

The Effect of Process Induced Variation of Nanostructure Sizes on the Superhydrophobicity of Modified C84400 Alloy Surfaces

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ABSTRACT

The sizes of the nanostructures formed by the reaction of the alloying elements in C84400 alloy with stearic acid varied with the reaction time and temperature. The determination of the characteristics of the nanostructures in terms of the chemical composition and morphology was done through the energy dispersive x-ray spectroscopy (EDX), the fourier-transform infrared spectrophotometric analysis (FT-IR), x-ray diffraction method (XRD) and through the scanning electron microscopy (SEM), respectively. The energy dispersive x-ray analysis showed the accumulation of carbon and oxygen on the surfaces after reaction of the C84400 alloy with 0.005 M stearic acid. This was further confirmed through the fourier-transform infrared spectroscopy that showed absorbance bands at 2915 cm⁻¹, 1535 cm⁻¹, 1460 cm⁻¹, 1396 cm⁻¹, 1105 cm⁻¹, 720 cm⁻¹ and 676 cm⁻¹ respectively for the samples treated at 30° C and 40° C and the absorbance frequencies at 1398 cm⁻¹ and 1536 cm⁻¹ were due to the symmetric and anti-symmetric COO⁻ stretch of cation-substituted carboxyl group while, the absorbance frequencies at 2915 cm⁻¹ and 2840 cm⁻¹ were assigned to the CH₂ stretching of the metallic stearates formed at these temperatures. This was further confirmed by the x-ray diffraction peaks in the long-arm spacing region at 2θ values of 2.5°, 4.1°, 5.9°, 8.1° and 10° respectively. At 30° C, the sizes of the nanostructures varied from 170±20 nm to 566±110 nm and at 40° C, from 178±120 nm to 842±110 nm. The changes in the sizes conformed to the alteration of the surface morphology and superhydrophobic behavior. The contact angles of water and hence the superhydrophobicity of the samples depended on the sizes of the nanostructures formed on the surfaces of the samples. The superhydrophobicity had maximum values of 154.8°±4.3° and 155.5°±3.6° for the C84400 alloys modified with stearic acid at the temperatures of 30° C and 40° C respectively. After these maximum values, the contact angles dipped, gradually reducing in values to below 150°. This dip in the contact angle values for superhydrophobicity is ascribed to the increasing fractional surface area available for wetting due to increasing nanostructure dimension (D_s).

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Introduction

The reaction of weak organic acids with metals, metal carbonates, and metal oxides can occur at elevated temperature and in excess water (Gonen, et al, 2005). Factors such as concentration of the weak acids, temperature and the reaction time are believed to affect the surface areas, morphologies and shapes of the metal salts generated by these organic acids. It is known that the nanostructures on the surfaces including rods, needles, belts etc. affect the wettability of such surfaces (Khranovskyy et al, 2012; Lee et al, 2012). To this end, simple chemical processes have been used in generating desired surface features for improved water and oil contact angles and these processes have been reported in literature (Guo et al, 2008; Lee et al, 2009; Escoba and Llorca-Isern, 2014; Latte et al, 2009, Zhang et al, 2010). These methods have become straight forward and easy ways of making surfaces with proper control of size, shape and dimensionality of the micro-and nanoscale structures. In this regard, superhydrophobic surfaces have been fabricated on a copper substrate through simple chemical oxidative method of immersing in n-tetradecanoic acid for about a week without further surface modification (Liu et al, 2007). Also, an optimized one-step wet synthesis using fluoroalkylsilane has been applied in fabricating superhydrophobic aluminium surfaces (Bernagozzi et al,

2014). Other workers have used different chemical processes and routes to generate various morphological features, for surface modification and superhydrophobicity (Qing et al, 2015; Wang et al, 2010; Liang et al, 2016).

C84400 alloy is important in the water reticulation components such as pumps and valves (Michels, 2006). As such, cheap, non-hazardous and effective means of modifying the surfaces of this alloy for superhydrophobicity can help solve the problem of fouling and corrosion associated with the alloy. In this research, we are reporting the effect of process induced variation of the nanostructure sizes on the superhydrophobicity of C84400 alloy surfaces modified with stearic acid.

