required for substitutional or self diffusion⁹. In subsequent steps c and d the B component diffuses away from the joint. As this occurs the liquid gap grows thinner and if the joint is given sufficient time, it will undergo an isothermal solidification where C<Cs. After the solidification, the joint must be allowed to homogenize and reduce the centerline concentration of B to below the room temperature solubility (C_R) in order to avoid precipitating unwanted phases upon cooling. While the developed process will be more complex, as it involves four component alloy systems, these fundamental concepts are still at work.



Figure 2- Stages of TLP Bonding¹⁰

TLP bonding has many of the advantages of soldering while avoiding some of its disadvantages. First, it is a capillary joining process. This allows some variability in surface preparation as the liquid phase can fill voids and surface irregularities. This liquid phase may also dissolve surface contaminants and thin oxide layers.

Next, TLP can be performed at relatively low temperatures. This will lessen the thermally affected regions on large assemblies to eliminate damage to heatsensitive components. As mentioned in the introduction, these lower bonding temperatures reduce residual stresses from thermal expansion mismatch. Third, TLP bonding can produce joints that remelt at a significantly higher temperature than their original bonding temperature. The literature documents cases in which TLP joint remelt temperatures were raised by several hundred degrees^{11, 12}. There are cases that produced joints with remelting temperatures that were 350°C higher than the bonding temperature (250°C), with a bonding time as little as one hour¹¹. One case documented a process dwell time of 36 hours and measured a remelt temperature that was more than 575°C higher than the original bonding temperature (400°C)¹². These increased remelt temperatures allow service temperatures above the bonding temperature and increased creep resistance.

Finally, TLP can create joints that almost match the mechanical properties of the parent materials. The diffusion that acts in the bonding process often serves to strengthen the mechanical properties of the joints when compared to the initial joint composition before bonding.

The reward of TLP's ability to offer the advantages of higher temperature bonding processes without their drawbacks is what motivates this research. A number of the findings presented in previous work were used in choosing fixturing conditions, potential alloy candidates, and general sample preparation.

Alloy Selection

It is known that spread characteristics of solders improve as the excess temperature above the melting point increases. Figure 3 shows this phenomenon for several binary solder alloy systems. Using this fact, a strong candidate for the alloy system to be used would have a low melting point to allow better substrate wetting. Extensive Thermo-Calc calculations¹³ were performed to model different systems and identify a system that would have a low melting point while excluding specific environmentally hazardous materials (Pb, Ga, Cd, etc.). Findings led most of the work to be centered on a composition near the ternary eutectic of the Bi-In-Sn system (see figure 5, label A).



Figure 3- Spread characteristics of binary solder alloys as a function of excess temperature above melting point¹⁴. The Pb-Sn alloy spreads easily with very little superheat while other alloys require excess heating to reach similar spread ratios.

Work was also done on two slightly different alloy combinations. One alloy was made with a 1% addition of Zn to the ternary eutectic which was intended to improve wetting characteristics (see figure 4). Another alloy was made with a composition that lies on the phase boundary line traveling between the ternary Bi-In-Sn eutectic and the binary In-Sn eutectic (see figure 5, label B) at 50% In, 43.6% Sn, 6.4% Bi. This choice was made to produce more rapid joint solidification and study the effect of lower bismuth content on mechanical properties of the joints.



Figure 4- Phase fraction Calculation of the In48-Bi35-Sn16-Zn1 system¹⁵. The 1% Zn addition was to increase the alloy's wetting of the substrate.



Figure 5- Calculated Bi-In-Sn liquidus¹⁶. Label A & B represent the ternary eutectic and low bismuth alloys used in bonding, respectively.

Experimental Procedure

3.1 Materials

3.1.1 Copper Substrates

Copper coupons ¹/₂" x ¹/₂" were wire EDM cut from alloy 110 electronic-grade copper sheets. The material was ordered with a mirror-like (#8) finish in 1'x1' sheets with a thickness of 0.062". After cutting, each coupon was dried and deburred along the edges. The coupons were cleaned with acetone immediately prior to bonding.

