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Electrospray deposition of AlN-PVA composite coating as thermal interface material

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ABSTRACT

In this study, aluminum nitride (AlN)-polyvinyl alcohol (PVA) composite coatings as a novel thermal interface material for electronic applications were fabricated by using the electrospray deposition (ESD) technique at room temperature. The influence of deposition time on the morphology and the thermal behavior of AlN-PVA composite coatings was investigated. The microstructural inspections indicate that homogeneous, highly dense, and paste-like AlN-PVA coatings were formed. Increasing the deposition time from 15 min to 30 min reduced the surface roughness of the AlN-PVA coating. Infrared thermography images revealed that the deposition of AlN-PVA composite coatings on aluminum alloy substrates dramatically improved its thermal effusivity. The thermal diffusivity of 15 min (38.767 mm^2/s) and 30 min (37.485 mm^2/s) coated samples were approximately 30% higher than the uncoated substrate (26.638 mm^2/s).

1. Introduction

Thermal management of electronic circuits has become a fundamental problem due to the ever-shrinking of modern electronic devices [1]. The commonly used method to rapidly remove the heat produced by a circuit is the application of thermal interface materials (TIM) in between a chip and its heat sink [2].

Functional polymer matrix nanocomposites have been developed for a wide range of applications such as electronic, medical, and energy applications [3,4]. In most cases, filler material plays a significant role in determining the final properties of composites. Aluminum nitride is one of the high thermal conductive semiconductor materials with a wide band gap energy. So, it was previously introduced as a suitable filler material alternative for fabricating polymer matrix composites as thermal interface materials (TIM) [5].

In the case of high thermal conductive nanocomposites, reaching up to a high volumetric filler density and providing a continuous contact between the filler particles are crucial steps [5]. However, fabricating thin composite films or coatings with more than 80 wt% filler content is a challenging procedure with conventional techniques.

Therefore, for the first time in the present work, AlN-PVA composite coatings as an alternative TIM were fabricated using a cost-efficient ESD technique at room temperature. Then, the structure and thermal properties of the composite coatings have been investigated and discussed.

2. Materials and methods

Analytical grade aluminum nitride (AlN, containing 1 wt% oxygen, particle size < 5 μm) and polyvinyl alcohol (PVA) powders were purchased from Merck KGaA Germany. For the fabrication of AlN-PVA containing suspension, 2.5 g of PVA was firstly mixed with 100 mL propanol under vigorous magnetic stirring at room temperature for 30 min. Then, 0.5 g of AlN powder and 100 mL propanol-PVA mixture were milled using a planetary ball mill for 3 h at 300 rpm. After this stage, a stable colloidal suspension of AlN-PVA in propanol was obtained. It is also possible to use different surfactants than propanol to obtain suspensions, but our preliminary studies showed that neither methanol nor ethanol could provide enough stability for AlN particles.

Aluminum alloy substrates with the dimensions of 10 mm × 10 mm × 1.5 mm were coated with AlN-PVA suspension using the ESD technique. The influence of ESD duration on the structure and thermal properties of AlN-PVA coatings was investigated by using two different coating duration (15 and 30 min). The flow rate of AlN-PVA suspension, working distance, and DC voltage between the nozzle and substrate were

