

Stacked Ceramic Capacitors for High Temperatures ($\geq 200^{\circ}\text{C}$)

John Bultitude, Lonnie Jones, John McConnell, and Abhijit Gurav
KEMET Electronics Corporation

2835 KEMET Way, Simpsonville, SC 29681, USA

Tel: +01-864-963-6450, Fax: +01-864-963-6492, e-mail: johnbultitude@kemet.com

Abstract

High temperature applications at 200°C or above in electronics for down-hole drilling are driving the development of capacitors with ever more reliable performance. Deeper wells with increased temperatures and pressures have resulted in exposure to harsher conditions for longer times for the electronics used in the extraction tools and deep-well control instrumentation. The capacitor solutions currently available for 200°C operation are reviewed by value and rated voltage. Some key reliability factors attributed of the various technologies are identified. The recent development of stacks made using multi-layer ceramic capacitors (MLCC) of Class-I COG type dielectric material with nickel inner electrodes are outlined with respect to their performance benefits at $\geq 200^{\circ}\text{C}$. Due to its linear dielectric nature this material exhibits highly stable capacitance as a function of temperature and voltage. The development of higher voltages and larger case size capacitors using this technology is discussed together with their incorporation into stacked ceramic capacitors by soldering on lead frames. Stacks of multi-layer ceramic capacitors (MLCC) allow capacitance to be maximized within the volume available. However, the solder interconnects must be evaluated to assess the long term reliability of the stacks at higher temperatures particularly with respect to maintaining mechanical and electrical integrity. The development of a custom high temperature shear test to evaluate the performance of different solder interconnects at temperatures from 200 to 260°C is described. Evaluations of two different HMP Pb-based solders are presented. The high and low temperature shear test data acquired for these solders is analyzed in terms of the strain and strain energy when force is applied. Changes in performance after exposure to temperatures $\geq 200^{\circ}\text{C}$ are assessed. The results are interpreted with respect to the values required to survive high g-forces and the performance of the different solder compositions. Performance considerations for high shear strength interconnects at 200°C and beyond are discussed.

Key words: stacked ceramic capacitors, BME MLCC, COG, HMP Solders, high temperature interconnects

1. Introduction

The oldest and largest user of high temperature electronics ($\geq 150^{\circ}\text{C}$) is the downhole oil and gas industry. In the recent past these applications have been limited to 175°C but as easily accessible reserves decline the exploration of more hostile wells with temperatures $\geq 200^{\circ}\text{C}$ and pressures > 25 kpsi has begun [1]. Since active cooling is not possible for the exploration tools the electronics must be capable of withstanding these harsh mission profiles. As with most electronics, capacitors are required to function reliably in these environments. To better understand the options available for capacitors rated for operation at 200°C a survey of the leading

capacitor suppliers was conducted in January 2014 and ranges of the different capacitor types is shown in Figure 1. The comparison shows the maximum capacitance limits by voltage rating but there is no consideration of the size of the capacitors that is a critical consideration. The leaded MLCC range closely follows that of the surface mounted MLCC except for the high voltage ratings. This is because larger case size surface mounted parts are more prone to mechanical damage such as flexure and this is mitigated using leads. It can be seen that Stacked MLCC can achieve even higher capacitance values over a broad range of voltages. The other types of

capacitor, wet Ta, solid Ta and silicon capacitors are limited to < 100V ratings.

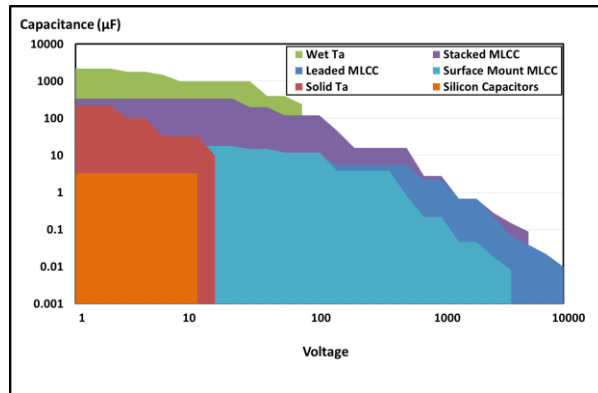


Fig. 1. Capacitance vs. Voltage ranges of different capacitor types rated at 200°C.

