Material screening for fully printed polymer-based thermocouples designed for use in harsh environments

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Abstract
Thermocouples are widely used as temperature sensors and most commonly made of two different metallic electrodes which are in contact at the measuring junction. In this work we present an approach to embed thermocouples in the painted surface of machine components, facilitating measurement directly at the point of interest for certain applications. The utilized spray process allows a cost-effective and fast fabrication method. In order to be competitive with available sensors, the spray-processed sensor ideally has to provide an output voltage in the same range as commercial ones and should withstand temperatures up to 200 °C while providing reliable adhesion to the surface at the same time. To meet these requirements, a material screening was performed including commercial as well as custom-fabricated paints. In particular, different commercial paints based on silver were combined with a carbon black polyamide-imide paint to form thermocouples which were then characterized regarding adhesion, noise and sensitivity (Seebeck coefficient). Furthermore, custom-fabricated paints based on iron and silver in a polymer binder were evaluated and compared to a commercial type J thermocouple (iron-constantan thermocouple). The paper reports on identified suitable material combinations and the associated sensor performances.

Keywords: high temperature, low cost, polymer-based, spray processed thermocouple

(Some figures may appear in colour only in the online journal)
In figure 1(a). The thermocouple consists of the conductive paths of paints 1 and 2, which are located on top of the insulation of the stainless steel substrate and Kapton strips (coated with the according conductive paint) facilitating the connection to the two electrodes. The sensitive area of the sensor is the junction between paint 1 and paint 2. Figure 1(b) shows the layer architecture of the temperature sensor. The following section gives an overview of the preparation of the insulation and the conducting paints which are divided into commercial (silver inks) and custom-fabricated paints (based on carbon black, iron or silver as conductive material).

2.1. Preparation of the insulation paint

The chosen insulation polymer was polyamide-imide. Due to its high temperature stability, continuous operation up to 250 °C and shortterm (1 h) exposures up to 300 °C are possible. The polyamide-imide was diluted with N-methyl-2-pyrrolidone (NMP) and p-xylene at a weight ratio of 10:12:8. To reduce sagging of the paint when processed on vertical substrates, 0.1 wt% of a thixotropic agent (Aerosil from Evonik) and to enhance the substrate wetting 0.3 wt% of a surfactant (BYK 310 from BYK) are added.

2.2. Commercial silver inks

The used commercial silver inks were Loctite EDAG PF 050 (further referred to as PF050), Pelco high performance silver ink 16047 (further referred to as Pelco) and DuPont Ka 801 (further referred to as Ka801). For spray processing, the paints PF050 and Ka801 were diluted with 50 wt% ethyl acetate, respectively. The Pelco ink was diluted with deionized water at a ratio of 1/1 and 1 wt% Tivida was added to improve the wetting properties of the paint.
2.3. Custom-prepared paints

The custom-prepared paints are based on polyamide-imide (already used as insulation material) or heat-resistant epoxy from Kwasny as a polymer matrix. Among the tested filler particles, acetylene carbon black and iron nanopowder turned out to be compatible with the polyamide-imide matrix. Before the polyamide-imide was mixed with the filler particles, 3 wt% of the surfactant BYK 310 and 5.5 wt% Nusperse 196 (enhances filler mixing in the paint) were added to the polymer solution, which was further diluted with p-xylene and NMP in a weight ratio of 10:28:24. Finally, carbon black and iron powder were incorporated into the paint in a volume content of 25 and 40 vol%, respectively. For better mixing, the paint was first placed on a magnetic stirrer for 30 min and afterwards placed in the ultrasonic bath for 8 h (iron paint was premixed on a vortex mixer without a magnetic stirrer and afterwards placed in the ultrasonic bath). The silver nanoparticles were not compatible with the polyamide-imide, but with the heat-resistant epoxy as polymer matrix. For the silver paint, silver nanopowder, the heat-resistant epoxy and acetone are mixed in a weight ratio of 2:5:2. The incorporation process was the same as for the carbon polyamide-imide paint.

