High-Reliability Solder Alloys' Impact on Pb-free TF Conductors

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ABSTRACT

Fired-on thick film conductors continue to be the preferred choice for electronic circuits in high-reliability applications. The demand for high-performance thick film circuits is consistently growing, especially in sectors such as automotive, aerospace, and military, making the need for reliable solder joints critical. The transition to lead (Pb)-free solder joints in thick film applications has been accompanied by reliability challenges, specifically with SAC (tin-silver-copper) alloys that have raised concerns in thermal aging and cycling performance. To address the reliability concerns, a series of test vehicles were manufactured to accurately evaluate the reliability of thick film and solder joints according to rigorous standards. These test vehicles – assembled on alumina oxide substrates – involved the combination of Pb-free silver-bearing thick film conductors, including Ag, AgPd, and APt alloys, with various SAC options such as SAC305 (used as a control), "HiRel A" alloy, and "HiRel B" alloy. The primary objective of this paper is to determine the most effective Pb-free solder/thick film combination through assessing these test vehicles after undergoing thermal cycling from -40°C to 150°C, as well as thermal aging at 150°C, via electrical, optical, and mechanical testing to meet the demands of high-reliability applications.

Key words: thick film, solder, lead free, high reliability

INTRODUCTION

Over the past few decades, the electronics industry has experienced an unstoppable demand for high-reliability materials across all markets. Thick film is seen as the leader for circuitry in markets from consumer products to defense and aerospace. The adhesion of the conductor to the substrate is of utmost importance, and solder joint reliability also plays a significant role in the overall circuit performance robustness. Simultaneously, the industry has been experiencing a global push towards lead-free materials, an initiative that has been largely driven by the installment of the Restriction of Hazardous Substances (RoHS) directive, which aims to address environmental and human health concerns tied with the use of Pb in electronics. Consequently, thick film and solder manufacturers have had to pivot to Pb-free formulations to ensure compliance with current regulations whilst increasing reliability performance.

There are already well known and readily available Pb-free solder alloys such as SAC being used in industry. However, the SAC solder alloy does not come without its challenges. The performance of SAC alloys in high-reliability settings has not been up to par, specifically during thermal cycling and aging, during which brittle intermetallics such as Ag_5Sn and Ag_3Sn are formed [1].

The following paper will review a reliability matrix of Pb-free thick film conductors and solder alloys after thermal cycling of -40°C to 150°C and thermal aging at 150°C for up to 1000 cycles and hours, respectively, to which the solder joints will be evaluated for cracking and fractures through optical, electrical, and mechanical tests.

MATERIAL SELECTION

SAC305 is a common Pb-free solder alloy, regardless of the reliability concerns. For this paper, two other Pb-free alloys, "HiRel A," a variation of the SAC alloy developed for PCB with high creep strength, and "HiRel B", a solder developed for alumina and high temperature environments, were selected to be tested against SAC305 performance, used as the control. Table 1 shows the solder selected for this paper.

Table 1. Solder Selection

SOLDER	*OPERATING TEMPERATURE [°C]*	*MELTING POINT [°C]*
SAC305	150	217
HIREL A	150	206-218
HIREL B	175	210-216

The adhesion of the thick film conductor to the substrate and the connection of the solder joint to the conductor are key players in reliable circuits. Thick film conductors come in a variety of metals and alloys, including but not limited to Ag, AgPt, and AgPd. The choice of thick film metal depends on the balance of performance and cost. For example, an AgPd conductor will be more resistant to solder leaching than just Ag alone but will be at a higher cost depending on the ratio. The Pb-free thick film conductors chosen for this paper vary by Ag content that cover multiple reliability and application requirements in the final circuit. Table 2 displays a list of the conductors used in this study, as well as their metal ratios.

Table 2. Conductor Selections

METAL	*RATIO*	*RESISTIVITY*
AG	-	< 3 mOhm/sq
AG:PT	99:1	< 5 mOhm/sq
AG:PD	30:1	< 6 mOhm/sq

EXPERIMENTAL SET-UP

For this study, a design of experiments (DOE) was developed to test the combinations of the three solder alloys and three Ag-based thick film conductors printed and fired on alumina test vehicles. Each test vehicle carried two different types of chip components – chip resistors and multilayer chip capacitors (MLCC) – of various sizes. Chip resistors and MLCCs were chosen for this study due to their difference in body material – alumina and barium titanate-based ceramics, respectively. These materials exhibit varying thermomechanical properties and compress and contract in distinct ways when exposed to changes in thermal conditions [2]. These test vehicles were then subjected to thermal cycling or thermal aging. Table 3 displays the variables of this DOE, which resulted in 252 individual test groups for this study.

Table 3. Experiment DOE

SOLDER ALLOY	*METAL*	*TREATMENT*	*CHIP SIZE*	*CHIP TYPE*
SAC305	Ag	Thermal Aging – 1000hrs	0402	MLCC
Hi Rel A	AgPd	Thermal Cycling – 48 cycles	1206	Resistor
Hi Rel B	AgPt	Thermal Cycling – 100 cycles		
		Thermal Cycling – 250 cycles		
		Thermal Cycling – 500 cycles		
		Thermal Cycling – 1000 cycles		
		Control – No treatment		

A total of 63 test vehicles (one board per solder/conductor combination per thermal treatment) were manufactured via screen printing an individual thick film conductor on a 96% alumina, 4x4" substrate, shown in Image 1. Conductors were dried in a box oven at 150°C for 10 minutes and then fired in a belt furnace with a peak firing temperature of 850°C for a 10-minute dwell time. Final fired thickness of the conductor traces was 11±1 microns.