2. Ceramic Materials Considerations

An important consideration for the MLCC ranges shown is that the highest capacitances reported are based for class 2 dielectrics of X7R or X8R that have significant loss of capacitance at 200°C and rated voltage. The capacitance at 200°C and rated voltage is usually $\geq 40\%$ the reported value at 25°C so is an important design consideration for the high temperature electronics. These class 2 ferroelectric dielectrics are based on barium titanate. In its pure form barium titanate undergoes a phase change from tetragonal to cubic above 130°C with subsequent loss of domains and so has less ability to store charge. MLCCs manufactured from class 1 paraelectric dielectrics usually based on rare earth titanates with precious metal electrodes (PME) do not undergo these phase changes so are more stable with temperature but have significantly lower capacitance [2]. A Class1 COG/NP0 dielectric based on a calcium zirconate dielectric compatible with nickel inner electrodes was developed with high reliability in thinner active layers than PME materials [3]. This allowed higher capacitance MLCC to be manufactured. In subsequent developments this technology was applied to high temperature surface mount MLCC [4], high voltage ($\geq 500\text{V}$ to 2000V) MLCC, and radial leaded MLCC [5] all rated to 200°C. Measurements of capacitance at rated voltage for these COG were compared to a competitor PME X7R as reproduced in Figure 2.

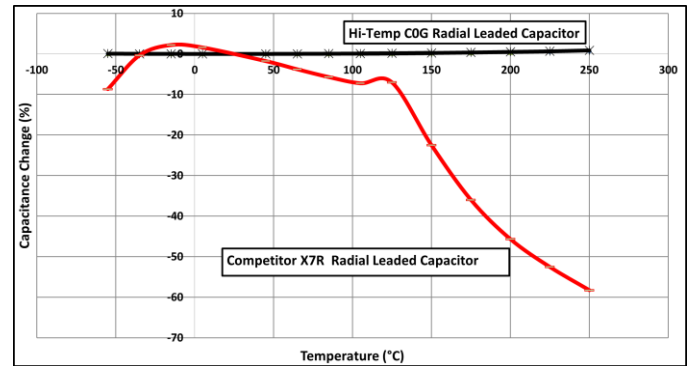


Fig. 2. Capacitance Change with Temperature for radial leaded HT COG (0.22µF) vs. competitor X7R (1.2µF) both rated 100V.

Above 200°C the competitor X7R has a significant loss of capacitance of over 45% compared to the rated value at 25°C. Furthermore if the capacitance per unit volume is considered when the rated voltage is applied then the CV per unit volume is higher for the COG capacitor (Figure 3.).

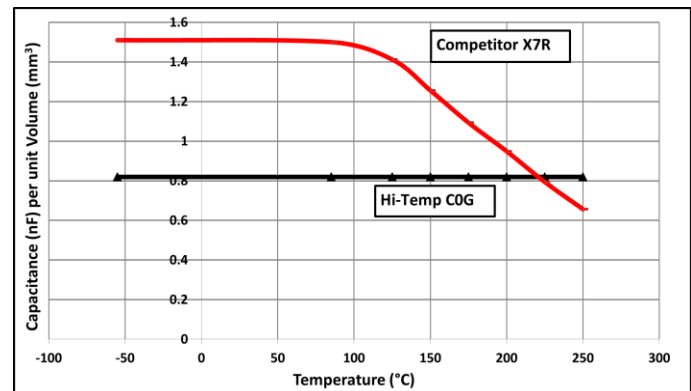


Fig. 3. Capacitance per Unit Volume for radial leaded HT COG vs. competitor X7R.

3. Stacked Ceramic Capacitors using HT COG

Even with the desirable combination of high reliability at high temperature coupled with high capacitance per unit volume there was a demand for even higher value leaded capacitors. For this reason we develop and offered stacked capacitors based on assembling multiple MLCC of ≤ 2220 case size MLCC into lead frames with high melting point Pb-based solders. A typical example of these stacks was previously presented [6]. The electrical properties of a stack of 2220 MLCC compared favorably to those

of a wet Ta capacitor of similar size and voltage rating and Table I and Figure 4 respectively.

Property	Wet Ta, T1, 4.7 μ F, 36V rating @ 200°C	HT COG Stack, 4.7 μ F, 50V rating @ 200°C
Max. ESR @ 25°C, 120Hz	9.3 Ω	0.060 Ω
Insulation Resistance	0.06 G Ω	1.6 G Ω
Max. Ripple @ 40kHz rms	0.525 A	10 A (Min.)

Table I. Electrical Comparison of Wet Ta to MLCC Stack made with HT COG.

Although much lower capacitance than can be realized than wet Ta technology by comparing similar sized and rated capacitors (Figure 4.). The stack has lower ESR, higher ripple current capability and lower leakage (Table I).

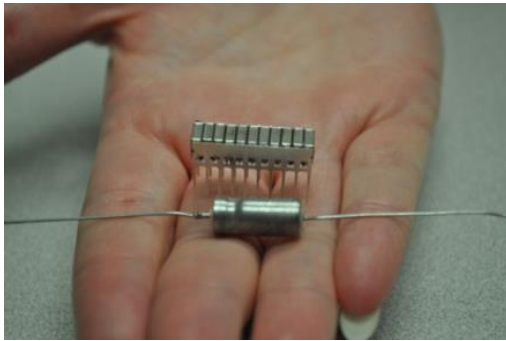


Fig. 4. Size Comparison of Wet Ta to MLCC Stack made with HT COG.

