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Novel Nanocrystalline Silver Alloy Coatings to Boost Performance of EV High Voltage Interconnects and Charging Interfaces

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Abstract

Electric vehicle performance needs challenge connector designers and powertrain engineers with new paradigms for performance under more rigorous operational conditions. Traditional connector design protocols direct the engineer to silver plating for the contact interface, but these coatings have a maximum interface temperature of 170 C (ambient temperature plus T-rise). To avoid thermal runaway, engineers have to derate the ampacity of powertrain connections, which reduces available energy delivery as the temperature increases. This is especially true during transient power events like regenerative braking and acceleration. The soft nature of silver coatings makes them well suited for power delivery and low contact resistance, but requires an engineering trade-off for wear durability. This is especially problematic for charging connectors which require tens of thousands of mating cycles before failure.

In this work, we demonstrate the performance enhancements that can be achieved using a novel nanocrystalline silver-tungsten alloy. The alloy was designed from fundamental thermodynamic principles to ensure stability at elevated temperatures, enhanced corrosion resistance and strength. Silver-tungsten resists softening up to 250 C, allowing significantly higher maximum operating temperatures compared to silver. Indentation studies at temperature reveal that Ag-W is twice the hardness of silver at room temperature and at temperatures up to 210 C. Long term aging tests, 4000 hours at 210 C, show that the contact resistance is low and stable while silver plating shows rapid increases. The stable nanocrystalline alloy has improved contact a-spot stability leading to a 5% improved transient and steady state ampacity at temperature. Lastly, while silver plating often fails through galling wear, the nanocrystalline silver alloy was designed to resist galling wear; this enables charger connector cycle life of tens of thousands of cycles or more.

Introduction

Battery electric vehicles have altered the landscape for power requirements in electrical connectors used in charging and power transmission applications. Voltages steadily increase towards 1000 volts with new demands on thermal capability, vibration and ampacity.

The reliability and performance of separable interconnects is enhanced through the use of surface coatings and platings, boosting corrosion resistance and managing the contact resistance at the interface. Silver plating has been the preferred material of choice for high power connectors as the fundamentally low resistivity provides for low resistance and thus low temperature rise from joule heating. [1] Silver is susceptible to corrosion and porosity, both of which are generally overcome through thicker deposits and higher applied normal force in the connector.

As the automotive industry moved away from gold plating as a cost savings measure, the replacements were tin and silver. For many automotive applications, the connector experiences very limited mating/unmating cycles during its expected life. This is fortuitous for silver in that the silver plating has very poor wear durability. The surface of silver is fundamentally sticky, leading to galling wear as the mated surfaces weld together. The surfaces eventually tear each other apart during vibration and high cycle wear. This wear is further exacerbated by the formation of silver sulfide and silver chloride corrosion products on the surface, which then accelerate wear as the corrosion product breaks up and enters the wear track.

Temperature is also an ongoing concern for connector applications. Tin plating has a maximum use temperature of somewhere between 105 and 130 C, limiting its use to lower temperature classes. [2] Silver has been used in applications up to 170 or 180 C, at which point the silver can locally soften and lose reliability. Connector designers can manage the reliability of these interconnections through an electrical derating process where the maximum ampacity of the connector is reduced as the operating temperature increases. The maximum use temperature of a contact material is related to the voltage at which the contact a-spots can lead to melting. [3] Since the current is restricted to flow only through the a-spots of the contact interface, all of the joule heating occurs at these spots. As current flows, the heat generated can be withdrawn by the surrounding material. Highly conductive materials such as silver are effective at drawing away the heat. As more current flows, the a-spots further heat up. The resistivity of the metals increases as they get warmer and the thermal conductivity of metals decrease as they get warmer. Hence there is a risk that additional heating will cause the rate of heat removal to go down which in turn increases the resistivity, which increases the joule heating and so on. The supertemperature, which is the difference between the local temperature of the a-spot and the temperature of the bulk conductor, is a design consideration when evaluating the maximum current a conductor can reliably accommodate.

We present here research into an alternative contact plating to improve upon the limitations of traditional silver plating. We have designed and built a new nanocrystalline silver-tungsten alloy which has improved hardness, thermal stability and wear compared to the standard silver materials.