3.1.2 Alloy Preparation

Precise amounts of alloy components were weighed and placed together in a graphite crucible in the glove box. They were then heated to above 200°C and stirred as they melted together. The alloy was subsequently poured on to a cold graphite plate to solidify. Diagonal cutters were used to cut the alloy into small cubes approximately 0.12" on a side.

3.2 Bond Preparation

3.2.1 Bonding Procedure

An aluminum fixture was designed with sixteen pockets cut into it by a plunge EDM process to keep a close tolerance on depth and parallelism (see figure 6). A small hole was drilled in the center of the fixture and a type K thermocouple was mounted to monitor the temperature. A flat piece of insulating, high-temperature plastic fiber board was cut to fit on to the aluminum base by mating with the steel points on the corners, and an aluminum shaft was mounted in the center to allow precise alignment of the load weights. Cast iron weights were used to apply the desired amount of pressure to the joints during bonding. The copper substrates were cleaned by scrubbing with a clean paper towel and acetone and then immediately loaded into the glove box. The fixture was heated on a hot plate to 125°C $\pm 3^{\circ}$ and the substrates were placed into the fixture pockets. A bead of bond alloy was placed on each substrate and an ultra-sonic lapper was used to spread the alloy. The lapper has a pencil-like tool that allows for various tips to be mounted thereon. The tip that appeared to work most effectively was a half inch strip of copper. The tool was scrubbed back and forth on the substrate slightly scoring the surface and ensuring complete alloy wetting of the surface. Both substrates were prepared with this method. After all of the bonds were prepared, they were placed together in a sandwich fashion and the flat insulating plate was positioned on top of the specimens. In order to control joint thickness and geometry, weights were placed on the fixture to transfer a 25psi load to the bonds. The recorded bonding time began when the load was applied. Some samples were made with 15 minute increments in dwell time between 0-120 minutes, and numerous samples were made at the 120 minute dwell time.



Figure 6- Test apparatus for fixturing the copper coupons and applying pressure



Figure 7- Inert atmosphere glove box where work was done. UHP nitrogen was used along with nitrogen based forming gas (5% H₂). The concentration of H₂O and O₂ were about <5ppm.

3.2.2 Bond Aging Procedure

Some two hour dwell time joints were subjected to a bond aging process to evaluate the effects of prolonged time at temperature and investigate the joint at stages closer to long-term equilibrium. An air oven was heated to the prescribed temperature (either 125°C or 150°C) and a thermal mass of cast iron was placed inside to reduce temperature fluctuations. The joints were then placed in the air oven without any fixturing pressure for 10, 50, 100, or 250 hours. After the specified aging time, the joints were removed and mounted for metallographic inspection and shear testing.

3.3 Shear testing

3.3.1 Room Temperature Tests

In order to replace conventional solder joints, the TLP bonds need to provide mechanical properties that are comparable or better than solders currently in use. To test the shear strength of the TLP bonds, an apparatus was designed to apply a variable shear load to the joints. Figure 8 shows this device before testing with a coupon in place (left) and after the test was run and the joint had failed (right). This device was placed into a load multiplier (Figure 9) that allows a testing range from 1,800psi to more than 16,000psi. Tests were performed by adding weight to the load bar in five pound increments.



Figure 8- Apparatus to apply shear load to the joints for room temperature and elevated temperature testing.



Figure 9- Large capacity load multiplier used in shear tests.

3.3.2 Low-melt Phase Exclusion Tests

After some DSC results showed there was a low melting phase $(T_M:~81^{\circ}C)$ present within the bond, shear tests were performed at an elevated temperature to determine bond strength when the low melting phase was liquid. This was done by instrumenting the apparatus with a resistive heater and thermocouple that fed into a simple, closed-loop control system to reliably heat the fixture.

Tests were performed with the same fixture from the room temperature shear tests but at a temperature of $\sim 100^{\circ}$ C to assure that any remaining low melting phase was not bearing part of the mechanical strength of the joint.

A smaller load multiplier with a capacity range of 70 to 800 psi testing was used in addition to the large multiplier used in the room temperature shear tests.

3.4 Temperature Reflow testing

An important metric for evaluation of bonds for electronic applications is the temperature at which the joining material will reflow. Bonding at low temperature is not helpful if the bond will fall apart while in service. To quantify the success of the diffusion joint in raising the reflow temperature, two types of tests were performed—shear based reflow tests and differential scanning calorimetry (DSC).