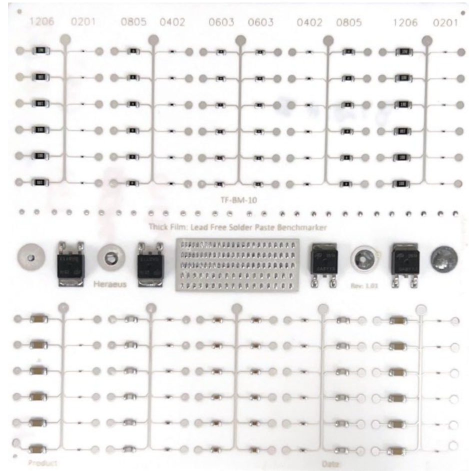

Image 1. Example of control test vehicles after solder reflow.

The solder alloys were then stenciled onto the substrate using a 4 mil stencil using a 1:1 solder pad to conductor pad ratio. Chip resistors and MLCCs, 12 of each size, were placed with resistors occupying the top half of the board and MLCCs in the bottom half. The use of a standard SAC linear solder reflow profile was kept consistent across all solder alloys so as not have solder processes be a variable in the DOE. Figure 1 shows the solder reflow profile.

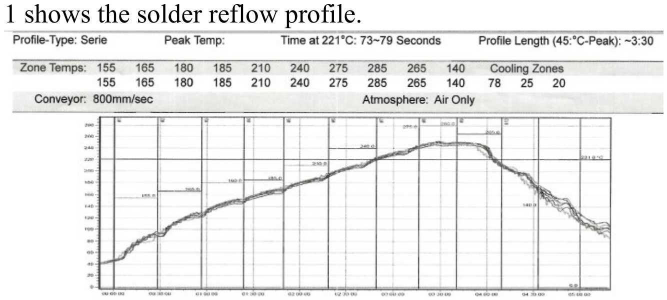

Figure 1. Solder reflow profile

Once built, the test vehicles and their chip components were imaged prior to going through either thermal cycling or aging. Initial electrical resistance and capacitance, for the respective component types, were also measured prior to beginning thermal treatments.

One board for each solder/conductor combination was placed in a box oven set at 150°C for 1000 hours for thermal aging. The other 45 boards were thermal cycled at -40°C to 150°C with a ramp of 5° per minute and a soak time of 15 minutes. Figure 2 shows the temperature cycle profile used.

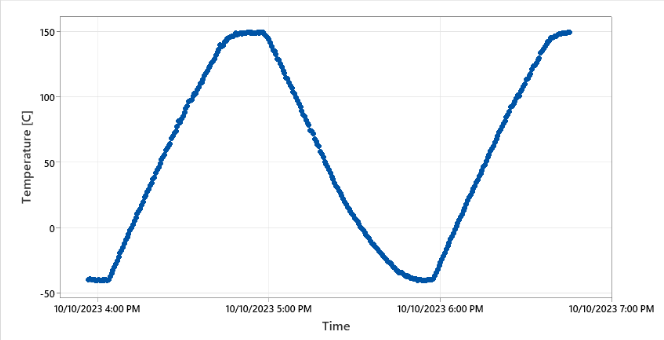

Figure 2. Thermal cycling profile

Vehicles were tested after 48, 100, 250, 500, and 1000 thermal cycles. After thermal treatment, the boards were imaged and electrically tested to detect cracking or fractures and changes in electrical values.

Shear testing was performed on the chips to determine changes in solder joint mechanical strength during and after the thermal cycling/aging tests.

THERMAL CYCLE TEST RESULTS

Thermal cycle testing aims to identify potential weaknesses, such as material fatigue, solder joint integrity, and electrical performance degradation, thereby enabling engineers to enhance the durability and robustness of electronic systems. The insights gained from thermal cycle testing play a pivotal role in ensuring the long-term reliability and resilience of electronic devices and systems across diverse applications and industries.

Optical Images

Below, images 2-4 represent chips before and after thermal cycling. Image 2 shows solders in combination with an Ag conductor at a 1206 case size, but the images are representative of external defects observed for all conductors and resistor case sizes.

After 1000 thermal cycles, both high-reliability solders look significantly better than the SAC305 control, which showed discoloration caused by oxidation.

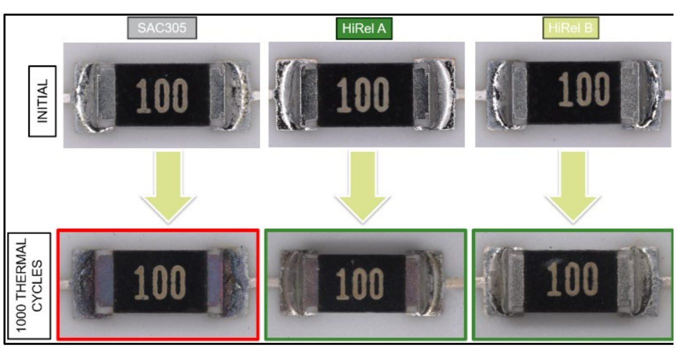

Image 2. 1206 chip resistors with each solder type, each soldered to Ag thick film conductor before and after undergoing 1000 cycles of thermal cycling at -40°C to 150°C Based on the cross-sectional images, it is evident that the chip resistors exhibit minimal cracking following thermal cycling, particularly with HiRel B. This outcome is likely attributed to the comparable CTE values of the chips and the substrates, which reduces the difference in expansion and contraction in the solder joint during cycling [2].

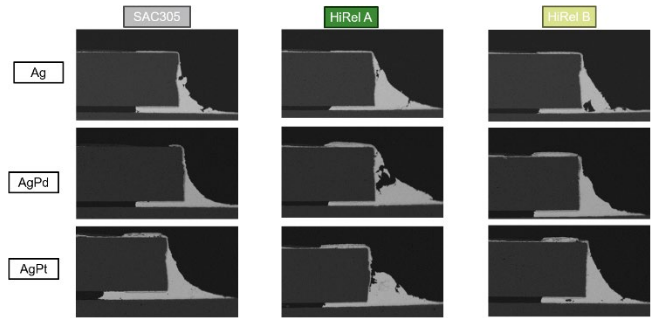

Image 3. SEM cross sections of 1206 chip resistors of each solder/conductor combination after 1000 thermal cycles at –40°C to 150°C

Opposingly, cracks can be seen underneath the MLCC bodies for each solder/conductor combination. Cracks in this area of the solder are usually due to thermomechanical stress during cycling, specifically the difference in properties between the component and substrate [3]. However, HiRel B in conjunction with the AgPt conductor has minimal cracking below the chip body.