Reducing the grain size of a metal material is well known to increase the hardness through the Hall-Petch relationship. Schuh has detailed the thermal stability improvements possible by carefully selecting the alloying agents which will reduce the overall energy of the material.[4] This leads to a fundamental improvement in thermal stability and often also improves the corrosion performance. [5, 6] The nanocrystalline silver alloy of this work is an alloy of silver and tungsten, where the tungsten alloying additions preferentially segregate to the grain boundaries of the material during fabrication. The tungsten atoms effectively pin the grain boundaries preventing them from growing after long term exposure at temperatures up to about 250 C. [7] This thermal stability and improved hardness has the potential to improve connector performance and cost.

Test Materials

The nanocrystalline silver alloy (NCSA) coatings were produced using the non-cyanide containing LUNA® plating electrolyte from Xtalic Corporation. All tested samples were generated using either the rack or barrel plating method

The pure silver coating used for the high temperature aging study was plated out of the LUNA® plating electrolyte without the addition of the alloying agent.

The silver coatings used for the durability, hardness at high temperature and current derating experiments were produced out of a Metalor MetSil® 100 bright silver electroplating bath. This is a cyanide based pure silver electrolyte.

A connector test vehicle (Figure 1. Silver plated EV charging style connectors used for durability testing) was designed to mimic the engineering features of typical electric vehicle charging connectors. The connectors were machined out of UNS C11000 copper substrate and were electroplated with both pure silver and NCSA for wear durability testing. The mating force of the connectors, as measured on a Chatillon DFS II, was between 6-8 N. The overall length of the connectors is 40 mm with six spring tines on the receptacle and the diameter of the mating plug pin is 6 mm. The contact gap of the receptacle as plated is 5.75 mm.

FIGURE 1 Silver plated EV charging style connectors used for durability testing.

FIGURE 2 NCSA plated and polished 1 cm x 1 cm x 0.5 cm test block used for hardness testing and crystallite size measurements.

Pure silver and NCSA were separately plated onto 1 cm x 1 cm x 0.5 cm copper pieces to be used for tests involving a hardness measurement as shown in Figure 2. Pieces were polished using a 0.5 μm diamond suspension after plating to ensure a uniform surface for measurements.

Test Methods

High Temperature Aging

Samples plated with minimum 20 μm Ag and NCSA were measured for hardness using a Wilson Tukon 2500 microindenter with a Vickers tip using a 10 g_f load. The crystallite size of the (111) plane of the face-centered cubic (FCC) silver structure of the test pieces was estimated using a Siemens D5000 X-Ray Diffractometer. The test pieces were then placed in an oven at 210 C. The samples were removed after prolonged high temperature exposure and remeasured for hardness and grain structure to characterize any material changes that have occurred. The samples were then placed back into the oven to allow to age in the oven until the next time interval. The exposure times after which the properties were tested were 0 (initial data), 200, 625, 1825, 3400, and 4150 hours. As it is typically deposited, the grains of cyanide silver are > 100 nm and thus cannot be measured using the Debye-Scherrer method for estimating crystallite size. The non-cyanide pure Ag electrolyte was chosen for this specific test to act as a more suitable control variable and help demonstrate the impact of the alloying element on performance of the deposit.

Hardness at High Temperature

Samples plated with Ag and NCSA were prepared and sent to Centaur Scientific, LLC for testing. Testing was conducted using a Bruker Hysitron TI 980 TriboIndenter equipped with the xSol High Temperature Testing Stage. Tests were conducted under load control; the force was increased monotonically to a peak load of 7500 μN in 5 seconds. Load was then held constant for 10 seconds to alloy creep to decay. The 7500 μN force was withdrawn in 0.5 seconds. Test measurements were conducted at ambient (30 C), 170, 180, 190, 200, and 210 C.

Current Derating

To compare the operating capability of NCSA with silver, test connector pairs (Figure 3) consisting of a pin and receptacle were plated with 5 μm of either NCSA or silver. The performance of the test connectors was conducted inside an oven at 95 C (Figure 4). Current was passed through the test connectors from 20A to 110A and the temperature rise of the test connectors was observed. Once the temperature had reached an equilibrium, the ambient temperature inside the oven and the temperature of the test connectors were recorded. Equilibrium is defined as when the temperature of the test connectors is constant for greater than five minutes.