These advantages have led to applications for these types of stacks for ratings ≤ 200 V. However, there is also a need for higher voltage > 500 V stacks that can be used at $\geq 200^\circ\text{C}$. These applications have until recently been exclusively serviced by stacks of 200°C rated class 2 X7R MLCC. However, as was noted earlier the class 2 X7R or X8R type materials loose at least 40% capacitance at 200°C rated voltage. For this reason we have extended the capacitance range of our COG HT Stacks by manufacturing and stacking larger case size MLCC (3040 – 6560) in lead frames to voltage ratings up to 1000V. The capacitance per unit volume of these high temperature rated COG stacks were compared to the catalog offerings of competitor X7R and COG stacks in Figure 5.

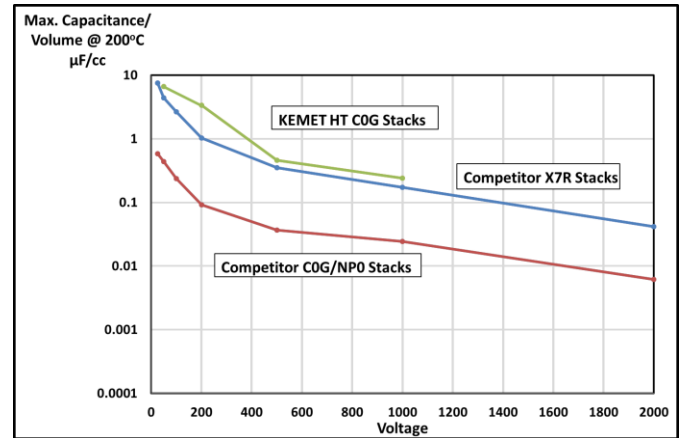


Fig. 5. Maximum Capacitance per Unit Volume of different stack types at 200°C .

The capacitance per unit volume of the high temperature COG stacks at 200°C are comparable to competitor X7R offerings and far higher than the competitor COG/NPO stacks. Furthermore, as already shown in Figure 3, the capacitance of X7R MLCC continue to decrease with temperature above 200°C resulting in lower available capacitance than the COG stacks at these elevated temperatures.

4. Solder Performance Testing

In order to realize reliable performance with respect to these high temperature COG stacks we embarked on an intensive study of lead attachment process and materials. High melting point (HMP) Pb-based solders have been traditionally used for lead attachment in high temperature stacks. Maintaining a reliable connection is of particular concern in downhole drilling where stacked capacitors may experience significant shear forces on the leads due to high vibration and shock loads present close to the drill head. The temperatures in this environment can exceed 200°C , but mechanical property data on solder alloys at these temperatures is not commonly available. Using mechanical properties of solder alloys measured at room temperature and solder alloy absolute melting temperatures are a guide to high temperature performance, but relying on this data solely to choose a solder alloy for high temperature applications is risky. Furthermore requiring large safety margins with respect to solder melting point may not be practical as it becomes desirable to increase the operating temperature of the electronics. A literature study of the reliability of die attach materials recommended using solders at 80% of their absolute melting temperature to avoid degradation due to creep effects [7]. Higher melting point Pb-free solders were deemed too expensive (AuSn, AuGe or

AuSi) or to have poor processability (BiAg or ZnAl). The selected solders for these studies and their melting points from supplier information are shown in Table II together with 80% of melting temperature.

Solder	Melting Temp, °C	80% of Melting Temp, °C
10Sn/88Pb/2Ag	290	232
93.5Pb/5Sn/1.5Ag	305	244
91.5Sn/8.5Sb	240	192
SAC 305	217	174

Table II. Properties of Selected Solders

The multiaxial loading on a solder joint of an MLCC stack in a high shock and vibration environment is complex, and is usually assessed through functional testing of partial or complete electronic assemblies. This approach is expensive, time consuming and does not always provide useful data that can be applied to improve the robustness of a stack design. To gain a basic understanding of mechanical property changes of solder joints at high temperatures and over long time periods, a test sample was prepared that is a good analog for a functional stacked MLCC on which shear testing of the stack solder joint could be performed at elevated temperatures. Shear testing simulates the most critical stresses that occur on solder joints during shock and vibration conditions.

The test sample consisted of a 4060 case size tin plated MLCC with two leads approximately 0.23" wide and 0.01" nominal thickness soldered to each side of the MLCC. The lead consists of phosphor bronze base metal overplated with a Ni barrier and finish coated with plated silver. Two lead based solders, 10Sn/88Pb/2Ag and 95Pb/3.5Sn/1.5Ag and two lead-free solders, 92.5Sn/8.5Sb and 96Sn/3.5Ag/0.5Cu (SAC 305) were used to attach the leads to the MLCC's. The MLCCs tested with the Pb containing solders were solder coated prior to assembly to remove the plated tin and minimize the change to these compositions. Since the solders have different densities and the solder pastes have different solids loading, volumes of the various solder pastes used for lead attachment were adjusted so as to consistently fill the joint so that valid comparisons of joint strength of the various solders can be made.