Experimental

Materials

The C84400 alloy used in these experiments was obtained from Baker Manufacturing, LLC (Evansville, WI, USA). The C84400 alloy consisted of copper (81 wt. %), lead (7 wt. %), tin (3 wt.%) and zinc (9 wt.%) as the alloying elements. Other chemicals used include stearic acid and ethanol solvent, all obtained from Sigma-Aldrich chemicals and of 99.9 % grade purity. These chemicals were used as received without further purification.

Method

The C84400 alloy was machined into sizes of 25 x 5 x 3 mm. To ensure the smoothness of the sample surfaces, after the machining and sectioning, these C84400 samples were ground and polished with various grit sizes of silicon carbide papers. The grit-sizes of the silicon carbide papers used included the 400, 600 and 1200 grades. The final polishing of the samples was achieved using a soft cloth covered with 1 micron alumina slurry. The samples were finally washed in an ultrasonic bath containing acetone and blown dry with compressed air. The direct chemical reaction process was carried out by the immersion of the samples in 0.005M stearic acid solutions for one to five days. The 0.005 M ethanol solution of stearic acid was prepared by dissolving precisely 1.6 g stearic acid in 1000 ml ethanol solution. Using a pressure reactor (the Parr pressure vessel, model no. 4601Q), the reaction between the C84400 alloy samples with the 0.005 M solution of the stearic acid at the temperatures of 30° C and 40° C was carried out. After the specified duration of one to five days, the samples were carefully removed from the pressure vessel and washed with acetone and distilled water, pending further characterization.

Characterization

The characterization the samples' surfaces altered during the reaction with stearic acid at 30° C and 40° C was done using various methods. The surface morphology was assessed through the use of the scanning electron microscope (Hitachi S-4800 model) at a high magnification. Furthermore, using the x-ray energy dispersive probe attached to the scanning electron microscope, the chemical compositions of the surface features were analyzed. Further characterization of the surfaces to elucidate the chemical nature of the surface features involved fourier-transform infrared spectroscopic and x-ray diffraction techniques. For the infra-red spectroscopy, the spectra were obtained in the region of 4000-500cm⁻¹ using the Pekin Elmer Grating Spectrophotometer. The x-ray diffraction analyses were done at a continuous count rate of 2 degrees per minute for 2θ values between 2.0° to 60° using the Scintag x-ray machine. Contact angle and surface roughness values were determined using the contact angle goniometer/tensiometer (Rame-Hart 250 model) and the surface roughness profilometer (SG-4500 model). The goniometer has the Dropimage advance software for image analysis and the determination of the contact angle. To ensure accuracy in the contact angle measurement, a micro-syringe that can place a water drop of specific volume was used. In the case of the average surface roughness, the average surface roughness was measured over a cut-off length (λ) of 5 μm. For each of the contact angle and the average surface roughness, (R_a), the averages of five measurements were taken.

Results and Discussion

Surface morphology evaluation

The SEM offered excellent insight on the surface morphologies and captured effectively the sizes and shapes of the nanostructures formed after the chemical reaction process at 30° C and 40° C, as shown in Fig. 1 and Fig. 2 respectively. It was observed that densely packed nanostructures were distributed, to some extent of

uniformity, on the surfaces of the samples, covering the entire surfaces. A gradual increase was observed in the sizes of the nanostructures formed on these surfaces as a function of time and temperature. At 30° C, the nanostructures on the surfaces evolved from thin tendril-like structures under the first 24 hours to coarse petal-like nanostructures after 120 hours of reaction with stearic acid.

Also at 40° C, the shape of the nanostructures evolved from tendril-like to petal-like and flake-like shapes as well as like a patchy surface on the C84400 alloy after 120 hours of reaction with stearic acid. This is consistent with the expectation that at higher temperature, the rate of the reaction of stearic acid with metals increases (Gonen et al, 2005). The accumulation and coarsening of the nanostructures on the surfaces are therefore attributable to the increase in the rate of the reaction of the acid with the alloying elements in the copper alloy and is believed to be continuous until the surface is sufficiently covered by the nanostructures, over a period. The continuous growth, accumulation and coarsening of the reaction products proceeded seemingly through a side-to-side attachment of the thin tendrils formed with the elemental constituents of the C84400 alloy. Therefore, the sizes of the nanostructures formed at 40° C were larger than those formed at 30° C due to a faster rate of accumulation and coarsening at the higher temperature. Using the dimensions of the nanostructures measured from the SEM images, an estimate of the rate of accumulation of the nanostructures at the two temperatures, k, was done using equation 1:

