



Novel Composite Coatings for Heat Sink Applications

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Novel composite coatings with interesting thermal properties were prepared by incorporation of phase change materials in electrodeposited metals. Such composite coatings combine a high thermal conductivity with a high heat absorption capacity and are potentially useful for heat sink applications where heat should be dissipated as fast as possible. Microencapsulation was used to make polymer particles with a core of phase change material which formed stable suspensions in the plating electrolyte and which incorporated well in copper deposits. It was found that under optimal processing conditions, copper coatings with 35 vol % of incorporated phase change material could be obtained. Such coatings have a heat absorption capacity of 10.9 J/g, as determined by differential scanning calorimetry.

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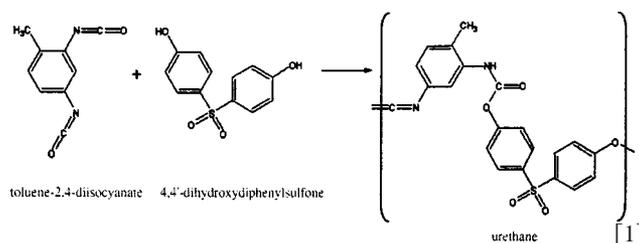
Integrated circuits such as computer central processing units (CPUs) often produce a lot of heat which should be dissipated as quickly as possible since failure of integrated circuits increases with their working temperature. Since integrated circuits often work in a boolean manner, switching on and off, thermal loads are often transient. This gives rise to thermal fatigue which also reduces the lifetime of integrated circuits. Therefore, the design of heat sinks is very important. The ideal material for heat sink applications combines a high thermal conductivity with a high heat capacity to absorb thermal spikes. Metals have a high thermal conductivity and hence are commonly used as heat sinks, but their heat capacity is low. Therefore, recently new heat sinks were designed which combine metals with phase change materials (PCMs).¹ PCM thermal energy storage is based on the latent heat absorbed or released when a material reversibly changes phase, usually between the solid and liquid state. During this phase change, the temperature of the PCM stays constant, which is ideal to absorb thermal spikes. Typical PCMs have melting temperatures between -15 and 190°C ,² which comprises the range of temperatures useful for cooling of integrated circuits. The latent heat of most PCMs tends to range between 150 and 250 kJ/kg.² Although the new heat sinks with PCMs have superior thermal properties, their performance is not optimal because they combine metallic heat sinks with bulk PCMs. Since the thermal conductivity of PCMs is low, better thermal properties could be obtained if the PCM would be finely and homogeneously dispersed in the metal. Therefore, novel metal matrix composite coatings containing PCM particles were developed in this work. A unique way to prepare such coatings is by electrocodeposition, a process where particles are incorporated in metal coatings which are deposited by electrolysis. Codeposition of particles has attracted scientific interest since the late 1960s.³⁻⁵ This interest was powered by the potential applications for composite coatings with new or improved material properties.⁶⁻⁹ Unfortunately, the process is not fully understood until now and sometimes a low or inhomogeneous particle incorporation is obtained. However, for certain types of particles, such as polymer particles or polymer microcapsules, a very high particle incorporation is often found.^{10,11} This is promising, since one of the ways to make micrometer-sized PCM particles is to microencapsulate PCM in a polymer shell. Microencapsulation can be done for various reasons, depending on the choice of PCM. For sticky PCMs such as paraffin waxes, micrometer-sized particles agglomerate during their preparation if they are not encapsulated. For other PCMs such as hydrated salts, microencapsulation might be used to prevent contact between the PCM and the metal in composite coatings, since this would lead to corrosion of the metal coating.