The shear test was accomplished using a Stable Micro Systems Texture Analyzer with a 250 kg load cell and crosshead position resolution of

0.001mm. A temperature chamber was used to heat samples up to 290°C to allow shear measurements at elevated temperatures. Low mass fixturing was designed to clamp the MLCC and lead firmly and squarely to the test head while minimizing heat loss to the test head and machine base. Thermocouples for temperature monitoring were located on the part clamp and heated air surrounding the part to ensure uniform and accurate heating of the joint. The shear area of the solder joint was approximately 0.096 cm². All shear tests were performed at a crosshead speed of 0.1mm/sec.

The as made samples of the Pb-based solders were shear tested at ambient (25°C) and at elevated temperatures of 85°C, 150°C, 200°C, 230°C, 260°C and 290°C. Samples were also prepared with the Pb-free solders SAC 305 and 91.5Sn/8.5Sb and shear tested in a similar way for reference. Samples of Pb-based solders were also exposed to temperatures of 200°C, 230°C and 260°C for 500 hours and then shear tested at these temperatures to evaluate the effect of a longer term temperature exposure on the solder joint shear strength. In all cases six shear measurements were performed for each solder at each condition.

5. Shear Testing Analysis

The sheared samples failed due to solder fracture in all cases as shown in Figure 6.

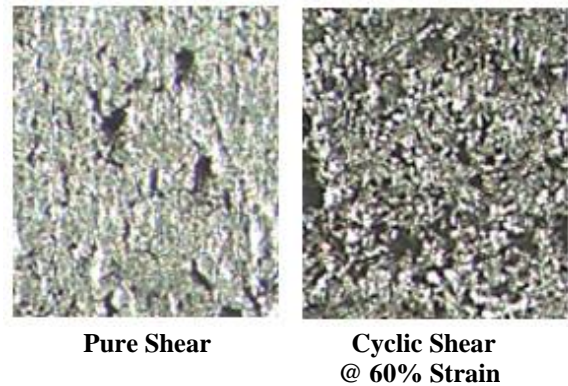


Fig. 6. Optical photographs of shear surfaces.

Although not readily apparent from these optical photographs the pure shear failures appear smeared consistent with an elongation to failure whereas the cyclic failures exhibit characteristics of brittle fracture.

To illustrate the data acquired, an example of the output from the shear test for a sample of 95Pb/3.5Sn/1.5Ag solder at 150°C is shown in Fig 7.

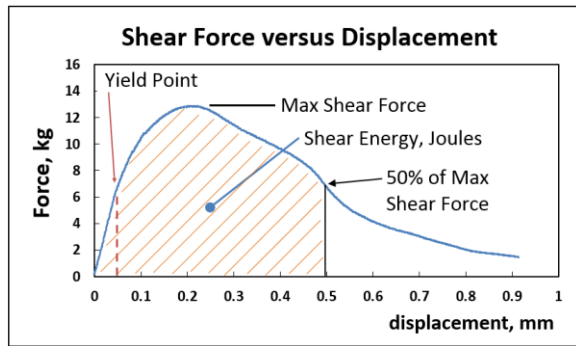


Fig. 7. Shear Test Output.

Based on the geometry of the test sample and the shear test data, the yield shear stress in MPa, the maximum shear stress in MPa, and the shear energy in Joules were calculated for each sample for each condition. Averages of these characteristics are plotted for each condition along with the coefficient of variation.

Shear stress is defined as the component of stress parallel to the cross section of the material [8].

$$\tau = \frac{F}{A}$$

where:

- T = the shear stress;
- F = the force applied;
- A = the cross-sectional area of the material with area parallel to the applied force vector.

The maximum shear stress was determined by dividing the maximum force recorded during the shear test in kg and dividing the force by the area of the solder joint. This value was converted to units of MPa.

The yield shear stress was determined by finding the shear force at the yield point of the sample (where plastic deformation begins to occur) and dividing this force by the area of the solder joint. This value was converted to unit of MPa.

Percent shear strain was calculated by dividing the measured displacement by the thickness of the solder joint (Figure 8). Mechanical fixturing was used to ensure the solder joint gap (thickness) for all samples was similar.