2.4. Paint processing

After the preparation process, the paints were suitable for spray processing. In this work an airbrush with a nozzle size of 0.3 mm was used to apply the paint. The first fabrication step was insulating the substrate with the polyamide-imide paint since the sensor was embedded onto a conductive stainless steel substrate. The applicability of the insulation paint on substrates improved after the coating step the mask was removed, and the paint was cured for 30 min at 250 °C. The curing takes 30 min at 260 °C for Pelco, at 150 °C for PF 050, at 200 °C for KA 801 and at 250 °C for the polyamide-imide based silver and iron paints as well as the silver epoxy paint. Finally, Kapton strips (used as flexible substrates) were coated with the according silver paint on top. The curing takes 30 min at 260 °C for Pelco, at 150 °C for PF 050, at 200 °C for KA 801 and at 250 °C for the polyamide-imide based silver and iron paints as well as the silver epoxy paint. Finally, Kapton strips (used as flexible substrates) were coated with the according conductive paint and were connected (a droplet of the conductive paint was used as adhesive) with the conductive paths of the thermocouple. These strips were used as connections for the measurement. A schematic representation of the layer architecture is represented in figures 1(a) and (b).

3. Characterization and results

The characterization of the processed thermocouples was performed in a temperature test rig consisting of an aluminum block with a heating cartridge, a resistance thermometer for measuring the junction temperature, and a liquid-cooled, electrically insulated aluminum block inside a housing. Figure 2 depicts the used characterization setup. The resistance thermometer is a calibrated PT 1000 resistor according to DIN EN 60751 from TE Connectivity and features an accuracy of ±0.3 °C. The thermocouple is placed with the junction side on the heating block and on top of the thermocouple junction the PT1000 is placed to measure the junction temperature. The connections lead to the liquid-cooled block where the connection temperature is kept constant at 25 °C.

During a characterization cycle the thermocouple was heated to a certain preset temperature; afterwards, the sample was cooled down again to ambient room temperature which took approximately 2h and 20 min. During the measurement, a box was placed over the test rig to protect it from air flow. The temperature difference ΔT in °C between the junction and the terminal (temperature of the external connection in the cooling block) and the according output voltage of the thermocouple were recorded. The noise of the thermocouples was quantified by calculating the standard deviation of the signal and the sensitivity was quantified by calculating the Seebeck coefficient of the material combination in order for the linear slope of the output voltage to be more precise. The linear region for all characterized sensors was at least up to a temperature of 60 °C. The adhesion of the thermocouple to the insulation is an important factor, as the temperature sensor should not easily peel off when stress is present. Thus, a tape peel-off test was performed in which a tape was placed on a sample consisting of a stainless steel substrate coated with polyamide-imide and a 10 × 10 mm square with the according silver paint on top. The adhesion was tested by rapidly removing the tape under a 180° angle. The adhesion is satisfactory when paint remains on the substrate and does not peel off with the tape.

3.1. Characterization of the commercial inks

The commercial inks have been characterized in combination with carbon black in polyamide-imide paint (Cb_PAi),
as this paint is stable due to the polymer binder (shortterm treatment 300 °C) and therefore suitable for this purpose. The Ka801 ink (which has already been used earlier [15]) is suitable for the spray process but is of limited use when it comes to high temperatures due to degradation of the polymer binder. Thus, two different silver inks were tested, PF050 and Pelco. The recorded measurement data are depicted in figure 3. Figure 3(a) depicts the temperature dependent output voltage of the Cb_PAi-Ka801 combination. The characterization was performed up to an absolute temperature of 200 °C while the terminal temperature was kept at 25 °C, which results in a maximum temperature difference ΔT between terminal and junction of 175 °C. The thermocouple shows a nonlinear characteristic at higher temperatures where the sensitivity increases with temperature. A maximum output of 3.37 mV is measured for a temperature difference of 175 °C. The noise of the output signal is in the range of ±2 µV and the calculated Seebeck coefficient is 15.47 µV K−1, therefore the temperature resolution of the sensor is below 1 °C.

The temperature characteristic of the output voltage virtually remains the same over the three measurement cycles, whereas the PF050 in combination with the Cb_PAi (depicted in figure 3(b)) shows a significant nonlinearity in the first measurement which changes somewhat for the two following repeated measurements.