A DC rectifier was used to supply the current through the test connectors. Terminal connectors were used to join the test connectors to the power source at the crimp of the copper wire (Figure 5). The thermocouple entered from above and made contact near the tip of the test connector receptacle (see closeup in Figure 6). The connector has a small indent in this location which made the placement of the thermocouple reproducible from test to test. The temperature rise of the test sample was recorded every second using an OMEGA thermocouple data logger.

At the end of each experiment, the experimental setup and temperature data were examined for any abnormalities and results were excluded if testing abnormalities are noticed. Abnormalities include but are not limited to the test connectors pulling apart, thermocouples moving from its position, and any fluctuations in the temperature data. Other common connector coatings (Sn and Au) were included for comparison in this testing.

FIGURE 3 Test connectors plated with NCSA.

FIGURE 4 Experimental current derating setup inside the oven.

FIGURE 5 Test connector pin attached in the terminal connector at the copper wire crimp.

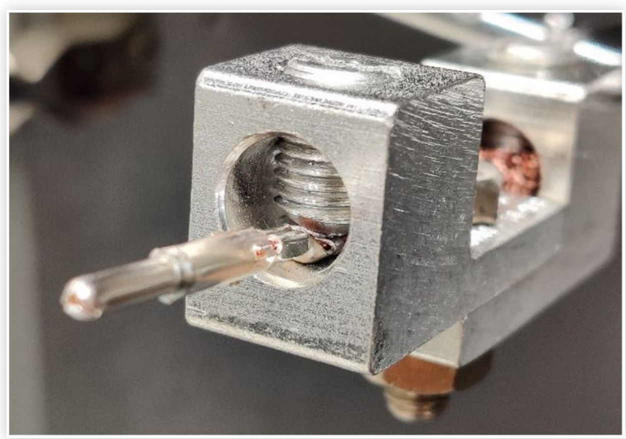
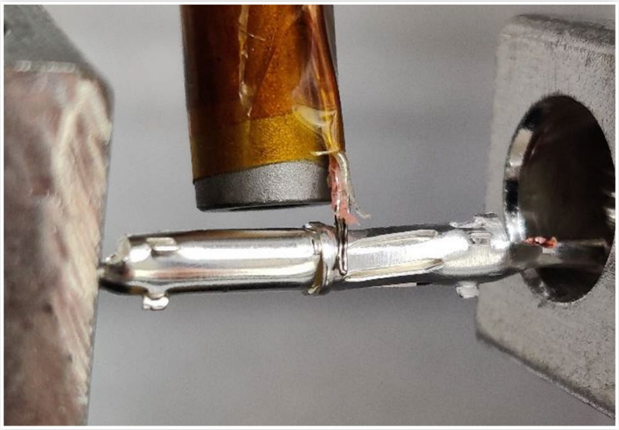


FIGURE 6 Thermocouple position adjacent to connectors for measuring temperature rise.



Wear Durability

EV connector pin and receptacle pieces were plated with NCSA and silver. The NCSA pieces included a 2um layer of Xtalic's nanocrystalline nickel-tungsten alloy (NCNTA), XTRONIC®, on the substrate followed by a NCSA coating of 5 µm in thickness. The silver pieces were plated with 20 µm of pure Ag, which is a typical plating stack for commercial connectors for EVs. Both sets had a self-assembled monolayer applied to the surface after plating to prevent tarnishing during testing, this was applied using Umicore Sealing 691 from Germany based Umicore. Tests were conducted without an added lubricant for both the NCSA and Ag pieces. Durability was then performed on a custom-built step motor driven wear tester, visible in Figure 7. The stroke length for these tests was 10 mm with a frequency of 500 cycles/hour. The pins were inspected by SEM periodically throughout testing to check the integrity of the coating. For the non-lubricated pieces, inspections were carried out at 2000 and 5000 cycles. A separate test was performed on NCSA plated pieces with a lubricant added to the surface to determine how long the coating could last when friction was reduced to a minimum.