$$k = \frac{D_s - D_s(24)}{\Delta t} \quad (1)$$

D_s and D_s (24) are the estimated sizes at (t) hours and 24 hours respectively while Δt is the change in time, in hours. The values of the estimated dimensions of the nanostructures are given in Table 1. Based on the relationship stated in equation (1), the estimated rate of accumulation of nanostructures is in the range of 1.29–6.27nm/hour for 30° C and 1.63- 10.29 nm/hour for 40° C, with the peak value occurring at the 72 hour. This confirms that the rate of accumulation of these nanostructures due to the reaction of the stearic acid with the alloying elements in the C84400 alloy samples, approximately doubled with the increase in temperature and this played a critical role in influencing the behavior of the contact angle of water observed thereof at 30° C and 40° C respectively. It is known that the initial surface roughness of the C84400 alloy would have an influence on the surface area exposed for reaction with the stearic acid solution. It should however be noted that the polished surfaces, with fine finishing of 0.1 microns at the initial point, ensured uniformity of the surface areas exposed for the reactions. Therefore we expect that the topography of surfaces of the C84400 alloy had no influence on the morphology and nature of the nanostructures.

Analyses of the chemical composition of surface nanostructures

Samples that were reacted in 0.005 M stearic acid at 30° C and 40° C for 5 days respectively were used as representative samples for the evaluation of the chemical nature and compositions of the nanostructures observed

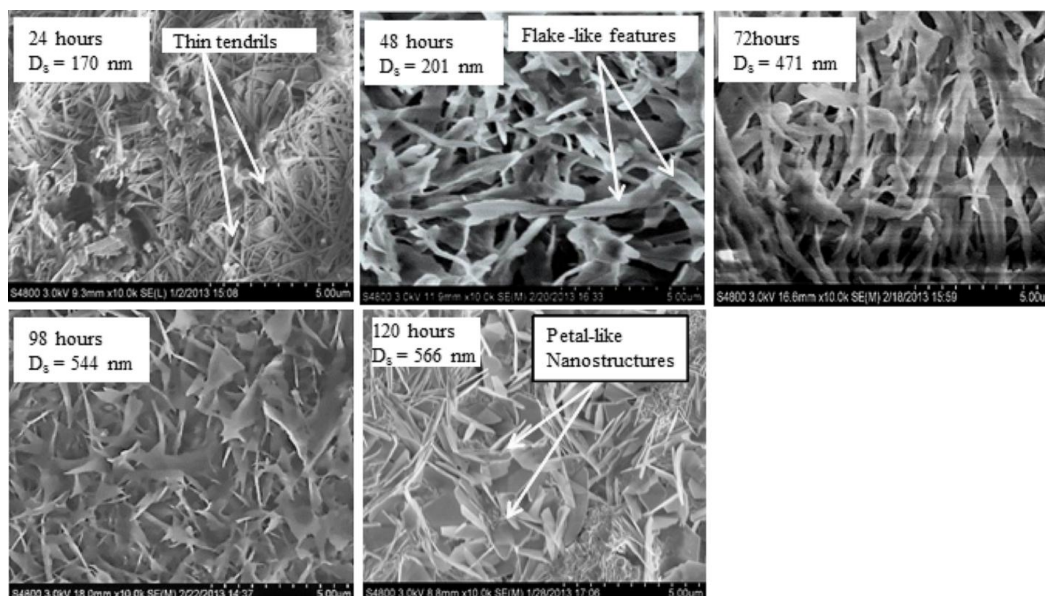


Figure 1: SEM images of C84400 copper alloy after surface modification in 0.005M stearic acid at 30 °C for 24-120 hours