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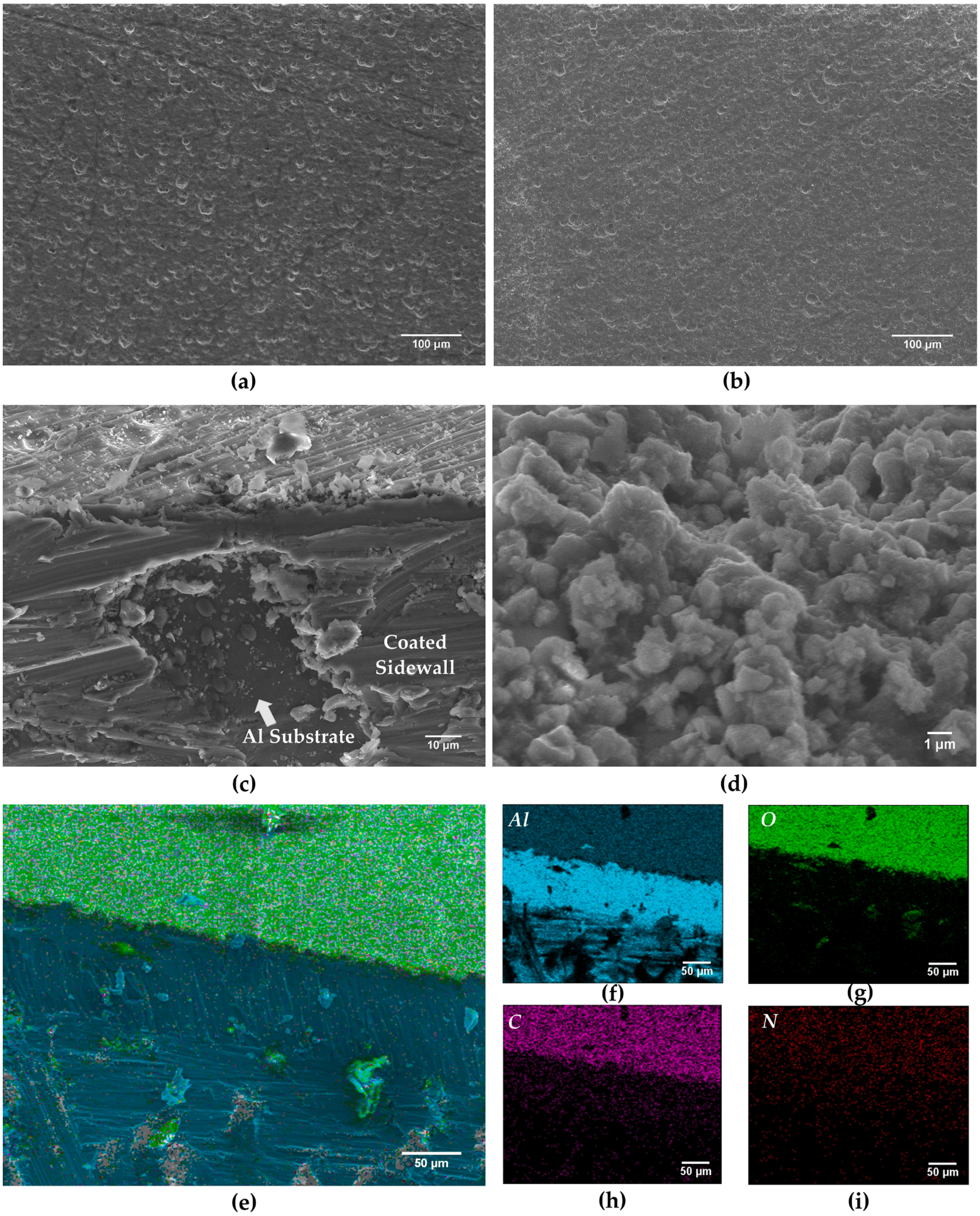

Fig. 1. SEM images of AlN-15 (a), AlN-30 (b–d), and EDX-mapping results of AlN-30 (e–i).

0.03 mL/min, 10 cm, and 6 kV, respectively. The morphology of AlN-PVA coatings was characterized by the field-emission scanning electron microscopy technique (FESEM, Jeol-JSM 7001F). Infrared thermography measurements of the samples were carried out using a thermal camera (Testo-883). Thermal diffusivities of the AlN-PVA coated samples were measured by laser flash technique (Netzsch-LFA 457) in accordance with the ASTM E1461 standard.

3. Results and discussion

SEM images of the top surfaces of 15 min (AlN-15) and 30 min (AlN-30) coated samples show that the whole surface of the substrates was coated homogeneously (Fig. 1-a and b). The formation of crater-like indents on both sample surfaces was seen and this texture might be formed because of the collision of highly accelerated suspension droplets to the substrate. The surface roughness of AlN-PVA coating was reduced by increasing coating duration. This observation indicates that increasing coating duration resulted in more AlN-PVA deposition on the surface of substrates.

The paste-like AlN-PVA composite coating was deposited even on the sidewalls of the substrate (Fig. 1-c). The damaged site of the coating suggests that approximately 10 µm thick coating formed after the 30 min ESD process. AlN particles were remarkably packed, and the particle-to-particle contact was established (Fig. 1-d). Most notably, even after the deformation, aluminum nitride particles with a size smaller than 1 µm maintained their strong binding with each other and the substrate because of the usage of PVA as a binder (Fig. 1-c.). The results of EDX-mapping analysis performed from the sidewall of the AlN-30 are shown in Fig. 1-e to i. Due to the reason that the sidewall of the sample was also coated, and the substrate is aluminum, the coating-substrate