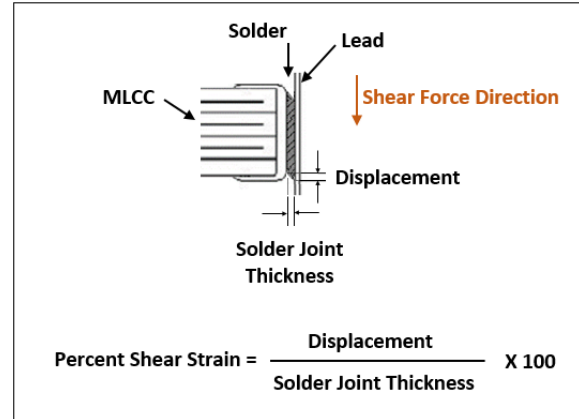


Figure 8. Illustration of Shear Test and Percent Strain Calculation.

It can be seen in Figure 7 that the solder did not exhibit a rupture failure mode but rather a continuing elongation to eventual failure. To facilitate a reasonable estimate of shear energy, solder joint failure was defined to occur when the shear stress decreased by 50% from the maximum shear stress. This behavior was observed in all the solders tested. Shear energy was determined by estimating the area under the stress/strain curve up to this defined strain limit and converting to units of energy, Joules.

The maximum shear stress values obtained with increasing temperature are shown for all 4 solders in Figure 9.

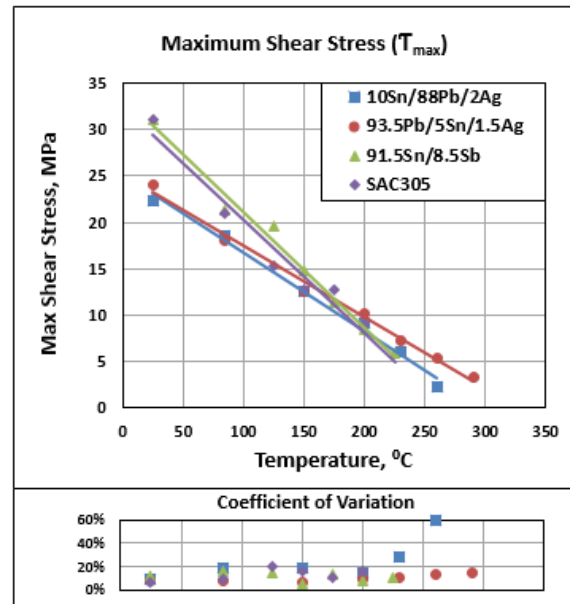


Fig. 9. Maximum shear stress vs. temperature for as made samples

The corresponding yield shear stresses are shown in Figure 10.

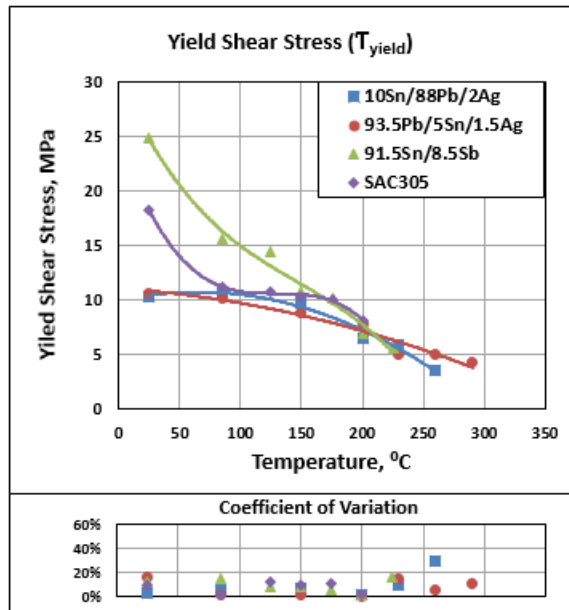


Fig. 10. Yield shear stress vs. temperature for as made samples

The Pb-free solders have higher maximum shear stress at ambient temperatures but these decline more rapidly at elevated temperatures closer to their melting points. The maximum shear stress of the 10Sn/88Pb /2Ag is lower than the 95Pb/3.5Sn/1.5Ag solder at 250°C and this corresponds to an increase in the coefficient of variation. The yield shear stress shows a similar trend to the maximum shear stress for all 4 solders tested. However, the yield shear stresses did not show a linear change with temperature.

Based on an understanding of the stress-strain behavior of the solder, shock and vibration mechanics can be employed to estimate the strain on the solder joint for assumed shock and vibration spectra. One simple approach is to estimate the shock load on the solder joint in shear for a given stacked MLCC design undergoing significant g-forces, estimate the shear strain on the joint and refer to the shear stress-strain relationship for the solder to estimate the behavior of the solder while experiencing the shear strain. For example, based on the weight of the 4060 size MLCC used in this shear testing and the solder joint area, the estimated shear stress associated with a 1000g shock is 0.75MPa. This stress is significantly less than the yield shear stress of the solders shown here, and the application of a single 1000g shock would therefore not be expected to permanently deform the solder joint. However, multiple cycles of shear force would

have to be applied for different strains to understand the cyclic fatigue life of the solder joint and confirmed through subsequent temperature cycling and vibration testing on design prototypes.