In this work, copper was used as the matrix material since copper

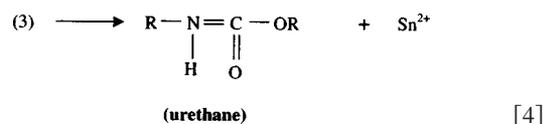
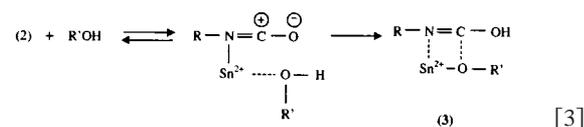
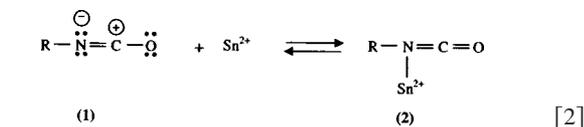
has a heat conductivity of 400 W/m K, which is high compared to most other metals.¹² As a phase change material, paraffin with a melting point of 54°C as specified by the manufacturer was chosen because of its high latent heat, good thermal stability, and nontoxicity.²

Experimental

Preparation of PCM microcapsules.—Paraffin microcapsules with an urethane shell were synthesized by emulsification of a solution containing molten paraffin, toluene-2,4-diisocyanate (TDI, Merck), 4,4'-dihydroxydiphenylsulfone (SDP, Acros), and dibutyltin dilaurate (DTD, 95%, Aldrich) in an aqueous solution of polyvinyl alcohol. When the emulsion is heated, the urethane shell around the molten paraffin droplets forms by polycondensation of toluene-2,4-diisocyanate and 4,4'-dihydroxydiphenylsulfone according to the following reaction



Dibutyltin dilaurate is used as the catalyst for the above reaction. The role of the catalyst in the above reaction is shown below



Practically, the synthesis was done by emulsification of an oily phase in an aqueous phase. The aqueous phase was made by dissolving 1 g polyvinylalcohol (PVA, 80% hydrolyzed, Mw 8000-10000, Aldrich) in 400 mL water at 60°C . The oily phase was made by dissolving 10 g of SDP in a solvent mixture composed of 40 g tetrahydrofuran (THF, Acros) and 2 g acetone. The resultant solution was heated to 60°C and thereafter, 50 mL of molten paraffin

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(melting point 54°C, Vel) was added. Finally 12 g of TDI and 12 drops of DTD were added. The DTD was used as a catalyst for the polycondensation reaction. After preparation of the oily and liquid phase, the oily phase was slowly added to the aqueous phase while vigorously stirring using an Ultraturrax (Janke & Kunkel, IKA Labortechnik). During this step, an emulsion of paraffin/THF droplets in an aqueous PVA solution was formed. This emulsion was kept at 65°C during 1 h while gently stirring with a paddle stirrer. During this heating, the TDI and SDP react at the interface between the aqueous and the paraffin/THF particles to form a polyurethane shell and the low-boiling THF solvent evaporates. After the reaction is completed and all solvent is evaporated, a dispersion of encapsulated paraffin particles in an aqueous PVA solution remains. This solution was washed six times with demineralized water of 60°C. Each washing cycle consisted of centrifuging the dispersion in order to separate the paraffin microcapsules from the aqueous phase and resuspending the particles in warm demineralized water.

Codeposition of phase change materials with copper.—Copper deposits with a thickness of 50 μm were made at room temperature. This was done using a copper electrolyte composed of 200 g/L CuSO₄·5H₂O and 50 g/L H₂SO₄ at current densities between 2 and 5 A/dm². The amount of particles added to the electrolyte was varied between 50 and 350 g/L depending on the experiment. Since the particles were hydrophobic, surfactant was added to the electrolyte in order to make the particles less hydrophobic and to prevent flocculation. The cationic surfactant, cetyltrimethylammonium hydrogensulfate (CTAHS, 99%, Aldrich) was used for this purpose. The cell used for codeposition experiments consisted of a glass beaker with a vertically suspended copper anode and a stainless steel cathode (Folien-Band, thickness 0.250 mm, Overtoom International Belgium N.V., Belgium). Prior to codeposition, the stainless steel cathode was degreased with a commercial alkaline cleaning solution (VR 6334-16, Henkel), rinsed with demineralized water, dipped in a solution of 10% HCl, and rinsed again with demineralized water. The active area of the stainless steel cathode was 10 × 10 mm. During codeposition, a paddle stirrer positioned in the center of the beaker was used to keep the particles well suspended. The rotation speed of the paddle stirrer was 90 rpm.