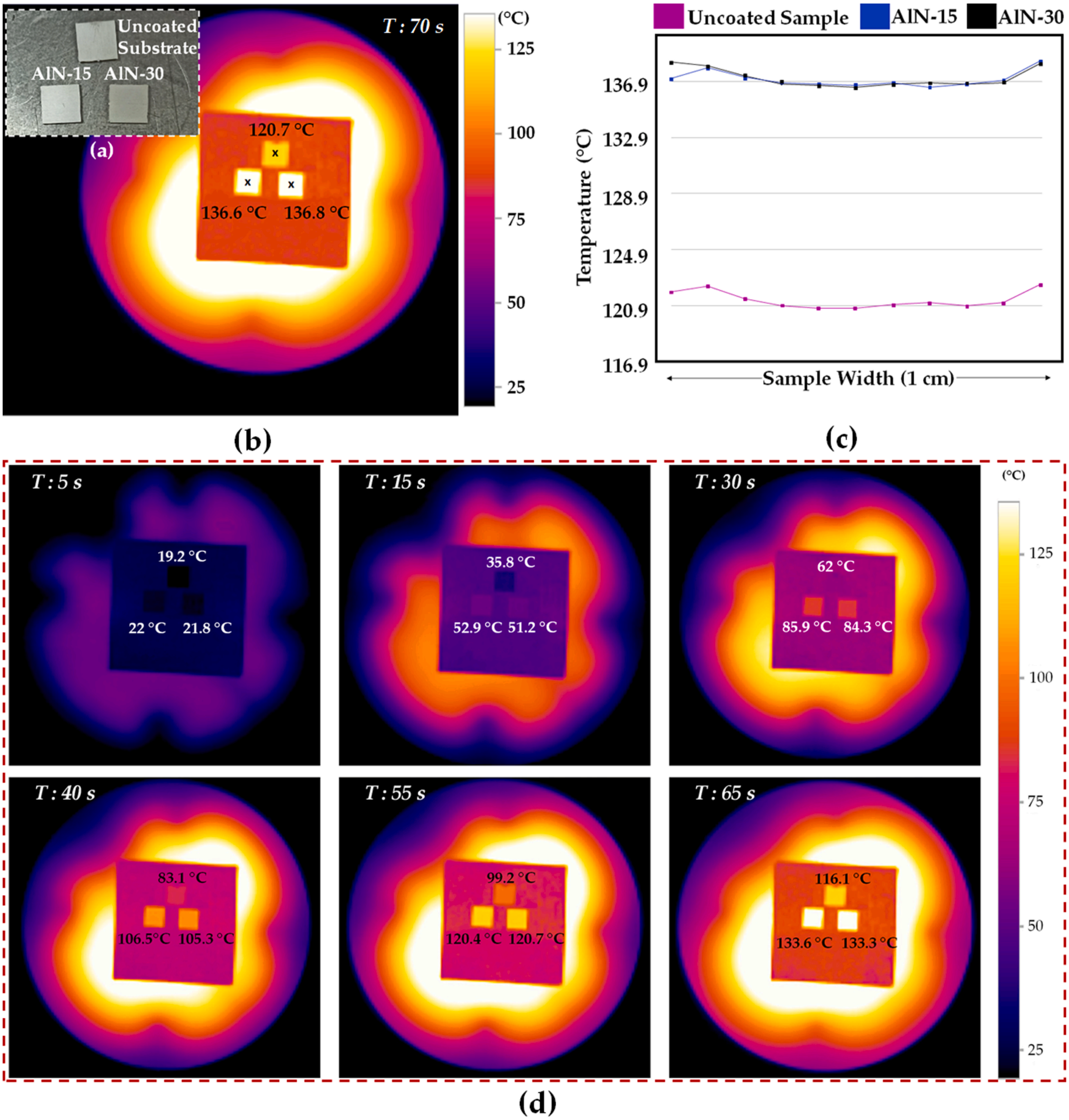

Fig. 2. A picture of samples on graphite foil (a), a thermograph captured after 70 s heating (b), temperature distribution graphs (c), thermographs captured after 5–65 s heating (d).

interface could not be clearly distinguished. Nevertheless, the color contrast in Fig. 1-e and the obtained aluminum, nitrogen, carbon, and oxygen (Fig. 1-f to i) signals indicate successful composite coating formation.

The infrared thermography image in Fig. 2-b shows that after 70 s heating, the surface temperature of the uncoated substrate became 120.7 °C. Contrarily, AlN-PVA composite coated samples' surface reached approximately 16 °C higher temperature than that of the uncoated substrate (Fig. 2-b). Besides, no dramatic temperature difference was detected between the 15 min (136.6 °C) and 30 min (136.8 °C) coated samples. The surface temperature distribution of the coated samples was also analyzed from captured thermographs (Fig. 2-c). Coated samples' linear surface temperature distribution is a sign of an even thickness gradient, well-established particle to particle contact (as also seen from Fig. 1-d), and defect-free structure (such as porosities or micro-cracks). Furthermore, even after the temperature reaches almost 140 °C, no visible deformation or thermal degradation of coatings was observed. Thermal degradation of neat PVA starts at around 225 °C and continues up to 370 °C [6]. So, it is expected that the fabricated coatings should be stable at least up to 200 °C.

A thermogram of the irradiated surface can give information about its thermal effusivity, defined as in Eq. (1) [7].

$$e = \frac{Q}{\Delta T(t)\sqrt{\pi t}} \tag{1}$$

Q; Dirac heat flux.
$\Delta T(t)$; Temperature change as a function of time.
t; Time.