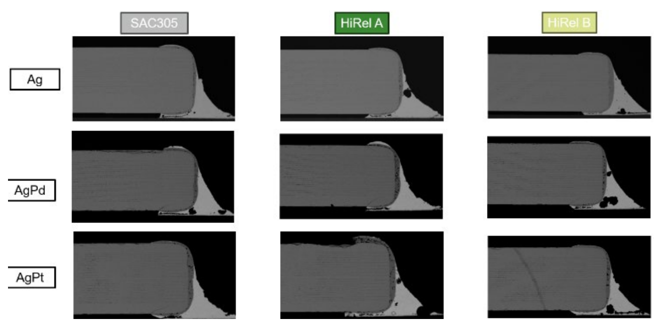

Image 4. SEM cross sections of 1206 chip capacitors of each solder/conductor combination after 1000 thermal cycles at -40°C to 150°C

Chip Resistor Data Analysis

Electrical analysis of the 1206 chip resistors after 1000 cycles at -40°C to 150°C show minimal change (<0.3%) in resistance before and after thermal cycling across all solder/conductor combinations. Shear values were shown to decrease between 0.5-25%. Percent change in resistance and shear strength after 1000 cycles are represented in Table 4. For both of these measurements, HiRel B/AgPd combination showed the least percent change, exhibiting only a 0.07% decrease in resistance and a 0.52% decrease in shear. This is respectively shown in Figures 3 and 4 below. Chip failure is defined by a >10% change in resistance. After 1000 cycles, 1206 chip resistors presented no failures.

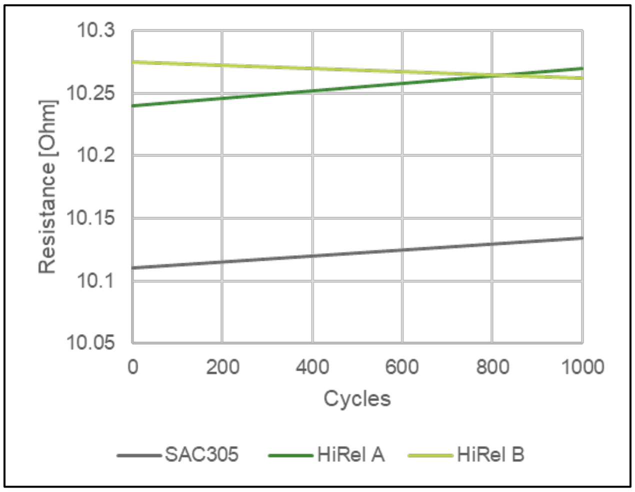

Figure 3. Resistance trend of 1206 chip resistors in combination with AgPd thick film conductor over 1000 thermal cycles at -40° to 150°C

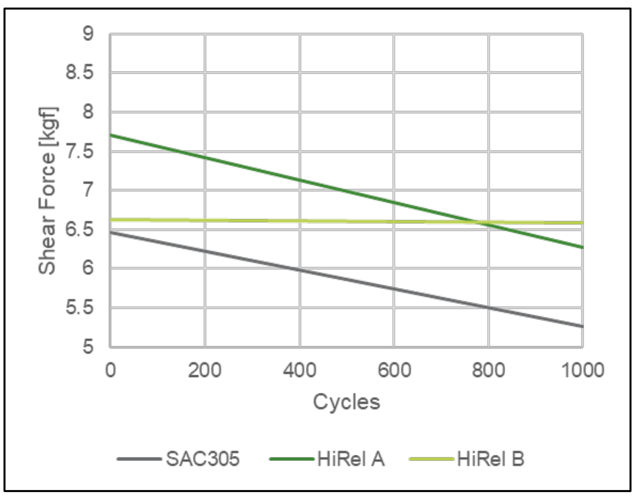

Figure 4. Shear force trend of 1206 chip resistors in combination with AgPd thick film conductor over 1000 thermal cycles at -40°C to 150°C

Table 4. Percent change of electrical and mechanical data for each solder/conductor combination for 1206 chip resistors after 1000 cycles at -40°C to 150°C

	Percent Change	Ag	AgPd	AgPt
SAC305	Resistance	0.138	0.098	-0.108
	Shear	-3.477	-20.58	5.01
HiRel A	Resistance	0.109	0.195	0.109
	Shear	-3.350	-20.55	-12.86
HiRel B	Resistance	0.158	-0.068	0.069
	Shear	-2.998	-0.521	18.411

Data results vary slightly when decreasing to a 0402 chip size, as shown in Figure 5. Unlike 1206 chip resistors, 0402 chip resistors presented chip failures after cycling, specifically with SAC305 and HiRel A solders.

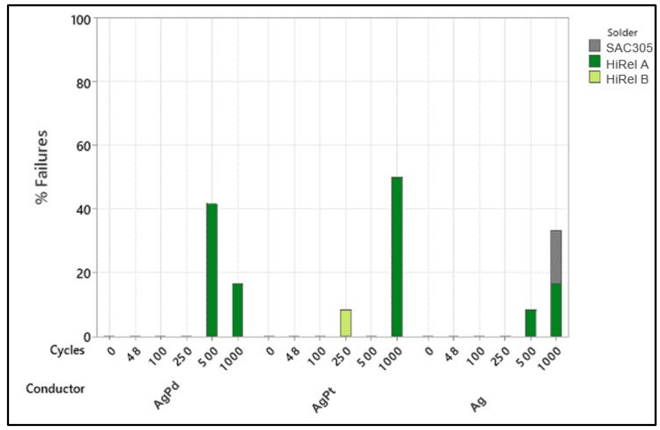

Figure 5. Percent of failed 0402 chip resistors with a percent change in resistance of >10% after 1000 cycles at -40°C to 150°C

Additionally, the overall percent change in resistance and shear force over 1000 cycles for 0402 chip resistors is higher than 1206 chip resistors, as shown in Table 5 below. HiRel B performs very well across all three conductors with minimal changes in both electrical and mechanical values, specifically in conjunction with AgPd (similar to 1206 chip resistors).