FIGURE 7 Wear durability testing equipment with plated connectors mounted into testing position.

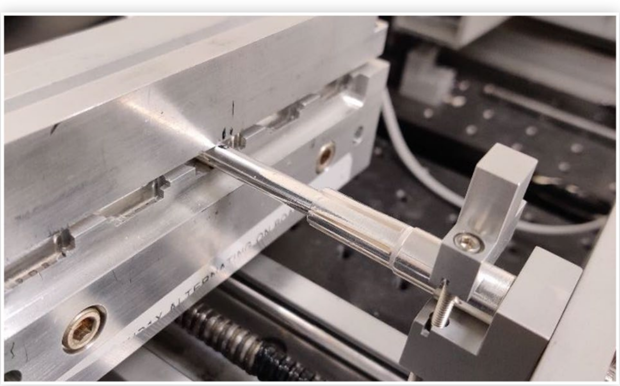
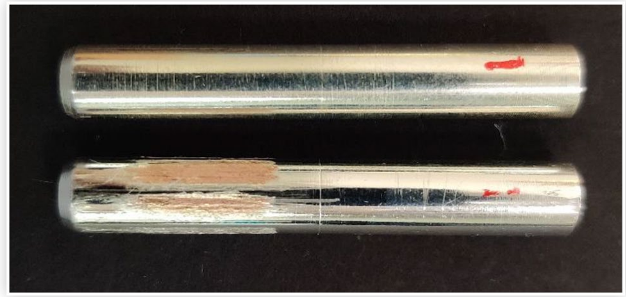


FIGURE 8 Top: NCSA plated pin connector after 2000 durability cycles showing intact coating. Bottom: Ag plated pin connector after 2000 durability cycles showing exposed Cu substrate.



Results

Wear Durability

After 2000 cycles the connectors were removed from the test equipment and inspected for wear. The Ag coated pieces showed heavy wear through to the copper substrate material while the NCSA coating remained intact. Figure 8 shows the pins after 2000 durability cycles.

Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS) images of the connectors after 2000 cycles show heavy galling wear in the Ag connectors (Figure 9). The EDS map shows the silver areas in blue and the exposed copper regions in red. The NCSA alloy samples have no wear tracks visible after 2000 cycles even with the plating being 25% of the thickness of the silver plating (Figure 10).

After 5000 durability cycles, the NCSA plated pin begins to show some wear through to the substrate material. The wear track (~1 mm width) that has occurred on the NCSA connector is not as wide as the silver-plated connector (~2.3 mm width) after 2000 cycles. Figure 11 shows the wear track development in the NCSA sample.

After 8000 durability cycles the NCSA plated sample exhibits wear thru comparable to the silver coated pin at 2000 cycles of wear.

With the addition of a lubricant to the connector surface, the NCSA coating is able to withstand > 60,000 durability

FIGURE 9 Left: QBSD SEM micrograph of silver pin showing galling after 2000 durability cycles. Right: EDS map of same area confirming exposed substrate material visible. Cu in red and Ag in blue.

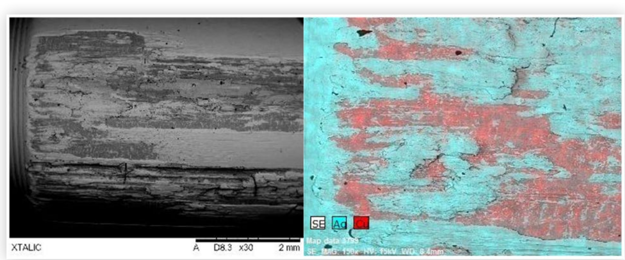


FIGURE 10 NCSA plated connector after 2000 durability cycles. The vertical lines in the image are machining lines from the manufacturing of the connectors. No evidence of galling wear on the sample.