Differential scanning calorimetry.—Samples for DSC measurements were weighed with a precision of ±0.01 mg on a microbalance (Mettler AE2400) and placed in aluminum pans with cover lids. The temperature in the measurement chamber was equilibrated at -20°C using liquid nitrogen as a coolant and thereafter, DSC measurements were done at a constant heating rate of 10°C/min up to a temperature of 120°C.

In this work, the amount of incorporated paraffin microcapsules in copper deposits was calculated from the latent heat of the microcapsules and the coatings which were determined by DSC measurements. The following formula was used for this purpose

$$L_{\text{coat}}m_{\text{coat}} = L_{\text{micro}}m_{\text{micro}} \quad [5]$$

with L_{coat} and L_{micro} , respectively, the latent heat of the coating and the microcapsules, m_{micro} the mass of the microcapsules in the coating, and m_{coat} the mass of the coating which is equal to $m_{\text{micro}} + m_{\text{metal}}$. Hence the mass fraction M_{micro} of particles in the deposit is given by

$$M_{\text{micro}} = \frac{m_{\text{micro}}}{m_{\text{coat}}} = \frac{L_{\text{coat}}}{L_{\text{micro}}} \quad [6]$$

To convert the mass fraction to a volume fraction, the density of the particle and the copper deposit is used.

Results

Using the above procedure to encapsulate paraffin, microcapsules with mean sizes ranging from 6 to 15 μm were obtained, depending on the stirring speed used for emulsification. Figure 1 shows a scanning electron microscopy (SEM) picture of paraffin

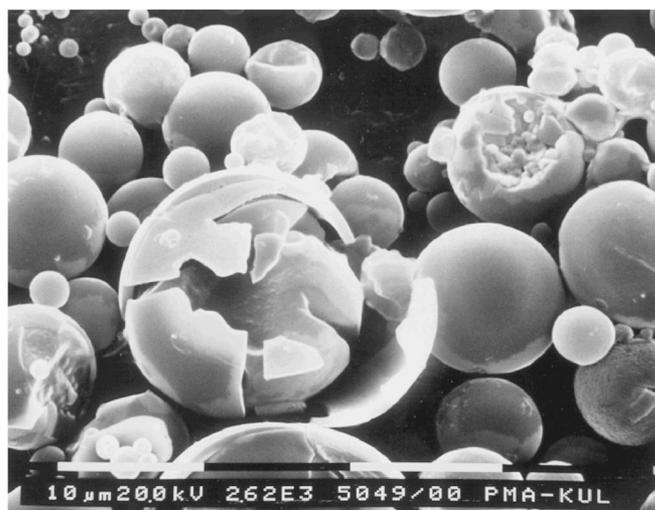


Figure 1. SEM picture of microencapsulated paraffin particles with a urethane shell. The particles were cryogenically fractured to show the thickness of the urethane shell.

microcapsules. The particles were cryogenically broken to show the thickness of the urethane shell. Typically, particles with a shell thickness of about 1-2 μm were obtained. Ideally, the urethane shell around the particles should be as thin as possible because the thermal conductivity of the shell is low (typical thermal conductivity for polymers ≈ 0.2-0.4 W/m K¹³). Therefore, heat conduction through the shell goes more slowly for thicker shells and hence it takes more time before the PCM becomes effective when the shell thickness is increased. Actually, to obtain the most performant thermal properties of metal composite coatings with incorporated PCM particles, the particles should have no polymeric shell at all. However, as already mentioned, this is not always feasible due to the difficulties of producing pure PCM particles or due to chemical incompatibilities between the PCM particles and the metal coating. The thermal properties of paraffin microcapsules prepared in this work were compared with the thermal properties of pure paraffin by differential scanning calorimetry (DSC) measurements. The results are shown in Figure 2. It was found that the DSC curve for pure paraffin has two peaks which indicates that the paraffin is a mixture of short and long chained alkanes with melting points of 41 and 59°C, respectively. The latent heat determined from the integration of the peaks in the DSC curve is 291 J/g. This corresponds well with values of the latent heat for paraffin found in literature.² The dashed baseline for the DSC measurement of paraffin in Fig. 2 is almost horizontal, which indicates that the heat capacity of paraffin is low. This is in agreement with literature where a value of 2.9 J/g K is found.¹⁴ The total heat Q which the paraffin takes up is given by