Table 5. Percent change of electrical and mechanical data for each solder/conductor combination for 0402 chip resistors after 1000 cycles at -40°C to 150°C

	Percent Change	Ag	AgPd	AgPt
SAC305	Resistance	2.856	0.327	0.607
	Shear	-41.44	-43.84	-15.22
HiRel A	Resistance	-0.788	8.456	1.849
	Shear	-29.09	-15.33	-18.65
HiRel B	Resistance	1.634	0.041	2.808
	Shear	-22.69	-33.32	-15.64

MLCC Data Analysis

Unlike the 1206 chip resistors that show an overall linear trend in resistance over 1000 cycles, 1206 MLCCs show an exponential decrease in capacitance, decreasing sharply in the first 100 cycles, and then steadying out at 250 cycles, displayed in Figure 6. This shift in trend may be due to the varying thermomechanical properties between the component and substrate, causing the components to undergo differential expansion and contraction compared to the chip resistors. Additionally, the percent decrease in shear force compared to the 1206 chip resistors is much more severe across all solder/conductor combinations, reaching as high as a 75% decrease, shown in Table 6. Overall, the electrical and shear data show that HiRel B has very stable values over 1000 cycles in combination specifically with the metal alloy conductors shown in Figures 6 and 7. With MLCCs, failures of >10% change in capacitance also occur, specifically in conjunction with Ag, shown in Figure 8.

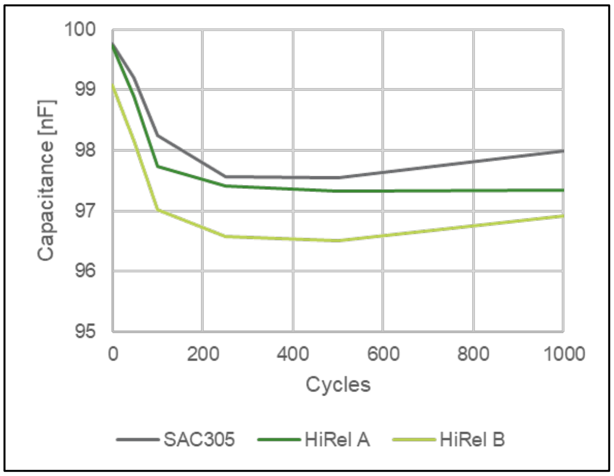

Figure 6. Capacitance trend of 1206 MLCCs in combination with AgPd thick film conductor over 1000 thermal cycles at -40°C to 150°C

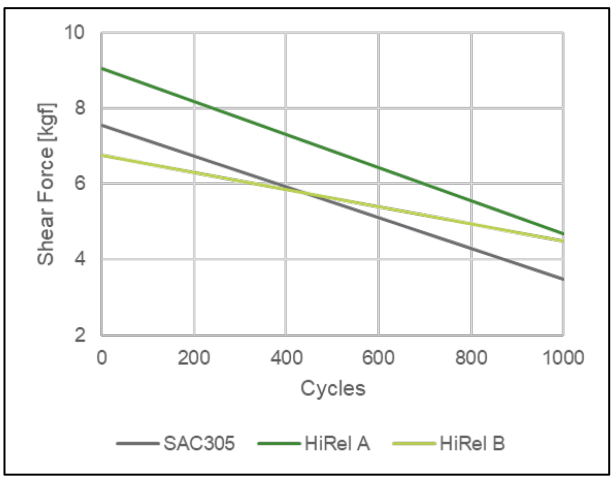

Figure 7. Shear force trend of 1206 MLCCs in combination with AgPd thick film conductor over 1000 thermal cycles at -40°C to 150°C

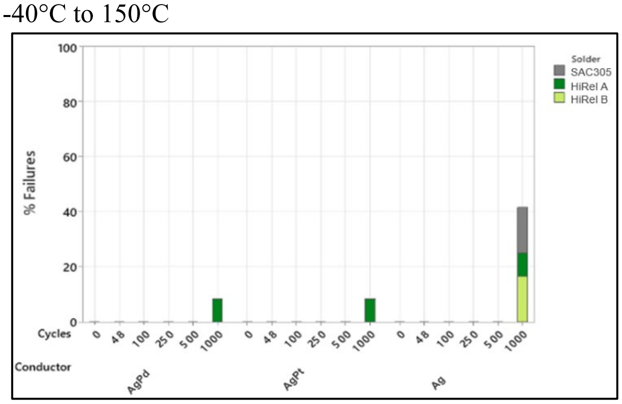

Figure 8. Percent of failed 1206 MLCCs that changed in capacitance of >10% after 1000 cycles at -40°C to 150°C

Table 6. Percent change of electrical and mechanical data for each solder/conductor combination for 1206 MLCCs after 1000 cycles at -40°C to 150°C

	Percent Change	**Ag**	**AgPd**	**AgPt**
SAC305	Capacitance	-2.017	-1.600	-2.141
	Shear	-50.76	-74.03	-57.40
HiRel A	Capacitance	-2.042	-2.348	-1.705
	Shear	-31.88	-63.85	-43.54
HiRel B	Capacitance	-2.923	-1.933	-1.968
	Shear	-16.80	-40.36	-28.56

Unlike the 1206 case size, 0402 MLCCs do not show an exponential decrease in capacitance over the 1000 cycles. Again, there are failures of >10% change in capacitance, specifically with SAC305 for this case size, shown in Figure 11. There is not an apparent pattern with the data to show that one solder/conductor combination is the most electrically and mechanically advantageous. From an electrical viewpoint, the HiRel A/AgPd combination showed the smallest percentage change (Figure 9), while from a shear strength perspective, SAC305/Ag demonstrated the least percentage change (Figure 10).