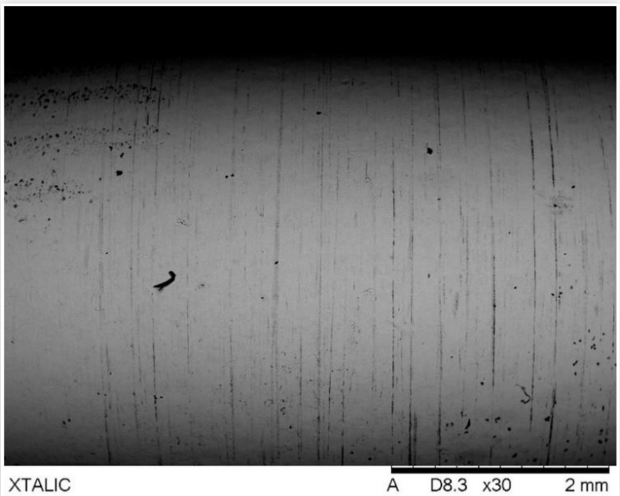
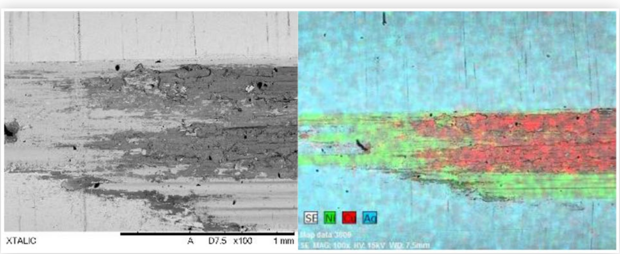


FIGURE 11 Left: QBSD SEM micrograph of wear track on NCSA coated pin. Right: EDS map confirming exposure of substrate material with Ni in green, Cu in red and Ag in blue.



cycles (Figure 12). The wear track begins to be visible on the NCSA with lubricant sample after 60,000 cycles but the type of wear is different than silver with no apparent galling. The EDS map confirms there is no exposed NCNTA or copper substrate visible through the NCSA layer.

Hardness at Elevated Temperature Prior to hot hardness testing, Vickers hardness was measured at room temperature. The NCSA sample had an average hardness of 154 HV_{10} while the Ag sample had an average hardness of 138 HV_{10}.

Across the range of temperatures tested, the NCSA sample was at minimum 45 % harder than the silver sample. The difference was further pronounced as temperatures rose higher; with the NCSA maintaining 2x hardness of silver at 190 °C and above.

Vickers hardness was measured again after the hot hardness testing. The Ag sample had a hardness of 85 HV_{10}. The NCSA sample had a hardness of 156 HV_{10}. The silver sample saw a 38 % drop in hardness from this short thermal excursion while no such drop was seen with the NCSA sample. The small change in hardness for the NCSA sample is a result of normal variability within the sample and test method.

FIGURE 12 Left: QBSD SEM image of wear track visible on NCSA pin after 60000 durability cycles with a lubricant applied to the surface. Right: EDS map of same area with Ag shown in blue.

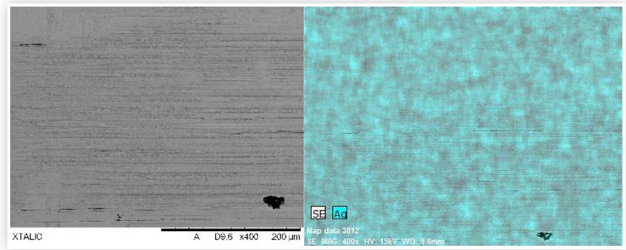


FIGURE 13 Graphical representation of NCSA and silver hardness as a function of temperature, from Bruker Hysitron TI 980 TriboIndenter.

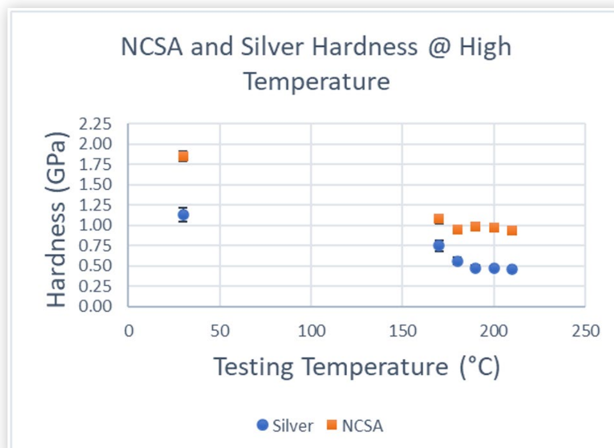


TABLE 1 Silver and NCSA hardness values measured at ambient and elevated temperatures.