$$Q = Lm + \int_{T_1}^{T_2} mc_p dT \quad [7]$$

with L the latent heat, m the mass, c_p the heat capacity, and T the temperature. The term with the heat capacity varies linear with temperature if c_p is temperature independent and corresponds with the dashed base line in Fig. 2. When c_p is small, the contribution of this term to the total heat flow is small and the dashed line is almost horizontal. Compared with pure paraffin, the latent heat for microencapsulated paraffin is smaller (Fig. 2). The reason for this is the fact that only the paraffin undergoes phase transformation while the urethane shell stays solid. Hence the urethane shell absorbs almost no heat because its heat capacity is low.¹³ The heat capacity of the urethane shell (≈ 1.3 J/g K¹⁵) is comparable to the heat capacity of paraffin, which is reflected in the horizontal baseline of the DSC curve (dashed line in Fig. 2). If the heat capacity of the urethane

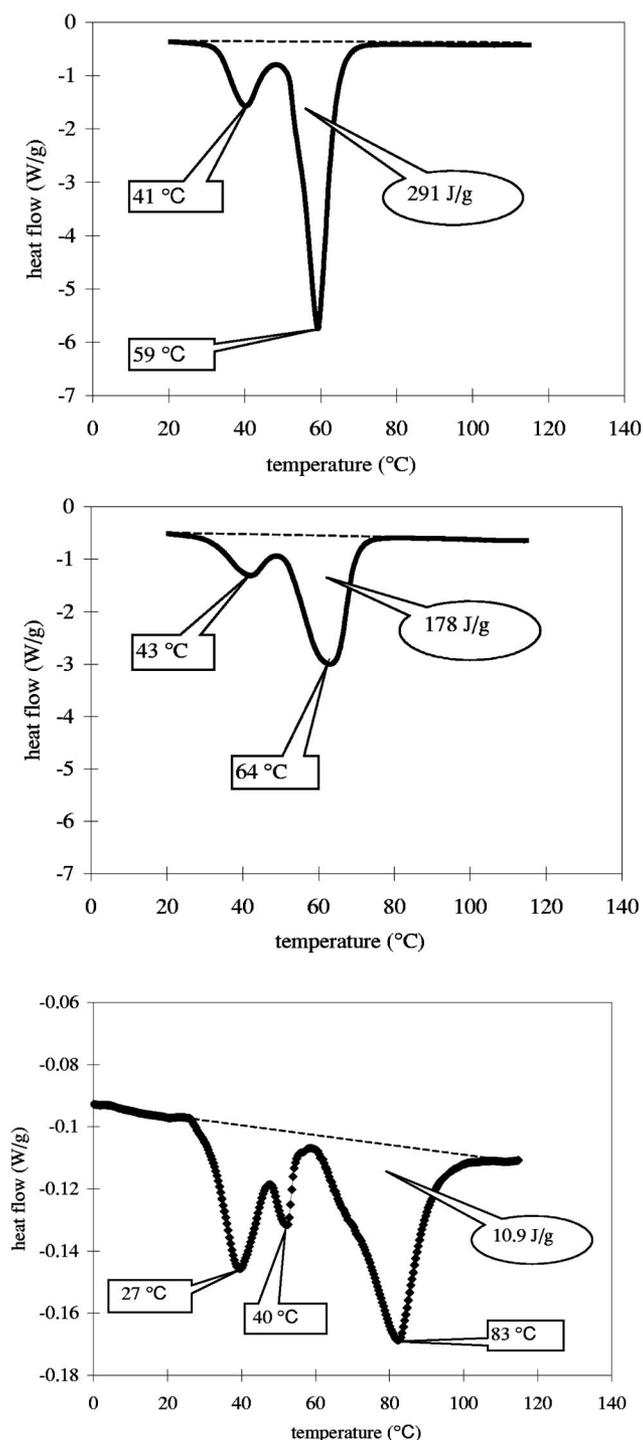


Figure 2. DSC measurements of pure paraffin (top), microencapsulated paraffin (center), and of a copper coating with embedded paraffin microcapsules (bottom). The measurements were done at 10°C/min.