3.4.1 Shear based reflow testing

In order to determine the temperature at which bond integrity would be compromised, a high temperature fixture was designed to place the joint in shear (5psi load) while the fixture was heated. In order to verify the temperature of failure accurately, a thermocouple was mounted inside the fixture near the mating surface of the coupon (Figure 11) and an electrical switch was designed to monitor resistance and remotely indicate the bond's failure. Both of these instruments were connected to a data acquisition system to record the information and store it on a laptop computer.

A furnace was prepared with a large cast iron plate in the base to act as a thermal mass and to increase the heat transfer rate in the test fixture. The furnace was allowed to heat to a uniform temperature of 400°C before the test fixture was placed inside. Once the test began, the data acquisition system logged the temperature of the thermocouple as well as the state of the failure switch at a sampling frequency of 1Hz.

The test was run until the joint failed or the fixture reached a temperature above 300° C (usually ~10min). Figure 10 shows the mounting of the coupon (a), the fixture loaded and ready to be placed in the furnace (b), and the failed coupon bond after testing (c & d).

A Pb-Sn eutectic joint was prepared with the same pressure and conditions as the test joints but without dwell time to allow diffusion. This joint was used to calibrate the accuracy of the test apparatus and procedure. The eutectic temperature of the alloy is 183°C and the test indicated a bond failure temperature of 183°C.



Figure 10- Schematic of different stages in shear based reflow tests. A) & B) Loading the sample before testing; C) & D) Failed sample after test.



Figure 11- Schematic of fixture for shear based reflow tests and data acquisition tools used to monitor the state of the joint and temperature of bond failure.

3.4.2 Differential Scanning Calorimetry

Since these bonds were somewhat heterogeneous in nature, possibly from bismuth segregation, it is possible for various parts of the bond to melt at different temperatures. This heterogeneity may create a situation where parts of the bond area are liquid while other portions are solid. The solid may maintain some of the bond's mechanical strength (See Figure 12). The shear based reflow tests determined the final temperature of bond melting and intrinsically defined failure as the temperature at which the highest melting portion of the bond became liquid. Another important portion of bond evaluation includes evaluating at what temperature the onset of melting would take place or when the liquid pockets begin to form.

A method was devised by which differential scanning calorimetry was used to evaluate when different phases of the bonding region were melting. Samples were prepared by shearing the bonds apart to expose the bond region. Small samples (generally .1-.2" on a side) from these shear tests were used because of the size constraints of the thermal testing apparatus. These samples were placed in Aluminum pans with the bond material contacting the bottom of the pan in order to maximize instrument sensitivity. A Pyrus Diamond DSC was used to plot the thermal response of the materials as the heat was measured and was transferred to the sample. By comparing the thermal response of the sample with a platinum reference standard, phase transitions were evident in the data. Figure 20 shows a plot of the DSC results for the primary alloy used for bonding (In-36Bi-17Sn).



Figure 12- Partial bonding diagram with liquid pockets and solid portions.

3.5 Microscopic Joint Analysis

3.5.1 Scanning Electron Microscopy

A variety of samples were mounted in a low temperature mounting epoxy with conductive filler. These joints were then polished using 400, 600, and 800 grit silicon carbide paper wheels followed by 9 and 3 micron diamond suspensions and finished with a blend of 0.05 micron alumina and colloidal silica. It was noticed that many bismuth rich areas tended to have pick out polishing artifacts and in these cases the final polishing stage was more of a detriment.

After sufficient polishing, the joints were examined in a scanning electron microscope (SEM) with energy dispersive spectrometry (EDS) capabilities. Particular attention was paid to diffusion profiles of the bond elements by linescan EDS as well as the identification of intermetallic compositions by point EDS.

3.5.2 Microfocus X-ray

Microfocus X-ray was used to scan some joints for voids or noticeable bismuth segregation. The initial copper coupons were too thick to allow sufficient x-ray penetration for imaging so the joint faces were polished until the total joint thickness was about 0.060 inches.