Temp (C)	Average Ag Hardness (GPa)	Average NCSA Hardness (GPa)
30	1.13	1.85
170	0.747	1.08
180	0.561	0.944
190	0.476	0.983
200	0.475	0.969
210	0.462	0.932

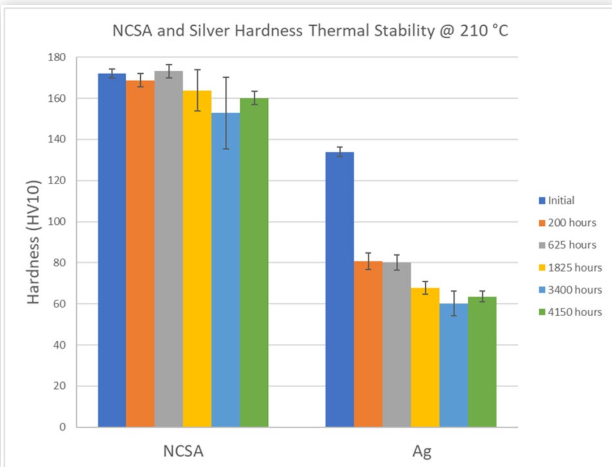
TABLE 2 Silver and NCSA hardness before and after hardness at temperature testing.

Sample ID	HV_{10} before test	HV_{10} after test	% ΔHV_{10}
Silver	138	85	-38%
NCSA	154	156	1%

Heat Aging

NCSA experiences a smaller drop in hardness relative to silver plating when exposed to elevated temperatures for a prolonged period of time. The NCSA samples used for this experiment

FIGURE 14 NCSA and silver hardness after prolonged exposure to elevated temperature. The error bars indicate one standard deviation of the measured values



had an average starting hardness value of 172 HV_{10}. The silver samples used for this testing had an average initial hardness value of 134 HV_{10}. After 200 hours thermal exposure at 210 C the average hardness for the NCSA samples was 169 HV_{10} while the average silver hardness was 81 HV_{10}. The NCSA exhibited a drop in hardness of ~1 % while the silver samples dropped on average by 40 %. This trend continued throughout testing. After 4150 hours of exposure at 210 C, the NCSA samples on average had lost ~ 7 % of their initial hardness compared to the silver samples which had lost ~ 53 % of their initial hardness values.

X-ray diffraction analysis shows a significant rise in crystallite size for the pure Ag plated pieces while the crystallite size for the NCSA pieces is relatively stable after thermal exposure. The change in hardness tracks well compared to the anticipated changes predicted by Hall-Petch.

Table 3 shows the relationship between crystallite size and time at temperature. After 200 hours of exposure at 210 C, the Ag samples were no longer nanocrystalline as their crystallite size had grown from an average of ~50 nm to more than 100 nm (note that the Debye-Scherrer method used to estimate crystallite size is no longer valid for crystallite sizes greater than 100 nm, thus values are reported as >100 nm). The NCSA samples were relatively stable with a modest increase from 27 nm to 38 nm. This slow growth trend continued as the oven exposure time increased with the NCSA crystallite size remaining close to 40 nm after 625 and 1825 hours oven exposure. The slight decrease from 625 to 1825 hours can be attributed to the measurement capabilities of the instrument.

TABLE 3 NCSA and silver crystallite size after varying exposure times at 210 C. Values shown are for measurements of the (111) diffraction peak.

Crystallite Size	NCSA (nm)	Ag (nm)
Initial	27	49
200 hours	38	>100
625 hours	43	>100
1825 hours	37	>100
3400 hours	35	>100

Repeatability and statistical significance were taken into consideration for the heat aging testing. There were 4 NCSA and 2 silver samples used in this testing. At each interval, 5 measurements were taken at various locations throughout the sample and an average of the measurements are reported. The slight increases in hardness at some time intervals can be attributed to normal error in the measurement for the Wilson Tukon 2500 microindenter. Slight decreases in the crystallite size measurements after 1825 and 3400 hours are also within the normal measurement error of the test equipment.