shell would be much larger than the one of paraffin, the slope of the dashed baseline would be larger for microencapsulated paraffin than for pure paraffin. The DSC results of the microencapsulated paraffin particles also show two peaks, corresponding with two melting temperatures (Fig. 2). However, the peaks occur at slightly higher temperatures than for pure paraffin. This is because the urethane shell around the paraffin has a large thermal resistance. Therefore, a larger temperature gradient is necessary to transmit heat from the outside

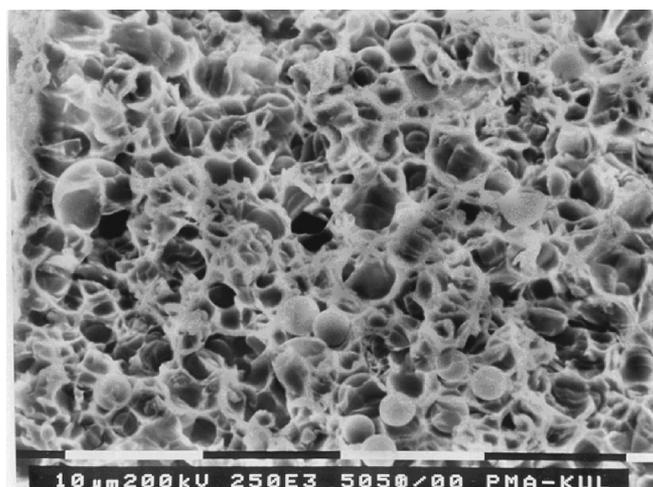


Figure 3. SEM picture of a cryogenic fractured copper coating with microencapsulated paraffin particles. This figure shows that the incorporation amount of paraffin particles is very high.

to the inside of the paraffin microcapsules, which implies that melting occurs at a higher temperature. Moreover, when pure paraffin particles start to melt, they flow onto each other which improves thermal conduction. Microencapsulated paraffin particles keep their shape during melting and hence the thermal conductivity stays low. This also contributes to the higher melting temperature of microencapsulated paraffin with respect to pure paraffin.

Figure 3 shows a SEM picture of a cryogenic fractured coating with incorporated paraffin particles. Almost the whole fracture area consists of cavities where particles had been positioned which fell out of the coating during fracturing. However, the picture clearly shows that the particles are homogeneously distributed and that the incorporation of paraffin particles is high. The volume fraction of paraffin particles in the coating is 35 vol % as determined by the surface fraction of particles on a polished cross section (Fig. 4). It was found that the incorporation of paraffin particles initially increases with increasing current density, reaches a maximum at a current density of about 3 A/dm², and then decreases with a further increase of the current density (Fig. 5). Such a maximum of the particle incorporation with current density was also found in literature for codeposition of polystyrene and Al₂O₃ particles with cop-

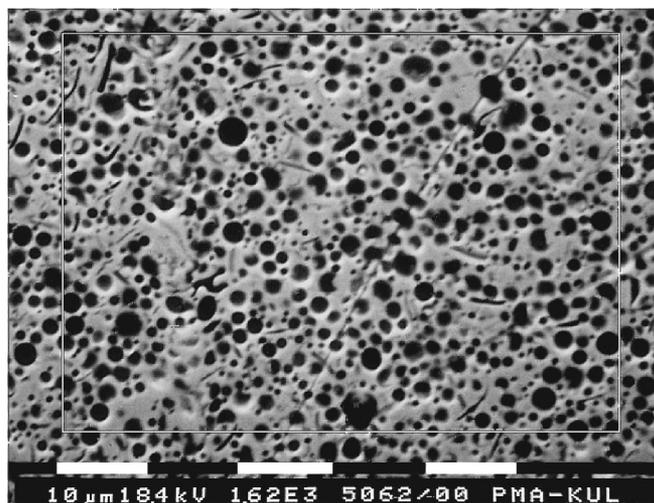


Figure 4. SEM picture of a cross-sectioned copper coating with embedded microencapsulated paraffin particles.