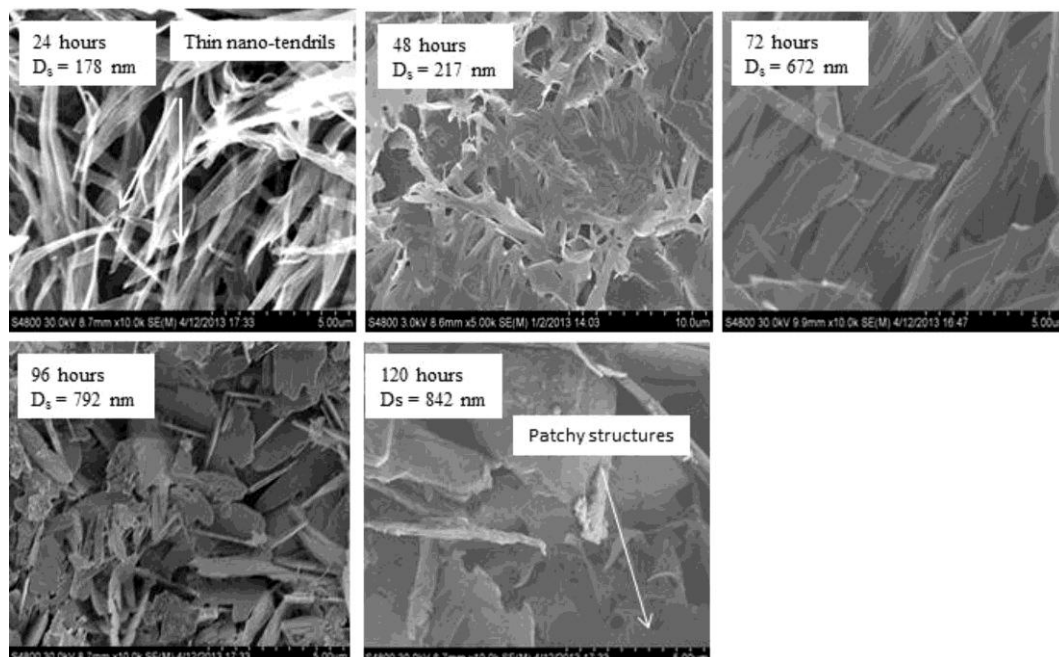


Figure 2: SEM images of C84400 copper alloy after surface modification in 0.005M stearic acid at 40 °C for 24-120 hours

with the scanning electron microscope, (SEM). From the EDX elemental analyses of these nanostructures, considerable amounts of carbon and oxygen (in weight percent) were present in the nanostructures besides the elements of copper (Cu), lead (Pb) and zinc (Zn), which constitute the C84400 alloy as seen in Fig. 3. The EDX did not show any considerable presence of Sn and this could be due to its rather limited amount in the alloy.

The immobilization of carbon that is from the extensive carbon-carbon chain of the stearic acid, on the surfaces confirms that these nanostructures are the products from the reaction of the alloying elements with stearic acid.

On further evaluation of the chemical composition of the nanostructures on the surfaces of the selected samples

with the FT-IR spectroscopic method, similarities were noted in the absorbance bands at 2915 cm^{-1} , 2848 cm^{-1} , 1536 cm^{-1} , 1460 cm^{-1} , 1398 cm^{-1} , 1105 cm^{-1} , 720 cm^{-1} and 676 cm^{-1} respectively for the samples treated at 30° C and 40° C, as shown in Fig. 4. It is known, and stated in various literature, that carboxylic acids show peculiar absorbance bands. To this end, carboxylic acids always show strong absorbance bands for O-H vibration at 3580-3180 cm^{-1} and another strong absorbance at 1800-1700 cm^{-1} for the C=O stretching frequency (Allara and Nuzzo, 1985; Pallacios and Monhemius, 2001; Robinet and Corbeil, 2006).

However, the infrared absorbance frequencies obtained from the fourier-transform infrared analyses did not have these distinct absorbance bands for carboxylic acids that

should have been a characteristic of the stearic acid. This implies that the alloying elements in the C84400 alloy effectively reacted with the low concentration stearic acid leading to stearates formation at both temperatures.