Experimental Results

4.1 Shear Tests

4.1.1 Room Temperature Tests

The room temperature shear tests yielded results as expected. There was a noticeable strengthening of the joints as dwell time progressed and more copper diffused into the bond region. It appears that the most noticeable strengthening started to happen between 10 and 50 hours of dwell time at 125°C.

Most joints were loaded until joint fracture. The exception is the 250 hour dwell time joints. All joints aged to this point exhibited bond strength that exceeded the strength of the copper coupons. In these cases the tests were stopped when the copper began to shear and/or buckle under the loading (see figure 13). The strengths plotted in figure 14 are therefore lower than the actual strength of the joint interface.



Figure 13- Deformation of copper substrate before debonding in 250 hr dwell time joints after room temperature shear testing



Figure 14- Results from shear tests performed at room temperature

The data suggest that the bonds have reasonable room temperature strength as soon as they are bonded. It is clear that this strength begins to improve after continued baking without pressure. At a point between 100 and 250 hours the bond strength exceeds that of the copper substrate.

4.1.2 Low-melt Phase Exclusion Tests

The 100°C shear tests showed that the bonds lost a considerable portion of their mechanical strength when heated. Large liquid portions were observed in the ternary eutectic joints for all dwell times up to the 100 hr baked joint.

This test used one of three test fixtures depending on the range of joint strength. Figure 15 shows the capacity of the various fixture configurations. In the cases that a joint withstood the maximum capacity of one method but failed at the minimum capacity of the next method, a range bar was plotted on figure 16 to represent the failure.

Shear Fixture Capacity (psi)			
	Minimum Load	Maximum Load	
Test Fixture Alone	1	5	
Fixture with small load multiplier	68	948	
Fixture with large load multiplier	1,808	16,000	

Figure 15- Capacity for various shear test fixtures

Elevated Temperature Shear Testing (100°C)



Figure 16- Low-melt phase exclusion shear test results

It is clear that the eutectic joints had low strength until they were baked at least 10 hours. Their strength continued to increase with further baking time and the 250h joint had a bond strength of 4,600psi.

The low bismuth alloy joints' strength was good at low dwell time and increased dramatically as that time increased—3,200psi at 100h and >7,400psi at 250h (test was stopped at substrate deformation).

4.2 Temperature Reflow Testing

4.2.1 Shear Based Reflow Tests

In doing the shear based reflow tests, it was found that joints with as little as 15 minutes of dwell time were able to withstand a 5psi shear load at temperatures of 300+°C. However, when the fixture was tapped when removing the sample, many of the joints that had low dwell times (<1.5 hr) would break. In these cases the bond surfaces were inspected immediately and it was clear that the joints had liquid regions. This result supported the theory of liquid pockets and solid columns (figure 12) and necessitated the DSC and Low-melt exclusion shear tests in order to refine our definition of "remelt" temperature.

4.2.2 Differential Scanning Calorimetry

The DSC results were somewhat complex. They showed that all of the bonds had at least some regions of low temperature melting. Bonds with less dwell time would be expected to have this low melting phase, but the components of longer dwell time joints should have diffused to a point that these low melting phases are eliminated.

The persistence of low melting phases in long dwell time samples is best explained by the theory that the immiscibility of bismuth in copper drives the bismuth away from the high-melting copper infused phases. These segregated bismuth areas retain some indium and tin from the original alloy. In a way, these bismuth domains are protected from the copper that would diffuse into the alloy to raise its melting temperature. As a result, the small low melting regions are preserved. This idea is supported by an observation from the low-melt phase exclusion shear testing. It was noticed that when the low dwell time joints would break, their fracture surfaces were largely liquid. However, the highest dwell time joints had no detectible liquid at the fracture plane.

4.3 Metallographic Analysis

By examining the joints at various dwell times (figure 20), some of the stages of joint evolution became evident. Joints with no dwell time were mostly uniform in composition with a small amount of copper beginning to enter into the joint edges. In these early stages of evolution (0-0.5 hr) it was noticed that the joints had some areas of cracking (figure 17). It is most probable that these areas were due to the thermal contraction of the liquid phase while some areas of the bond were already solidified and constrained the bond thickness preventing shrinkage. Because no cracks were found in joints with dwell times above one hour, it can be inferred that these cracks heal as the diffusion further homogenizes the bond.