Thus, the PF050 is not suitable for high-temperature environments as the sensitivity continuously decreases. Nonetheless, the thermocouple is stable at low temperature regions and shows a Seebeck coefficient of 12.47 µV K−1 and a noise of ±3.99 µV. The Pelco in combination with the Cb_PAi features reproducible characteristics during the three measurement cycles; a slightly nonlinear response to temperature with increasing sensitivity at higher temperatures could be observed. The maximum output voltage reached in the measurement is 4.1 mV, the Seebeck coefficient within the first 60 °C is 14.4 µV K−1 and the observed noise is in the range of ±2.5 µV. Although the Pelco shows a lower sensitivity than KA801 (15.47 µV K−1 versus 14.4 µV K−1), it is not limited to lower temperatures and it shows furthermore a low noise in the output voltage which allows a temperature resolution below 1 °C. Thus, when it comes to high-temperature applications, the Pelco paint is the most suitable commercially available silver material tested in
Figure 4 depicts the samples before and after the tape peel-off test. The adhesion of the Ka801 was not satisfactory as it was possible to remove the complete paint layer. The Pelco paint was also easy to peel off in the adhesive tape test. The only commercial paint with satisfactory adhesion on the polyamide-imide was the PF-050. As the tested commercial paints either show poor adhesion on the insulation (Ka801 and Pelco) or do not have sufficient temperature stability (PF-050 and Ka801), an additional two custom-fabricated paints were prepared and tested.

3.2. Characterization of the custom-prepared inks

Three thermocouples were prepared consisting of Cb_PAi in combination with iron in polyamide-imide (Fe_PAi), Cb_PAi in combination with silver in heat-resistant epoxy (Ag_hr), and iron in polyamide-imide in combination with silver in heat resistant epoxy. All three thermocouples are at least stable up to 250 °C and for short-term (1 h) exposures up to 300 °C. The recorded measurement data for these thermocouples are shown in figures 5(a)–(c). The thermocouple in figure 5(a) (made out of the Fe_PAi and the Cb_PAi) shows an increasing sensitivity with increasing temperature. The maximum output is 14.3 mV at a junction temperature of 250 °C and a terminal temperature of 25 °C resulting in a temperature difference $\Delta T$ of 225 °C. The determined Seebeck coefficient in the linear region is 52 $\mu$V K$^{-1}$ and the noise in the output signal is $\pm 5.9$ $\mu$V, which allows a temperature resolution below 1 °C. The characteristic remains stable over the three repeated measurement cycles. The thermocouple consisting of Fe_PAi in combination with the Ag_hr has a nonlinear response at higher temperatures, which can be seen in the three measurements in figure 5(b). The achieved output at a temperature difference $\Delta T$ of 225 °C is 10.7 mV, which is slightly below the output of the carbon black/iron thermocouple. The Seebeck coefficient is 40 $\mu$V K$^{-1}$ and the noise $\pm 5.6$ $\mu$V, which is allows a temperature resolution below 1 °C. The lowest output of the custom-prepared paints of 4.25 mV at a $\Delta T$ of 225 °C was observed for the Cb_PAi/Ag_hr thermocouple, the temperature voltage characteristic of which is depicted in figure 5(c). The determined Seebeck coefficient is 14.8 $\mu$V K$^{-1}$ and the noise $\pm 2.5$ $\mu$V. Figure 5(d) compares the recorded outputs of the thermocouple combinations made out of the custom prepared inks. To determine the compatibility of the custom-prepared paints with the insulation paint, again the tape peel-off test was performed. Figure 6 depicts the CB_PAi, the Fe_PAi and the Ag_hr before and after the tape removal. All three paints survived the peel-off test without ablations, which indicates sufficient adhesion strength.
The signal quality (low noise compared to the output voltage) is in the same range or even better for the thermocouples based on custom-prepared paints compared to the thermocouples using carbon black/commercial paints. In comparison to the commercial inks and the custom-prepared silver ink, the advantage of the custom-prepared silver is better adhesion (no ablation after tape peel off) to the substrate. When it comes to the thermocouple based on iron in polyamide-imide and silver in heat-resistant epoxy, the output voltage could be more than doubled compared to the carbon black/silver thermocouples. An additional increase in sensitivity is achieved by the combination of the iron and carbon black paint. Furthermore, these paints provide the best compatibility with the substrate as the substrate insulation and the conductive paints are based on the same polymer binder (polyamide-imide) and no ablation in the tape peel-off test was observed. As the thermocouple should be embeddable and therefore useable in harsh environments, the adhesion of the paint layers is essential; also a high output voltage is of advantageous for the readout of the sensor. Thus the iron/carbon black (Fe\textsubscript{PAI}/Cb\textsubscript{PAI}) thermocouple turned out to be the most suitable thermocouple of the tested combinations when it comes to sensitivity (52 $\mu$V K$^{-1}$), adhesion and noise ($\pm$5.9 $\mu$V noise compared to a sensitivity of 52 $\mu$V K$^{-1}$), which allows a temperature resolution below 1 °C of the fabricated thermocouple.