The maximum shear stress of the Pb-based solders is compared to samples exposed to 200°C, 230°C and 260°C for 500 hours in Figure 11.

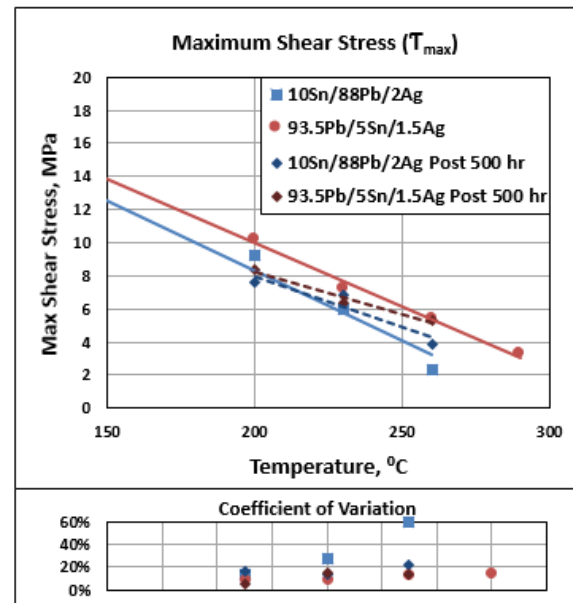


Fig. 11. Maximum shear stress vs. temperature for Pb-solder samples as made and after high temperature exposure.

The exposure of the 10Sn/88Pb/2Ag and 95Pb/3.5Sn/1.5Ag solders to these elevated temperatures does not appear to have resulted in a significant decline in their maximum shear stress.

The shear energy change with temperature for the as made solders is shown in Figure 12.

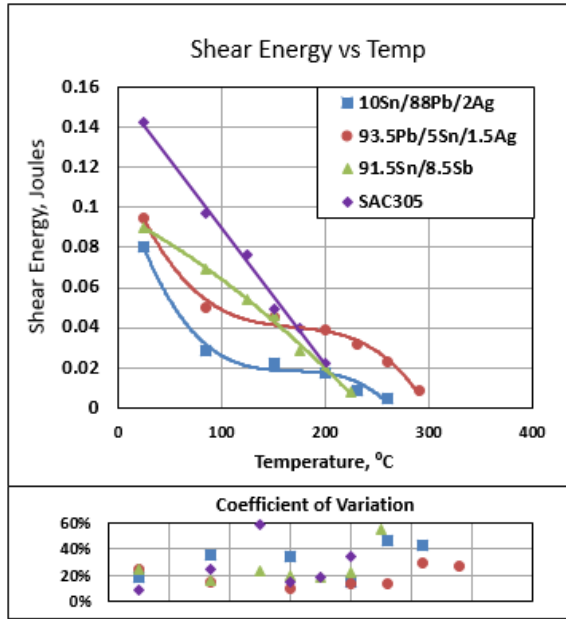


Fig. 12. Shear energy vs. temperature for as made solders.

At ambient temperatures the shear energy of the SAC 305 Pb-free solder exceeds that of Pb-based solders but this declines rapidly with temperature. Above 200°C both Pb-free solders have lower strain energy than Pb-based solders.

The strain energies of the Pb-based solders is compared to samples exposed to 200°C, 230°C and 260°C for 500 hours in Figure 13.

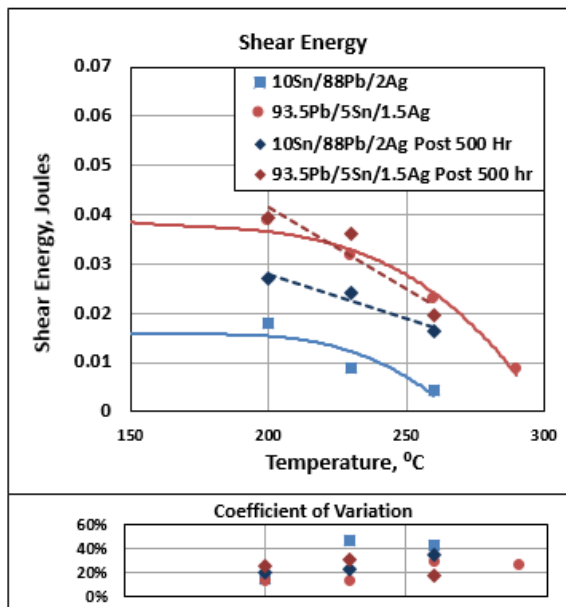


Fig. 13. Shear strain energy vs. temperature for Pb-solder samples as made and after high temperature exposure.

Exposure of the 10Sn/88Pb/2Ag to solders at these elevated temperatures appears to increase the strain energy compared to the as made samples. The root cause for this change is not known at this time.