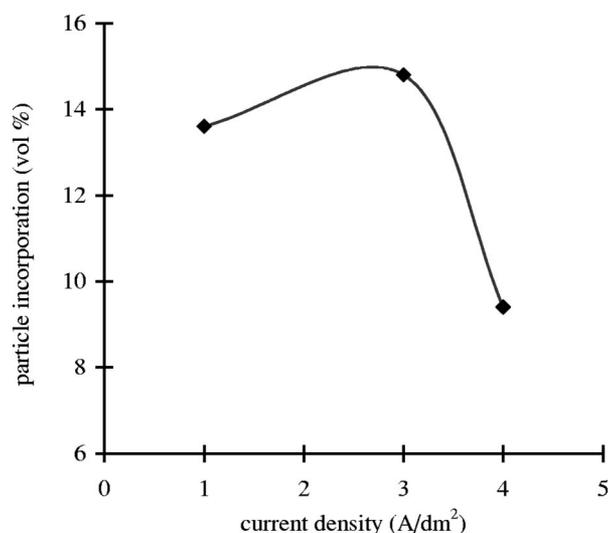


Figure 5. Amount of particles incorporated in the copper deposits as a function of the current density at which the deposits are made.

per, albeit at a current density between 1 and 2 A/dm².^{4,11} According to literature,^{5,11,16} the codeposition maximum can be linked to the potential of zero charge (pzc) of the electrode which lies at a cathodic overpotential of 110 mV. It was also shown in Ref. 5 and 11 that the pzc occurs at a current density of about 2 A/dm² for a copper electrode in a copper sulfate electrolyte. In Ref. 11 it is assumed that the maximum incorporation at the pzc is related to the hydration force which impedes particle incorporation and which is smallest at the pzc. Figure 6 shows the incorporation of PCM particles in copper deposits as a function of the particle concentration. It was found that the incorporation increases with increasing particle concentration and finally reaches a plateau value for high particle concentrations. The increased incorporation with increasing particle concentration is because more particles are transported to the electrode for higher particle concentrations and hence more particles get the chance to incorporate. Once the concentration is very high, further increase of the particle concentration no longer influences particle incorporation because particle-particle interactions start to play a role. At very high particle concentrations, particles which are

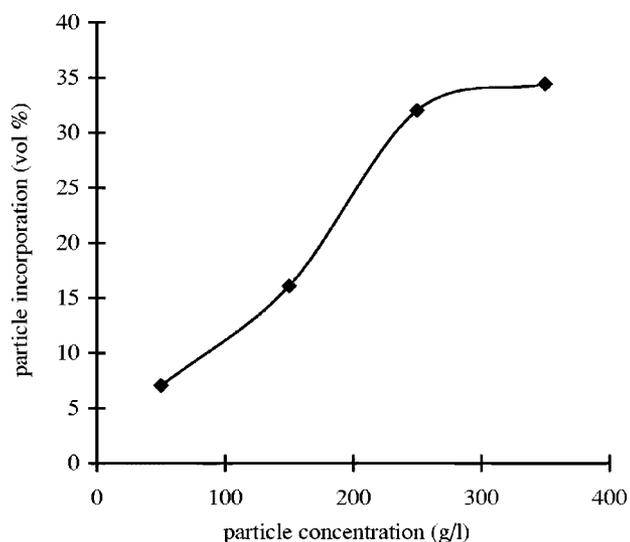


Figure 6. Amount of particles incorporated in the copper deposits as a function of the concentration of particles in the electrolyte.

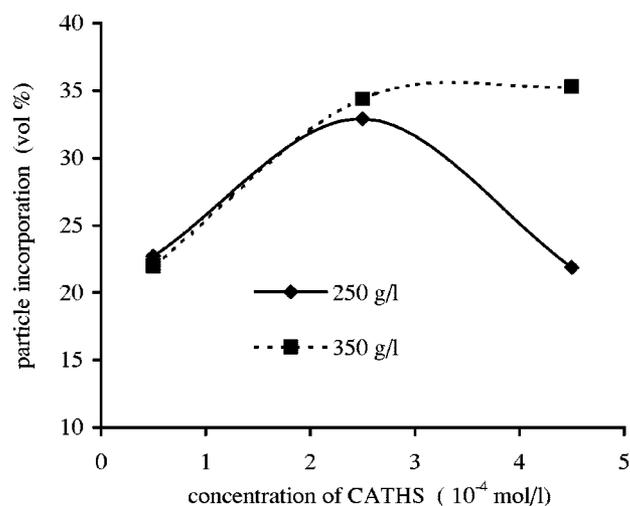


Figure 7. Amount of particles incorporated in the copper deposits as a function of CTAHS concentration in the electrolyte. Results for two different particle concentrations are shown.