Current Derating Upon initial application of current, the temperature rise is rapid and nearly equilibrates after 10 seconds. Figure 15 shows the temperature rise of silver and NCSA plated connectors when 100 A is applied. At a starting ambient temperature of 25 C, NCSA experienced a 3 C lower temperature rise than silver after the first 15 seconds.

Table 4 and Figure 16 show the performance of NCSA and silver coated connectors with applied current. Individual datum for each test run are shown on the graph along with an average result for each coating. As currents increased above 60 A, NCSA began to show lower temperature in the connector for the same current. At 110 A, NCSA demonstrates a 10% lower temperature rise than silver.

FIGURE 15 Graphical representation of the initial temperature rise with applied current of NCSA and silver at ambient temperature.

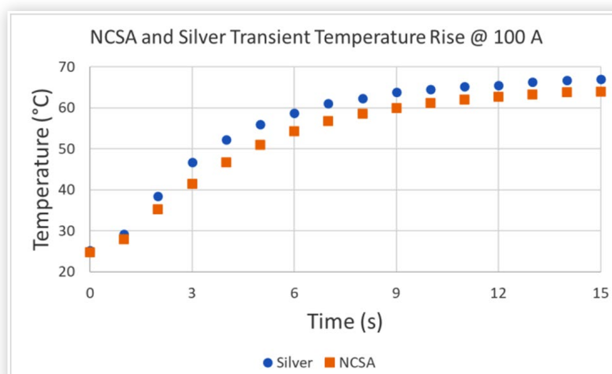
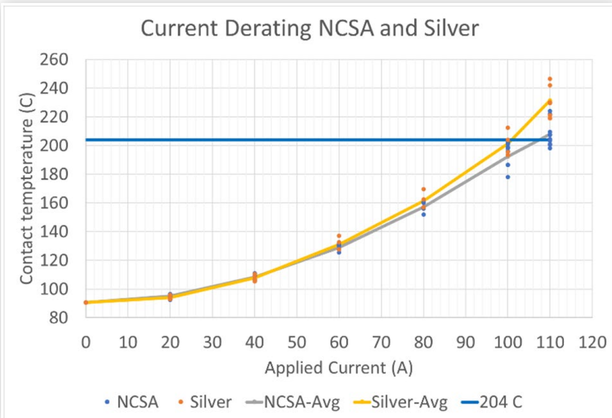


TABLE 4 NCSA and silver temperature rise at varying current.

Current (A)	Average NCSA Temperature @ Equilibrium (C)	Average Ag Temperature @ Equilibrium (C)
0	90.5	90.5
20	95.2	94.0
40	108.3	107.8
60	129.0	129.2
80	157.1	161.5
100	193.4	201.4
110	207.8	231.3

FIGURE 16 Graphical representation of the temperature rise with applied current for various connector coatings.



We considered the repeatability of the tests to evaluate the significance. For the higher current tests there were six replicates, sufficient to mathematically evaluate significance using the student t-Test for means. The Pstat value is 0.0097 showing significance in the difference between Ag and NCSA coated replicates.

Conclusions

1. A new nanocrystalline silver alloy has been developed and evaluated on electric vehicle style connectors.
2. Nanocrystalline Ag-W alloy outperforms cyanide silver plating in terms of improved wear durability, showing more than 60,000 mating cycles before wear through.
3. Nanocrystalline Ag-W alloy has improved thermal stability and hot hardness. This hardness leads to a more robust contact interface and allows for operation at higher temperature.
4. Nanocrystalline silver alloy coatings provide the potential for ampacity improvement in connectors at elevated temperature. We report here approximately 10% increase in ampacity at a temperature of 204 C.

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Acronyms Used

EV - Electric vehicle
NCSA - Nanocrystalline silver alloy
UNS - Unified Numbering System
FCC - Face-centered cubic
DC - Direct current
NCNTA - Nanocrystalline nickel-tungsten alloy
SEM - Scanning electron microscope
EDS - Energy-dispersive X-Ray diffraction
QBSD - 4 quadrant backscatter detector
HV_{10} - Vickers hardness measured using a 10 g_f load

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