These values are listed in Table 7. Additionally, HiRel B was the only solder not to have any test components fail with a >10% change in capacitance.

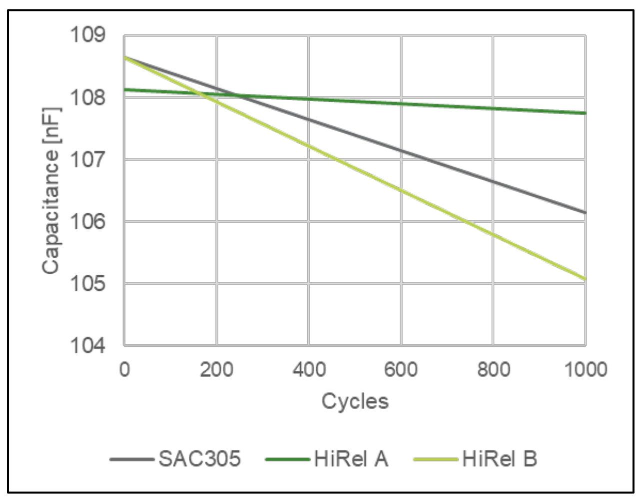

Figure 9. Capacitance trend of 0402 MLCCs in combination with AgPd thick film conductor over 1000 thermal cycles at -40°C to 150°C

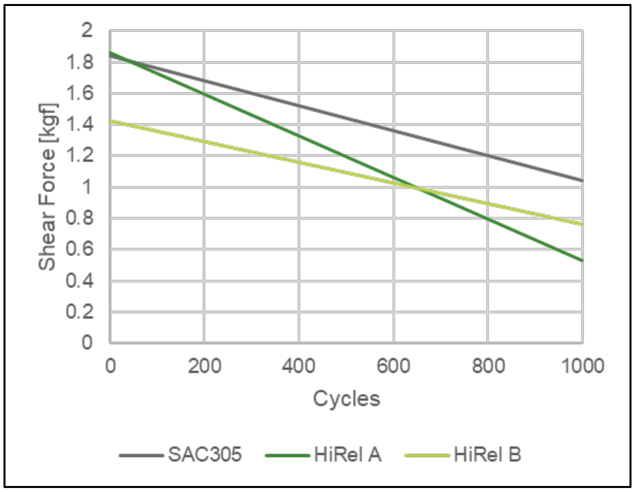

Figure 10. Shear force trend of 0402 MLCCs in combination with Ag thick film conductor over 1000 thermal cycles at -40°C to 150°C

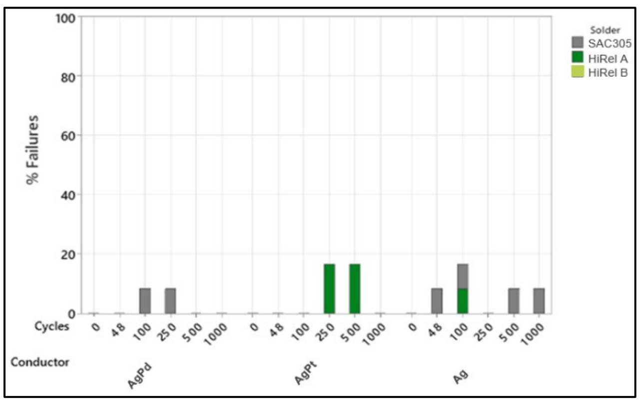

Figure 11. Percent of failed 0402 MLCCs that changed in capacitance of >10% after 1000 cycles at -40°C to 150°C

Table 7. Averages of percent change of electrical and mechanical data for each solder/conductor combination for 0402 MLCCs

	Percent Change	**Ag**	**AgPd**	**AgPt**
SAC305	Capacitance	-3.305	-2.326	2.323
	Shear	-43.45	-33.02	-30.18
HiRel A	Capacitance	-1.357	-0.350	1.175
	Shear	-71.60	-80.17	-65.17
HiRel B	Capacitance	0.590	-3.325	-2.268
	Shear	-46.71	-61.17	-43.35

Thermal Cycle Testing Summary

It was observed that across all test groups, HiRel B exhibited the most stable performance throughout 1000 thermal cycles, especially when paired with the AgPd conductor. While HiRel A demonstrates high shear values across all conductor combinations, it also shows a significant percent change in shear over 1000 cycles compared to HiRel B.

THERMAL AGING

Thermal age testing enables analysis of the solder/conductor combinations through accelerated life testing to speed up the formation of intermetallics, which are potential failure areas due to embrittlement. Similar to thermal cycle testing, the goal of this test is to pinpoint material fatigue caused by interactions at the solder/conductor interface.

Optical Imaging

After aging the chips for 1000 hours at 150°C, no external cracks or fractures were detected in either the SAC305 control or the high-reliability solders, regardless of the conductor used.

Image 5 shows the combination of solders with Ag conductors in a 1206 case size. However, the images represent external defects observed across all conductors and case sizes.