The thermographs captured as a function of heating duration are evident that AlN-PVA composite coatings promote accelerated heat ex-

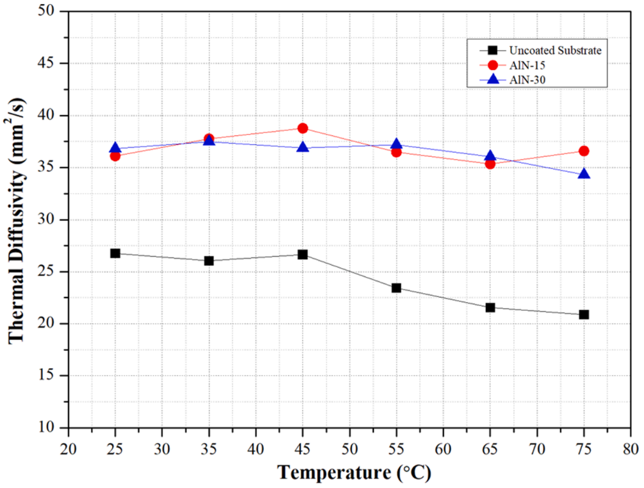

Fig. 3. The thermal diffusivity values of the uncoated substrate, AlN-15, and AlN-30 as a function of temperature.

change between the hot plate and substrate (Fig. 2-d). Lower $\Delta T(t)$ results in higher thermal effusivity. The thermal effusivity is directly proportional to the thermal conductivity (Eq. (2)) [8]. Thereby, it can be inferred that electrospray deposited AlN-PVA composite coatings enhance the substrates' thermal conductivity.

$$e = \sqrt{\lambda \rho Cp} \tag{2}$$

λ; thermal conductivity.
ρ; density.
C_p; heat capacity.

According to the laser flash measurement results (Fig. 3.), AlN-PVA composite coating improved the thermal diffusivity of the substrates up to 10.069 mm^2/s at 25 °C and 15.791 mm^2/s at 75 °C. At larger than 45 °C, the thermal diffusivity values of all samples decreased with increasing temperature. The thermal diffusivity of uncoated substrate decreased 21.6% in the temperature range of 45 to 75 °C, while that of AlN-15 and AlN-30 had only reduced by 5.61 and 6.9%, respectively. This phenomenon can be explained by Umklapp scattering, which decreases the thermal diffusivity of crystalline materials by reducing the mean free path of both electrons and phonons as a function of temperature increase [9]. There was no dramatic difference between the thermal diffusivity values of AlN-15 and AlN-30, which supports the results of infrared thermography analysis. Even though the increased ESD duration (from 15 to 30 min) should increase the coating thickness, contrary to the expected, it did not decrease the thermal diffusivity of coatings. The equal thermal diffusivity of AlN-15 and AlN-30 might be because AlN-30 has a relatively smoother coating surface, or well-established particle to particle contact prevents thermal diffusivity loss even in the thicker coating. Additionally, the observed slight fluctuation in the thermal diffusivity values might be because of the surface roughness. It is noteworthy that the thermal diffusivity of most thermal paste materials varies in the range of 1 to 10 mm^2/sec [10]. The measured thermal diffusivity values of the fabricated AlN-PVA composite coatings were relatively higher than some of the conventional silver, aluminum oxide, boron nitride, or zinc oxide containing thermal paste materials [10]. Hence, we can say that electrospray deposited composite coatings have a great potential to replace conventional thermal pastes as new-generation permanent thermal interface materials.

4. Conclusion

AlN-PVA composite coatings were deposited on aluminum alloy substrates using the ESD technique at room temperature. It was observed that well homogeneous, highly dense, and paste-like AlN-PVA coatings formed after both 15 min and 30 min coating processes. The results indicate that the AlN-PVA composite coatings greatly improved both thermal effusivity and diffusivity of substrates. The measured highest thermal diffusivity values of 15 min and 30 min AlN-PVA composite coated samples were 38.767 mm^2/s and 37.485 mm^2/s, respectively. These values are approximately 30% larger than that of the uncoated substrate (26,638 mm^2/s). It is concluded that electrospray deposited AlN-PVA composite coatings can provide faster heat exchange between a heat source and a heat sink. Therefore, AlN-PVA composite coatings might be a suitable alternative for conventional thermal interface materials used in electronic applications. Furthermore, because the electrospray deposition technique is a large-area scalable and cost-effective process, the presented AlN-PVA coatings would be economically feasible for the mass-production of the new generation thin electronic packages.

CRediT authorship contribution statement

Suna Avcıoğlu: Conceptualization, Investigation, Visualization, Writing – original draft, Writing – review & editing. **Pınar Uyan:** Investigation, Data curation. **Onur Yontar:** Investigation, Data curation. **Sinem Çevik:** Supervision, Resources, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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