6. Cyclic Stress-Strain Fatigue Evaluations

Cyclic stress-strain testing is another tool that can be used to highlight differences in the mechanical performance of solder alloys [9].

A Stable Micro Systems Texture Analyzer was used to perform low shear strain cyclic testing on a test piece made using the same lead as described in section 4 above except a 4540 size MLCC was used with one lead per side. Three solder alloys were used to attach the leads to the MLCC, two lead based solders, 10Sn/88Pb /2Ag and 95Pb/3.5Sn/1.5Ag and one lead-free solder, 96Sn/3.5Ag/5Cu using the same methods as the stress test samples. The solder paste volumes were adjusted to fill the solder joint volume. As before the solder joint area was approximate 0.096cm². The test fixture was designed to hold the MLCC and lead parallel and square to the test head and to minimize flexing of the lead during cycling.

Levels of strain were chosen based on the relative strengths of the solders so that the measured cycles to failure ranged from approximately 5 to 25000 cycles. Because the amounts of strain were small relative to the resolution of the crosshead encoder, absolute movement of the lead clamp was independently verified using a digital micrometer with resolution of 3 microns. The measured strain was corrected using this method to ensure accurate reporting of the strains used to generate the cycles to failure data.

An example of the stress-strain hysteresis loop obtained by this method is shown in Figure 15 for the 95Pb/3.5Sn/1.5Ag solder tested at ambient temperature for a shear strain range of 45%.

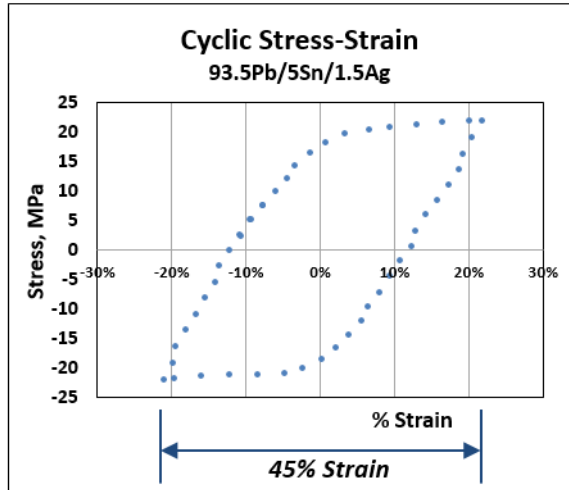


Fig. 15. Example Stress-Strain Hysteresis Loop.

In order to make this evaluation the shear tester used for the previous measurements was programmed to apply different displacements at one cycle per second, and the number of cycles to failure, N , was recorded [9]. The fatigue failure was defined as a 50% reduction of the maximum shear force. This work was performed on the Pb-based and SAC 305 solders at ambient temperature as shown in Figure 16.

In addition, stress-strain cycling was performed at elevated temperatures of 150°C and 200°C to determine how the fatigue resistance of the 95Pb/3.5Sn/1.5Ag and SAC 305 solders change with temperature as shown in Figures 17 and 18, respectively.

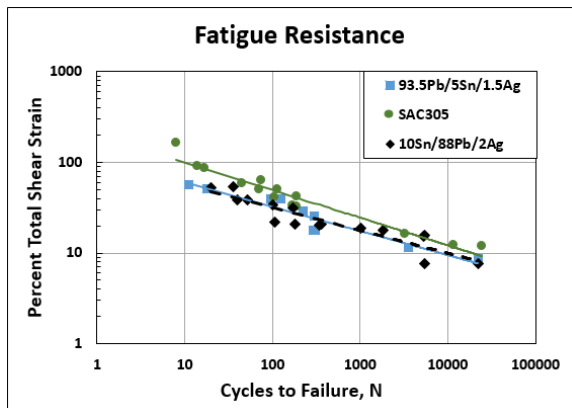


Fig. 16. Fatigue Resistance of Different Solders

At ambient temperatures the SAC 305 solder has higher fatigue resistance than the Pb-based solders.

The 10Sn/88Pb /2Ag and 95Pb/3.5Sn/1.5Ag solders have very similar fatigue performance at ambient temperatures.

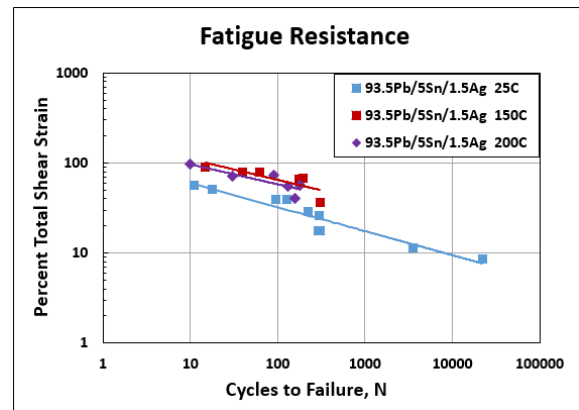


Fig. 17. Fatigue resistance of 93.5Pb/5Sn/1.5Ag solder at three temperatures.