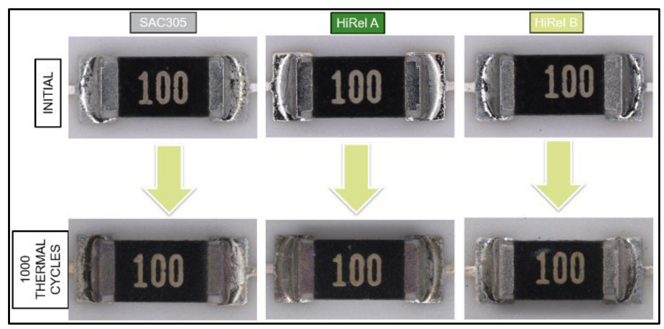

Image 5. 1206 chip resistors of each solder type before and after thermal aging 1000 hours at 150°C

As shown in the cross section of Images 6 and 7, all solder/conductor combinations show no aggressive cracking or propagation of cracking in the solder beneath the components. However, there is some voiding and crack propagation in the MLCC body for HiRel A solder (Image 7). The crack propagation could be a result of an improper reflow profile for this solder's thermomechanical properties.

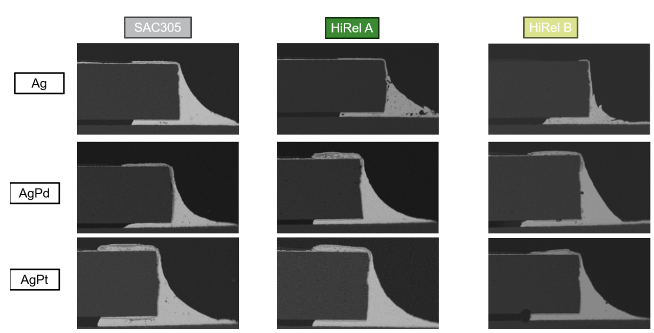

Image 6. SEM cross sections of 1206 chip resistors of each solder/conductor combination after 1000 hours at 150°C

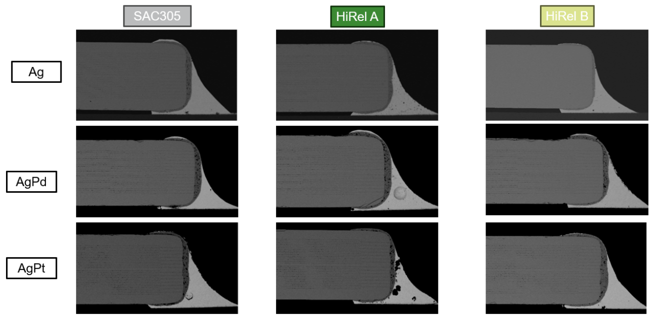

Image 7. SEM cross sections of 1206 MLCCs of each solder/conductor combination after 1000 hours at 150°C

Chip Resistor Data Analysis

HiRel B performed well for both 1206 and 0402 chip resistors, regardless of the conductor alloy. 1206 chip resistors had an average of <5% change after 1000 hours for both resistance and shear strength with the HiRel/AgPd combination, shown in Figures 12 and 13.

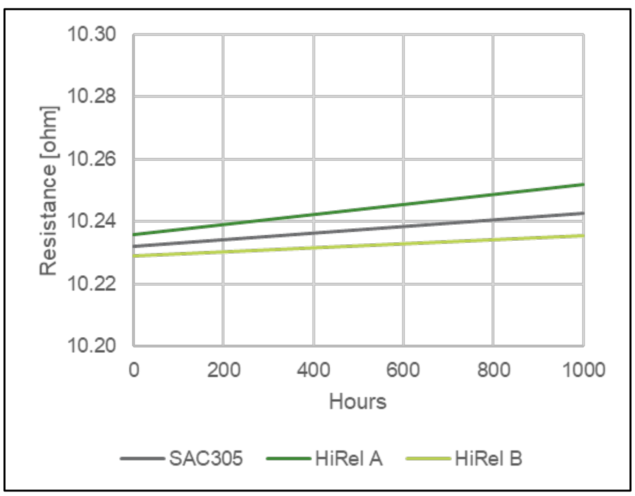

Figure 12. Resistance trend of 1206 chip resistors in combination with AgPd thick film conductor over 1000 thermal aging hours at 150°C

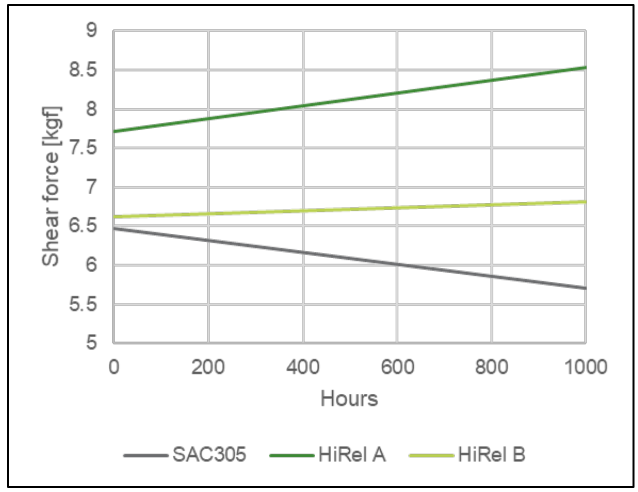

Figure 13. Shear trend of 1206 chip resistors in combination with AgPd thick film conductor over 1000 thermal aging hours at 150°C

Table 8. Percent change of electrical and mechanical data for each solder/conductor combination for 1206 chip resistors after 1000 hours at 150°C

	Percent Change	Ag	AgPd	AgPt
SAC305	Resistance	0.168	0.103	-0.150
	Shear	5.548	-12.47	-12.47
HiRel A	Resistance	-0.002	0.157	0.024
	Shear	12.56	10.19	-14.64
HiRel B	Resistance	0.212	0.062	-0.252
	Shear	9.985	2.274	4.74

Same as for the thermal cycle testing, chip failure is defined as >10% change in electrical measurement. For 1206 chip resistors, 20% of the components tested with SAC305 and HiRel B in combination with the AgPd conductor showed failure (Figure 14).