Concluding an aging test and comparison with a commercial type J thermocouple (iron–constantan) were performed with this particular thermocouple. To see at what extent aging of the thermocouple affects their characteristics, the thermocouple was stored at standard laboratory conditions for 4 months without encapsulation so that oxidation could potentially occur. After these 4 months, three repeated measurements were performed in the same way as before the aging process. The measured data recorded for the new and the aged Fe\textsubscript{PAI}/Cb\textsubscript{PAI} thermocouple are depicted in figure 7(a). The insets in this figure show the deviation of the recorded thermocouple outputs. The deviation of the single measurements to a calculated average is below 0.1 mV up to a $\Delta T$ of 160 °C. Only at even higher temperatures the deviation increases to 0.25 mV, which is in total 1.7% of the output signal, meaning that no significant change in the characteristics of the thermocouple was observed although it was stored without encapsulation. Figure 7(b) shows the Fe\textsubscript{PAI}/Cb\textsubscript{PAI} thermocouple in comparison with a commercially available type J thermocouple (iron–constantan). Compared to the type J thermocouple, the custom-fabricated one shows a comparable signal quality (noise of the type J thermocouple was determined to be $\pm$4.5 $\mu$V compared to $\pm$5.9 $\mu$V of the Fe\textsubscript{PAI}/Cb\textsubscript{PAI} thermocouple) and an even higher output voltage at higher temperatures. These properties make it suitable for many applications where the integration of the sensor is required or favorable.
In this work, the Fe_PAICb_PAII thermocouple was processed on stainless steel using a polyamide-imide insulation layer. But the sensor is not limited to this particular substrate. For nonconductive substrates, the insulation layer can be omitted, and the sensor directly processed on the substrate, e.g. Kapton foil or ceramics. Due to its thin layer height and the polymer binder, the thermocouple can also be used in applications where flexibility is required. The adhesion is guaranteed for these substrates as no ablation in the tape peel-off test was observed. Figure 8 depicts the Fe_PAICb_PAII thermocouple processed on stainless steel insulated with polyamide-imide, Kapton foil and ceramics before and after the tape peel-off test.

4. Conclusion

In this work we presented the enhancement and detailed characterization of polymer-based thermocouple sensors in terms of output voltage, high temperature stability and adhesion properties. The most promising sensor type with respect to adhesion, noise compared to sensitivity and output voltage is based on polyamide-imide and contains either carbon black or iron nanopowder as filler material (Fe_PAICb_PAII thermocouple). The observed noise was in the range of ±5.9 µV and the sensitivity was 52 µV K⁻¹ in the linear region up to 60 °C and even higher in the non-linear region above this temperature resulting in a maximum output of 14.3 mV at 250 °C (terminal temperature 25 °C resulting in a ΔT of 225 °C). The devised Fe_PAICb_PAII thermocouple shows an output voltage which is higher than that of the characterized commercial type J thermocouple (iron–constantan) benchmark (≈13 mV at 250 °C). In applications where the sensor is used on conductive surfaces, the insulation layer is made from the same polymer as the conductive paints, which guarantees adhesion of the layers; as verified by the tape peel-off test where no ablation of the paint was observed. The used polymer binder allows applications with temperature exposures up to 250 °C (continuously) and 300 °C for at least 1 h. The fabrication process is a low-cost and fast spray process. The sensor is applicable to most common high-temperature stable surfaces (Kapton, metal and ceramic) and showed no significant aging when stored without encapsulation for a couple of months.

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