Figure 17- SEM image (1.0kX) of half hour dwell joint with thermal mismatch cracking

The interaction of copper and bismuth play a major role in the evolution of the bonds. Bismuth has very little solubility in copper (30ppm) and copper has virtually no solubility in bismuth¹⁷. The study of the joints at different dwell times revealed that the bismuth underwent a noticeable phase separation when copper diffused into the region. In the early joints (<1 hr dwell time), the bismuth seemed to remain in solution with the indium and tin while migrating away from the boundary areas where copper was able to penetrate. There is a point between one and two hours of dwell time when the copper penetrates so far into the joint that the concentration of bismuth is above the solubility limit and it begins to precipitate. As dwell time increases (2-10 hr), the bismuth congregates near the center of the joints. At a point near fifty hours of dwell, spherical regions that are rich in bismuth form near the centerline of the joint (figure 18). As time evolves further (>250 hr), the copper penetrates completely (~60% Cu concentration at the joint centerline) and the bismuth tends to be broken up from the large pockets into very small particles. These particles group themselves near the boundary of the bond and the substrate. This process can be seen in figure 19 where the previously large bismuth rich regions have been penetrated by the bulk material. The pockets of lightest color were analyzed and found to be pure bismuth.



Figure 18- SEM image (1.5kX) of 50 hour baked joint with bismuth congregation



Figure 19- SEM image (500X) of 250 hour baked joint with bismuth dispersion



Figure 20- EDS results of elemental intensity for variable dwell time joints

Conclusions

The work presented in this thesis shows that LTTLP bonding is a viable process for electronic packaging applications. The goal of creating a joint in 2 hours dwell time at 125°C that would exhibit no remelting below 200°C was not achieved with the systems that were explored.

However, it was found that strong bonds can be made in the 2 hour time limit. The room temperature properties of these joints are good immediately after bonding. When viewed in comparison with conventional solders (Pb-Sn & Sn-Ag), the room temperature bond strength is better after approximately 85-150 hours of baking at a temperature of 125°C or greater. These properties are reduced at elevated temperature (100°C) because of persistent low melting phases in the bond. With sufficient baking (~200-250h) the bonds will not break before substrate deformation, even at the elevated testing temperature. It is possible that a higher fixturing pressure or an alloy with some initial copper component would help to accelerate the formation/maturation of the bonds as it would reduce the average required diffusion distance.

Wetting was not noticeably increased with the addition of 1% Zn but the alloy with 6.4% Bi was found to wet the substrates more readily than the 36% Bi alloy probably because of the immiscibility of Bi and Cu.

LTTLP bonding with the In-Bi-Sn system is capable of producing good joints that are almost defect free. Since the joints' mechanical properties improve over the life of the joint, care should be exercised in implementing such a process without an appropriate baking procedure to strengthen the bond. The small regions of low melting components may serve to reduce thermal stresses, but could in time coagulate and lead to joint deterioration. Ultimately, the process must be analyzed for specific applications and considered with all of its advantages and risks.

In making the LTTLP bonds, care must be exercised to ensure that:

- 1. the substrates are flat and have been cleaned and degreased immediately prior to bonding
- 2. the atmosphere is dry and free of oxygen
- 3. the alloy wets the substrate completely in the ultrasonic scrubbing step
- 4. the pressure is applied in an even fashion

Future Work

This thesis provides a basis for the development of a LTTLP bonding process by which heat sensitive electronics may be joined at low temperatures and without the use of chemical fluxes or environmentally restricted metals. Ideally, the process would wet the substrate without the use of an ultrasonic lapper, bond at a lower temperature, and diffusion strengthen with less dwell time. To this end, further investigations into many aspects of the joining process are necessary and include

- 1. Optimizing the applied pressure in joining to maximize mechanical strength and minimize dwell time for solidification/strengthening
- 2. Further surveying the alloy system to find the ideal amount of bismuth (and copper) to be included in the initial bonding alloy
- 3. Studying joint formation at even lower temperatures (~75°C) to determine the feasibility of ultra low temperature bonding
- 4. Refining tensile/shear testing to study mechanical properties of the joints
- 5. Investigating creep resistance of the bonds

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