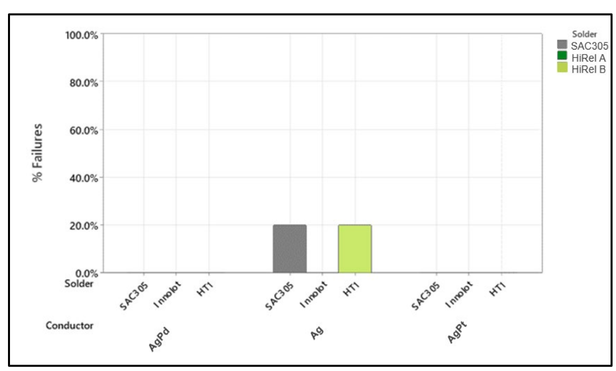

Figure 14. Percent of failed 0402 chip resistors that changed in resistance of >10% after 1000 hours of thermal aging at 150°C

0402 chip resistors presented much higher percent change averages for all solder/conductor combinations. However, the HiRel B/AgPt combination exhibited minimal electrical and mechanical change over 1000 hours (Figures 15 and 16). These values are presented in Table 9.

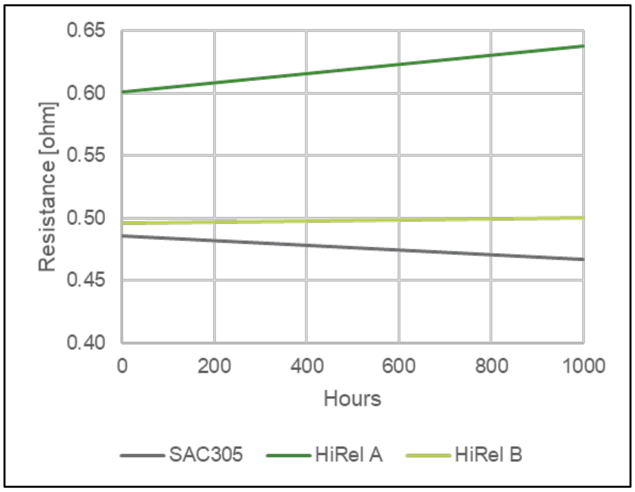

Figure 15. Resistance trend of 0402 chip resistors in combination with AgPt thick film conductor over 1000 thermal aging hours at 150°C

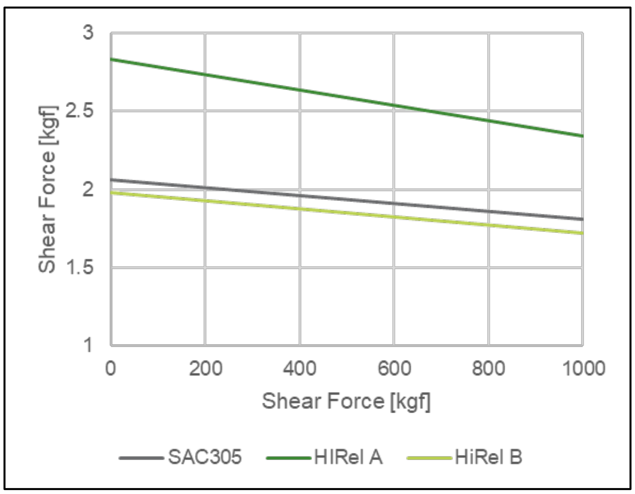

Figure 16. Shear trend of 0402 chip resistors in combination with AgPt thick film conductor over 1000 thermal aging hours at 150°C

Table 9. Percent change of electrical and mechanical data for each solder/conductor combination for 0402 chip resistor after 1000 hours of thermal aging at 150°C

	Percent Change	Ag	AgPd	AgPt
SAC305	Resistance	2.353	7.841	-4.016
	Shear	-16.08	-33.94	-13.18
HiRel A	Resistance	-0.381	1.309	6.052
	Shear	-27.10	-29.74	-19.20
HiRel B	Resistance	3.665	-1.946	0.644
	Shear	-10.41	-30.51	-14.17

MLCC Data Analysis

In the case of thermal aging MLCCs for 1000 hours of thermal aging at 150°C, it was shown for 1206 case size that the HiRel A/Ag combination worked the best, shown in Figures 17 and 18, specifically in shear values over 1000 hours at 150°C. Additionally, both SAC305 and HiRel B in combination with AgPt showed a <10% change in electrical and mechanical values after 1000 hours of aging at 150°C. The percent change of capacitance and shear strength are shown in Table 10.

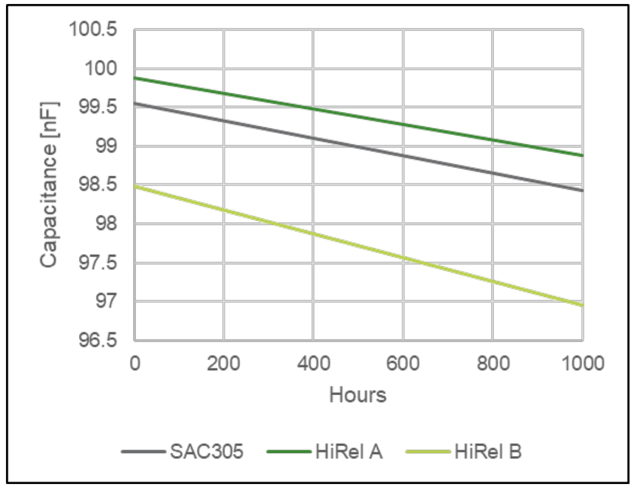

Figure 17. Capacitance trend of 1206 MLCCs in combination with Ag thick film conductor over 1000 thermal aging hours at 150°C