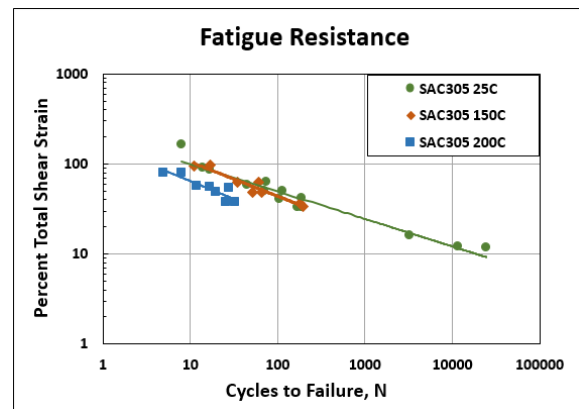


Fig 18. Fatigue resistance of SAC 305 solder at three temperatures.

The 95Pb/3.5Sn/1.5Ag solder shows higher fatigue performance at both 150 and 200°C at relatively high strains. The SAC 305 had similar fatigue performance at ambient and 150°C but showed a significant degradation at 200°C. This higher temperature may be too close to the melting point of SAC 305.

7. Summary

Ceramic stacks manufactured with HT COG MLCC were shown to have higher available capacitance at temperatures $\geq 200^\circ\text{C}$ compared to other available ceramic stacks. The HT COG stacks offer some performance benefits over other capacitor types and their high voltage performance $> 200\text{V}$ is of particular interest. Shear test evaluations were made on 4 different solders up to 290°C to better understand their performance as lead attachment on the ceramic stacks. At elevated temperatures above 200°C the properties of Pb-free, SAC 305 and SnSb solders are significantly lower than the Pb-based solders tested. The 95Pb/3.5Sn/1.5Ag solder appears to retain its useful properties above 250°C whereas the 10Sn/88Pb/2Ag solder approaches its useful limit at this temperature. Interestingly the strain energy associated with 10Sn/88Pb/2Ag solder increased on 500 hour exposure at elevated temperatures $\geq 200^\circ\text{C}$ for reasons that are not fully understood. Stress-strain cycle fatigue testing was explored and SAC 305 showed a significant degradation at 200°C whereas 95Pb/3.5Sn/1.5Ag maintained its fatigue performance at this temperature.

8. Future Work

These evaluations indicate that the Pb-free solders tested have limited performance above 200°C . The high temperature shear and shear-strain tests developed should allow us to compare other solder and interconnect materials with the long term goal of identifying viable Pb-free high temperature interconnects. In the future we hope to compare and correlate the Pb-based solder testing to application specific tests.

9. References

- [1] J. Watson, et al., "High Temperature Electronics Pose Design and Reliability Challenges," p1-7, *Analog Dialog*, 46-04, April 2012.
- [2] I. Burn., "Ceramic Capacitor Dielectrics" p1102-1118, *Engineered Materials Handbook; Ceramics and Glasses*, Volume 4, 1991.
- [3] X. Xu, et al., "Robust Class 1 MLCCs for Harsh Environment Applications," p2636-2643, *IEEE Transactions on Industrial Electronics*, Volume 58, No.7 July 2011.
- [4] J. Magee, et al., "High Voltage Multi-Layer Ceramic Capacitors for Use at High Temperatures," p263-274, *Proceedings of the 33rd Symposium for Passive Components (CARTS USA 2013)*, Houston, TX, USA, March 25-28, 2013.
- [5] R. Phillips, et al., "High Temperature Ceramic capacitors for Deep Well Applications," p69-77,

Proceedings of the 33rd Symposium for Passive Components (CARTS USA 2013), Houston, TX, USA, March 25-28, 2013.

- [6] A. Gurav, et al., "Ceramic Capacitors and Stacks for High Temperature Applications", p30-37, *Proceedings IMAPs International Conference on High Temperature Electronics Network (HiTEN 2011)*, St Catherines College, Oxford, UK, 2011.
- [7] M. Knorr, et al., "Reliability Assessment of Sintered Nano-Silver Die Attachment for Power Semiconductors", p56-61, *IEEE Proceedings of 12th Electronics Packaging Technology Conference*, Shangri-La Hotel, Singapore, December 8-10, 2010.
- [8] R.C.Hibbler, *Mechanics of Materials*, p32, New Jersey, USA 2004 ISBN 0-13-191345-X
- [9] Y. Kariya et al., "Low Cycle Fatigue Properties of Ni added Low Silver Content Sn-Ag-Cu Flip Chip Interconnects", p689-694, *Material Transactions*, Volume 45, No. 3, 2004.