transported to the electrode might collide with particles already residing on the electrode, waiting to be incorporated. As a consequence of collisions, some of the particles on the electrode become dislodged and reenter the bulk electrolyte. The effect of cetyltrimethylammonium hydrogen sulfate (CTAHS) surfactant added to the electrolyte is given in Fig. 7. This figure shows that for a particle concentration of 250 g/L, the incorporation reaches a maximum at a surfactant concentration of about $3 \cdot 10^{-4}$ M. This maximum probably corresponds with a monolayer of surfactant on the particles. Based on the molecular structure of a CTAHS molecule it can be estimated that the molecule has a projected surface of about 0.25 nm². Assuming that only 54% of the particle surface can be covered by surfactants (i.e., for a monolayer adsorption) based on a random packing of surfactant molecules on the surface,¹¹ it can be calculated that the monolayer concentration of CTAHS is about $3.5 \cdot 10^{-4}$ M for 250 g/L particles which is slightly larger than the concentration of maximum particle incorporation in Fig. 7. Nevertheless, since the difference between the calculated monolayer concentration and the maximum of particle incorporation is small, the maximum probably corresponds with a monolayer of adsorbed surfactant. For the particle concentration of 350 g/L, no maximum is found for the surfactant concentrations used in this work. This is because the surfactant concentration at which a monolayer adsorbs on the particles increases with particle concentration. Hence the highest surfactant concentration used in this work was too low to form a surfactant monolayer on 350 g/L of particles. The effect of surfactant on particle incorporation can be described as follows. The surfactant molecules consist of a hydrophobic hydrocarbon chain and a hydrophilic end group which is positively charged for CTAHS. The first surfactant layer adsorbs with the hydrocarbon chain on the particles and hence the positively charged end group is directed toward the solution. Therefore, the particles become positively charged by adsorption of a surfactant monolayer. The positive charge on the particles increases the attraction between the particles and the electrode which is negatively charged and hence particle incorporation is increased. When more surfactant is added to the electrolyte, a second layer of surfactant starts to adsorb which decreases the positive charge on the particles and hence decreases the attraction to the electrode. This leads to a decrease in particle incorporation. The maximum particle incorporation obtained in this work lies around 35 vol %. To investigate the thermal properties of coatings with paraffin microcapsules, DSC measurements were done. A result of such measurement is given in Fig. 2, which shows a DSC curve of a copper coating containing 35 vol % of paraffin microcap-

sules. The DSC curve has peaks at 40 and 83°C. The first peak occurs at around the same temperature as for free paraffin microcapsules, while the second peak occurs at a much higher temperature than the one found for free microcapsules. The difference in melting temperature between embedded and free microcapsules might be due to the difference in thermal expansion of the paraffin microcapsules and the copper coating. When the coating is heated, it exerts a pressure on the paraffin particles which is described by the following equation^{17,18}

$$P = \frac{\Delta\alpha\Delta T}{\left(\frac{1 + \nu_m}{2E_m}\right) + \left(\frac{1 - 2\nu_p}{E_p}\right)} \quad [8]$$

with $\Delta\alpha$ the difference in thermal expansion of copper and paraffin, ΔT the temperature range over which the composite coating is heated, ν_m and ν_p the Poisson ratios of copper and paraffin, and E_m and E_p the elastic moduli of copper and paraffin. The elastic modulus, thermal expansion coefficient, and Poisson ratio of copper have values of 117 GPa,¹² $17 \times 10^{-6} \text{ K}^{-1}$,¹² and 0.34,¹⁹ while for paraffin, values for the elastic modulus and thermal expansion coefficient of 240 MPa²⁰ and $130 \times 10^{-6} \text{ K}^{-1}$ ²¹ were found in literature. The Poisson ratio of paraffin was not found in literature and therefore, it was assumed that the value is about 0.4 based on Poisson moduli of other hydrocarbon materials. For the above values, the equation predicts a pressure of 52 atm for a coating heated from room temperature to 64°C, which is the melting temperature of the paraffin microcapsules. This pressure leads to an increased melting temperature according to the Clausius-Clapeyron equation²²