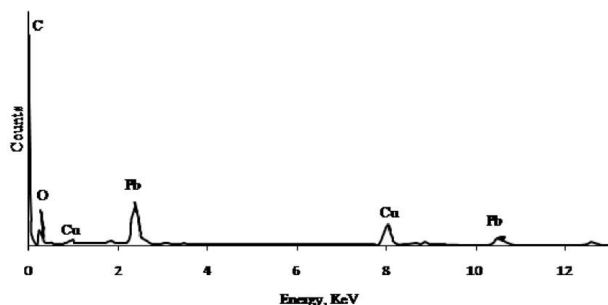


Figure 3: EDX of surfaces of C84400 copper alloy chemically modified in 0.005M stearic for 5 days at 30 °C/ 40° C

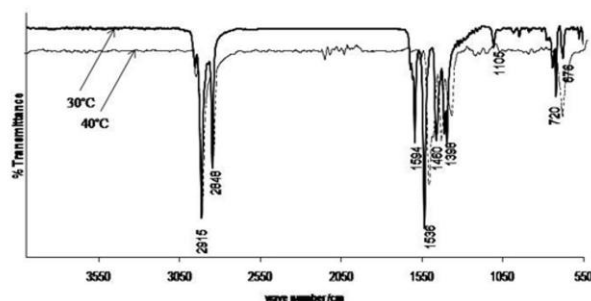


Figure 4: IR spectra of surface of C84400 copper alloy after reaction in 0.005M stearic acid solution

Therefore, the absorbance bands at 1398 cm⁻¹ and 1536 cm⁻¹ are attributed to the COO⁻ symmetric and anti-symmetric stretching due to the substitution of a cation in the carboxyl group. The presence of these absorbance bands distinctively confirms the formation of metal stearates nanostructures. The absorbance bands at 2915 cm⁻¹ and 2848 cm⁻¹ are due to the CH₂ stretching frequencies of the stearates formed (Nakamoto et al, 1959; Otero et al, 2014). The bands at 676 cm⁻¹ show that the alkyl chains of the stearates are extended in a trans zig-zag structure (Snyder and Schachtschneider, 1963). Metal stearates are known to present absorbance peaks from 1530 cm⁻¹ to 1570 cm⁻¹ due to the asymmetric vibration stretching of the carboxylic group coordinate through the oxygen atom with the metal (Lu et al, 2002). This means that the metal stearates are formed by the coordination of the oxygen with the bivalent metal ions in a chelating form as shown in equation (2) and Fig. (5).

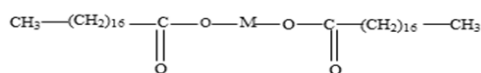


Figure 5: Structure of metal stearates formed by coordination of oxygen with the alloying elements in C84400 alloy. (M= Cu, Zn, Pb and Sn in the +2 oxidation state)

The chemical equation in (2) shows the reaction of alloying elements in C84400 alloy with stearic acid (with M= Cu, Zn and Pb in the +2 oxidation state).

The formation of the stearates on the surfaces is expected to depend on the ease of the reactivity of these different alloying elements with stearic acid (Raman et al, 2010). The FT-IR analyses, as stated in this paper, only confirm that the alloying elements of Cu, Zn, Pb and Sn reacted with the stearic acid to form the corresponding stearates. However, the analyses provide no information on the extent of reaction of these alloying elements with the stearic acid under the process conditions.

The x-ray diffraction peaks observed in the x-ray diffraction analyses of the samples after the chemical reaction processes at 30° C and 40° C were identical, as seen in Fig. 6. The x-ray diffraction patterns were seen in two distinct regions, the long-arm spacing and the short-arm spacing regions. The former included 5 orders of (00l) Bragg peaks, indexed as (001), (002), (003), (004) and (005) planes of the stearates formed, at 2θ values of 2.2°, 2.5°, 4.1°, 6.0° and 8.1° respectively. These peaks still confirm the formation of well-defined stearate structures. Furthermore, the diffraction peaks observed at 43.0° and 49.8° are due to the α-phase of the C84400 alloy. It is known that the C84400 alloy consist of a single phase solution of the α-phase, which is noted from the phase diagram of CuZn alloy systems (Bagherian et al, 2016; R. J. Davies, 2001). The peaks observed in the long-arm spacing region were weak, with low intensities signifying a thin layer of the stearate nanostructures.