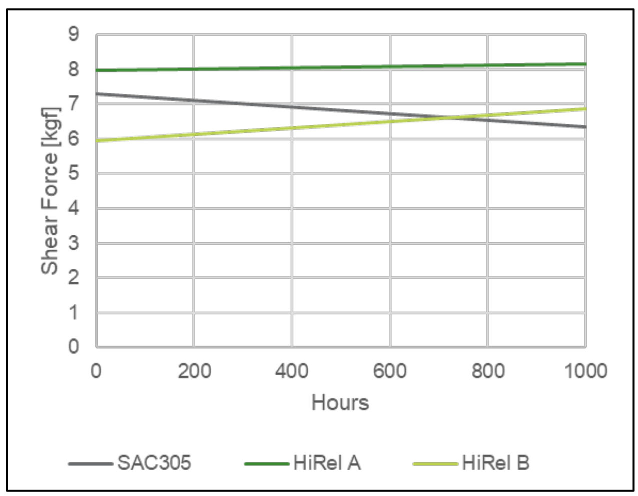

Figure 18. Shear trend of 1206 MLCCs in combination with Ag thick film conductor over 1000 thermal aging hours at 150°C

Table 10. Percent change of electrical and mechanical data for each solder/conductor combination for 1206 MLCCs after 1000 hours of thermal aging at 150°C

	Percent Change	**Ag**	**AgPd**	**AgPt**
SAC305	Capacitance	-1.134	-0.047	-0.527
	Shear	-13.67	-16.06	-5.077
HiRel A	Capacitance	-1.006	-2.271	-0.134
	Shear	2.06	-27.98	-12.87
HiRel B	Capacitance	-1.548	-0.229	-1.098
	Shear	-14.31	-33.38	-5.420

The AgPt conductor also performed well with all solders for 0402 MLCCs; however, the HiRel B/AgPd combination shows the least percent change between both capacitance and shear strength (<5%) over the 1000 hours, shown in Figures 19 and 20, and highlighted in Table 11.

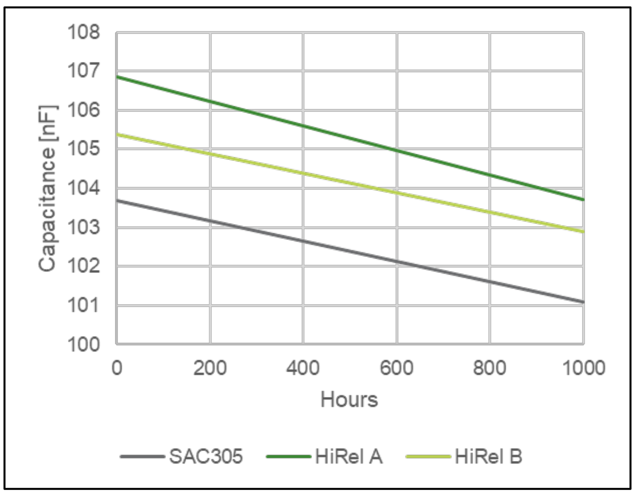

Figure 19. Capacitance trend of 0402 MLCCs in combination with AgPd thick film conductor over 1000 thermal aging hours at 150°C

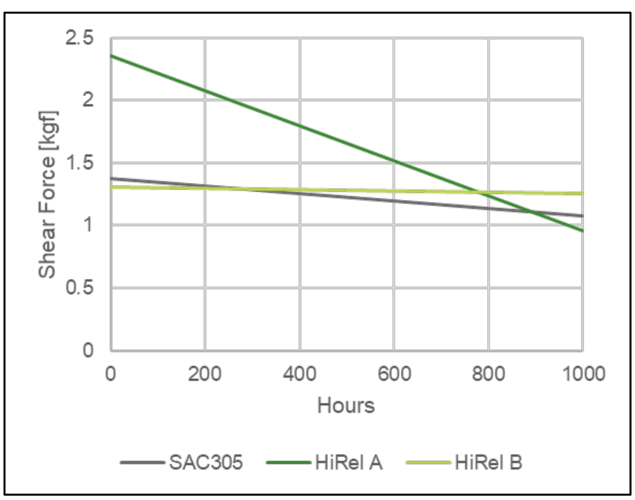

Figure 20. Shear trend of 0402 MLCCs in combination with AgPd thick film conductor over 1000 thermal aging hours at 150°C

Table 11. Percent change of electrical and mechanical data for each solder/conductor combination for 0402 MLCCs after 1000 hours of thermal aging at 150°C

	Percent Change	**Ag**	**AgPd**	**AgPt**
SAC305	Capacitance	-2.588	-2.510	-2.343
	Shear	-18.65	-23.84	-21.23
HiRel A	Capacitance	-3.220	-2.988	-2.686
	Shear	-58.77	-84.69	9.76
HiRel B	Capacitance	-1.882	-2.368	-2.250
	Shear	-5.960	-3.950	-14.30

No MLCCs, regardless of case size, changed in capacitance more than 3% and, therefore, showed no failures.

Thermal Age Testing Summary

Similar to the thermal cycle testing, it was observed that HiRel B across all test groups performed well, specifically with the alloy conductors, compared to the other solder options. No cracking in the solder joint was observed optically; however, while large decreases in shear strength exceeding 30% (even reaching as high as 85% for HiRel A) show that there is some degradation to the solder joint over elongated periods at high temperatures, the magnitude depends on the solder/conductor combination.

CONCLUSION

The main objective of this paper was to identify a solder (specifically Sn-based and high reliability) and thick film combination to improve overall reliability of thick film hybrids. This was done by conducting rigorous thermal testing. The work conducted for this paper served as an initial exploration into this area of study. It demonstrated that certain solder and thick film conductor combinations displayed favorable results across various tests and test groups. Specifically with HiRel B that has advantages such as being able to withstand high operating temperatures up to 175°C and the mixed metal conductors that showed better performance in most testing compared to an Ag-only conductor, even at high Ag ratios. Factors such as using optimal reflow profiles and solder pad geometries could further improve the reliability of HiRel B in thick film circuits. Further work and continuous improvement projects for this study include investigating the above factors as well as a study into the formation of the intermetallic layer between the solder and thick film conductors.

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