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H} \quad [9]$$

with T the equilibrium temperature during melting, ΔV the volume change during melting, and ΔH the change in enthalpy with phase transformation. For paraffin microcapsules with a melting temperature of 64°C, the above equation predicts an increase of the melting temperature with pressure of about 0.383 K/atm. Hence, the pressure of 52 atm which the coating exerts on the particles increases the melting temperature from 64 to 84°C, which is in correspondence with the DSC measurement. When designing new composite coatings with a certain melting temperature, the pressure dependency of the melting temperature should hence be taken into account. The latent heat of the copper coatings with 35 vol % of incorporated paraffin microcapsules was 10.9 J/g. However, potentially, the latent heat of composite coatings could be increased to about 20 J/g if paraffin microcapsules with thinner shells would be used.

Discussion

A back-of-the-envelope calculation shows that coatings with a latent heat this high are useful for heat sink applications. For instance, a Celeron processor (Intel Corp.) produces 21.7 W of heat. When this processor works continuously during 10 s, 217 J of heat are produced which have to be dissipated. Two coatings with the same mass are compared: a pure copper coating and a copper coating containing 35 vol % of paraffin microcapsules. The experimentally determined value of the latent heat of the paraffin microcapsules is 178 J/g, the heat capacity of the paraffin microcapsules is 2.9 J/g K according to literature,¹⁴ and the heat capacity of copper is 0.385 J/g K.¹² A coating with a mass of 8.9 g was used for the calculations, which corresponds with a pure copper coating having a surface area of $10 \times 10 \text{ cm}$ and a thickness of 100 μm . For a composite coating with a total mass of 8.9 g and 35 vol % of paraffin microcapsules, the mass of copper is 8.4 g and the mass of paraffin is 0.5 g, assuming that the density of the particles is 1 g/cm³. The temperature increase for the pure copper coating and the composite coating is calculated according to the following equation

$$Q = m'_{\text{Cu}}c_p^{\text{Cu}}\Delta T' = m_p c_p^{\text{p}}\Delta T + m_p L_p + m_{\text{Cu}}c_p^{\text{Cu}}\Delta T \quad [10]$$

with m'_{Cu} the mass of the pure copper coating, m_{Cu} the mass of copper in the composite coating, m_p the mass of the paraffin microcapsules in the composite coating, c_p^{Cu} the heat capacity of copper, c_p^{p} the heat capacity of the paraffin microcapsules, and L_p the latent heat of the paraffin microcapsules. For $Q = 217 \text{ J}$, a $\Delta T'$ of 66°C is found for the pure copper coating while a ΔT of only 29°C is found for the composite coating, provided that the end temperature is above the melting temperature so that phase transformation took place.

Although the above values give an indication of the temperature reduction by using PCMs, the calculation was only indicative. In real cases, the heat is adsorbed by the PCM which is melting, and since the melting front moves, the conduction of heat in the PCM also plays a role. Also, the fact that PCM is distributed in the metal complicates exact calculations of the heat flow.

Conclusion

It was shown that microcapsules composed of a paraffin core with a urethane shell can be prepared by interfacial polycondensation. Particles prepared in this way formed stable suspension in an acidic copper plating electrolyte and could be incorporated in copper coatings. The resulting composite coating is useful for heat sink applications since it combines the high thermal conductivity of copper with the high heat absorption capacity of PCMs. The effect of current density, particle concentration, and concentration of surfactant on the amount of particle incorporation was investigated and it was found that under optimal conditions coatings with a particle concentration of 35 vol % could be obtained. Such coatings have a heat absorption capacity of 10.9 J/g, as determined by DSC.

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