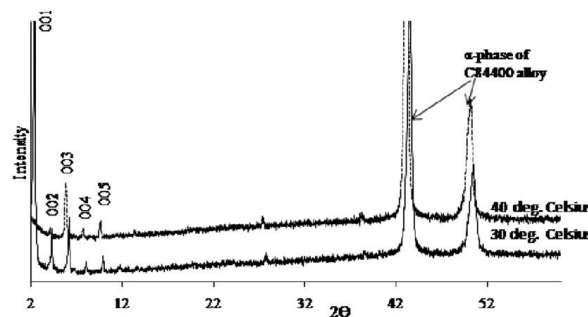


Figure 6: XRD of surface layers of C84400 copper alloy after modification in 0.005 M STA at 30° and 40°

Effect of reaction parameters on the growth of the metallic stearates

Here we discuss the key parameters of temperature and reaction time that affect the formation, morphology and sizes of the metal salts of Cu, Zn and Pb after the reaction of the stearic acid with the C84400 alloy. In terms of the reaction time, it is noted that larger sizes of the stearates nanostructures are formed with increase in the reaction time. Therefore, the dimensions of the stearates given by D_s were higher at longer times of reaction. The D_s values, signifying the sizes of the nanostructures formed, were also of higher values when the temperature of the process was altered from 30° C to 40° C. As much as the sizes of the nanostructures formed increased with time, this time - dependent increase was more at 40° C than at 30° C. The stearic acid reaction rate with the alloying contents in the C84400 alloy was therefore controlled predominantly by

the temperature. These results show that by increasing the temperature, the kinetic energy of the reacting alloying species and the molecules of the stearic acid increases resulting in enhanced collision probabilities. This increases the effectiveness of the chemical interaction and of course growth of the metallic stearates (M. Fallah et al, 2017).

Influence of the nanostructures on the contact angle of water (θ_{av}) and the average surface roughness (R_a)

The main factors that determine the wettability of the surfaces are the surfaces energy, the surface roughness and the fractional surface area of the nanostructures (Bhushan et al, 2008). The C84400 alloy surfaces are hydrophilic in nature. In this work, change in the hydrophilicity of the C84400 alloy surfaces to superhydrophobicity, was due to the hydrophobic properties of the metal stearates and the micro/nanoscale hierarchical structures of the metal stearates. While the low energy of the metal stearates formed induced anti-wetting behavior of the surfaces, the sizes of the nanostructures influenced the fractional surface area wetted and the roughness of the surfaces. To this end, the contact angle of water (θ_{av}) and the average surface roughness values (R_a) of the surfaces studied as a function of time and process temperature showed specific trends. The contact angle of water increased with the immersion time up to a maximum value at both temperatures, beyond which they start to reduce. This is seen in the plot of the θ_{av} against the immersion time for the two temperatures, in Fig. 7. These maximum values in

the contact angles were observed after 48 and 72 hours of the process, as $154.8^\circ \pm 4.3^\circ$ and $156.4^\circ \pm 0.7^\circ$ at 30°C and 40°C respectively.

This is due to more effective coverage of the surfaces by the metal stearate nanostructures at the higher temperature. Beyond these maximum values, increasing sizes of the nanostructures equally resulted in the increase in the values of the fractional surface area, f_{sl} , as calculated from equation [3] and stated in Table 1. It should be noted that the $54.7^\circ \pm 1.2^\circ$ being the contact angle for the polished samples was used as the value of θ_o . From the Cassie-Baxter model, given by equation 3 (Cassie and Baxter, 1948), the fractional surface area must be small ($f_{sl} < 1$) for superhydrophobicity to be sustained. This can be appreciated from the values of f_{sl} stated in Table 1, where superhydrophobicity was sustained at f_{sl} values 0.14 and 0.09 for the C 84400 samples treated at 30°C and 40°C respectively.

$$\cos \theta_{av} = f_{sl}(\cos \theta_o + 1) - 1 \quad (3)$$

Therefore, beyond the D_s values of $201 \pm 20\text{ nm}$ and $217 \pm 140\text{ nm}$, representing the alloy samples processed at 30°C and 40°C , the values of the contact angle of water tend to slip out of the superhydrophobic region. We can therefore infer that beyond these values of D_s , the fractional surface areas due to the metallic stearates nanostructures formed on the alloy surfaces cannot sufficiently sustain a Cassie-Baxter superhydrophobic state.

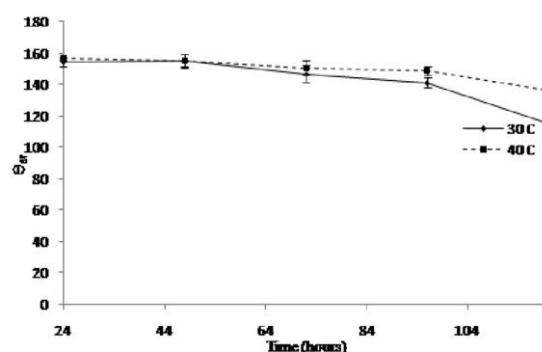


Figure 7: Plot of contact angle of water against immersion time (in hours)

Table 1: Table of the various contact angles of water, θ_{av} , D_s , f_{sl} and R_a at 30°C and 40°C

Time (hrs.)	30 °C					40 °C			
	θ_{av}	D_s (nm)	R_a (μm)	f_{sl}		θ_{av}	D_s (nm)	R_a (μm)	f_{sl}
24	$154.3^\circ \pm 2.6^\circ$	170 ± 20	0.21	0.06		$156.4^\circ \pm 0.7^\circ$	178 ± 120	0.95	0.05
48	$154.8^\circ \pm 4.3^\circ$	201 ± 20	0.51	0.06		$155.5^\circ \pm 3.6^\circ$	217 ± 140	2.89	0.06
72	$146.9^\circ \pm 7.8^\circ$	471 ± 30	1.08	0.10		$150.8^\circ \pm 7.9^\circ$	672 ± 100	1.87	0.08
96	$141.4^\circ \pm 2.9^\circ$	544 ± 130	0.84	0.14		$148.6^\circ \pm 2.8^\circ$	792 ± 150	1.38	0.09
120	$115.0^\circ \pm 3.4^\circ$	566 ± 10	12.25	0.37		$136.3^\circ \pm 3.2^\circ$	842 ± 110	1.43	0.27

This explains the gradual reduction in the water contact angles as seen in Fig. 7 and Table 1. The values of the average surface roughness increased to a maximum. To this end, the highest R_a value of 2.25 micron was recorded after 120 hours of the reaction process. Between 72 and 96 hours, the average surface roughness values of the samples processed at 30°C where comparable in values at 0.8 and $1.08\text{ }\mu\text{m}$. At 40°C , the average roughness values were generally higher than those observed at 30°C . The highest

maximum value of the surface roughness was 2.89 microns. This deviates from the expectation that the maximum surface roughness value will be seen on the surface with the highest value of D_s . The specific reason for this may be a result of uneven accumulation of the metal stearate nanostructures on this surface thus generating an uneven surface texture. However, the surface roughness had limited effect on the contact angle behavior to the extent that water contact angles were reducing, after a maximum

value, even with increasing average surface roughness values, R_a .

Conclusions

The nanostructures formed by the immersion of the C84400 in the stearic acid were confirmed through IR studies to be stearates of Cu, Pb and Zn. The stearate nanostructures were formed through the coordination of the alloying elements with the oxygen atom of the carboxyl group in the stearic acid chain. The continuous growth of the nanostructures on the surfaces depended on the immersion time as well as the temperature. Therefore, the dimension (D_s) and the fractional surface area, f_{sl} of these nanostructures increased with the immersion time and temperature. The D_s increase from 170 ± 20 nm to 566 ± 110 nm and from 178 ± 120 nm to 842 ± 110 nm for 30°C and 40°C respectively over a period of 120 hours. As the D_s and f_{sl} increased, there was a gradual reduction in the contact angle of water out of the superhydrophobic range (that is, $< 150^\circ$). This contact angle behavior was noted after the 48th and 72nd hours of reaction at 30°C and 40°C respectively. The reason for this was attributed to the dominating effect of the increase in the fractional surface areas available for wetting by the water drops due of the growth and size increase of the stearate nanostructures.

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