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THERMAL DECOMPOSITION OF SILVER FLAKE LUBRICANTS

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Abstract

There is a thin layer of organic lubricant on commercial silver flake surfaces. This lubricant layer is a fatty acid salt formed between a fatty acid and silver flake surfaces. Thermal decomposition behavior of the silver flake lubricant is investigated in this study. The heat flow and mass loss of a silver flake are studied using differential scanning calorimetry (DSC) and thermogravimetry (TG), respectively. The silver flake is also oven heated to different isothermal temperatures (150, 190, 250 and 300°C) for one h. Then chemical nature of the lubricant of the heated silver flake sample are studied using diffuse reflectance infrared Fourier transfer spectroscopy (DRIFTS). Based on the results, a mechanism of thermal decomposition of the silver flake lubricant is proposed. It is found that decomposition of the lubricant – the fatty acid salt – includes the release of the fatty acid, formation of short chain acids by decomposition of hydrocarbon moiety of the fatty acid, and formation of alcohols through decarbonation of the short chain acids.

Keywords: conductive adhesive, fatty acid salt, lubricant, mechanism, silver flake, thermal decomposition

Introduction

There has been tremendous effort to develop electrically conductive adhesives (ECAs) as a potential alternative to tin/lead solder in electronic packaging [1–4]. ECAs consist of an insulating adhesive and a conductive filler. Silver (Ag) flakes have been widely used as conductive fillers in ECAs [5–7]. There is a layer of organic lubricant on the silver flake surfaces after the production of the silver flake. This lubricant layer can help lower the viscosity of the ECA formulations and improve dispersity of the silver flakes in the adhesives [7–9].

A previous study indicated that this layer of lubricant was not a free fatty acid but a fatty acid silver salt formed between the fatty acid and silver flake surfaces [10]. During thermal curing of an ECA, the chemical nature of this lubricant layer may change. There-

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fore, it is of great interest to study the thermal decomposition behavior of the silver flake lubricant. In Lovinger's investigation of one commercial silver powder, he proposed that decarboxylation of the fatty acid followed by vaporization was the possible mechanism of decomposition of the lubricant. But no strong evidence was provided [9]. In this study, the DRIFTS technique was employed to monitor the change of chemical nature of the lubricant during heating at different isothermal temperatures. A mechanism for decomposition of a silver flake lubricant was proposed.

Experimental

Materials

An in-house silver flake was fabricated using a ball-milling process [10]. The lubricant of this silver flake was stearic acid. Stearic acid and infrared grade potassium bromide (KBr) were purchased from Aldrich Chemical Company. These chemicals were used as received. A silver stearate (purity 95%) was purchased from the Bodaman Industries and contained a small percentage of free stearic acid. The stearic acid was removed by washing the silver stearate with an acetone solvent for 24 h [11].

Study of lubricants of silver flakes using DSC

A differential scanning calorimeter (DSC) from TA Instruments, model 2970, was used to study the lubricant of a silver flake. A sample of approximately 10 mg was placed in an aluminum DSC open pan. After the sample was put in the DSC cell, the temperature was raised from 25 to 350 at a heating rate of 10°C min^{-1} in an air purge gas and heat flow was recorded.

Study of lubricants of silver flakes using TG

The silver flake lubricant was studied using thermogravimetry (TG) from TA Instruments, model 2950. A silver flake sample of about 100 mg was placed in a platinum TG pan. The sample was heated from 25 to 400 at a heating rate of 10°C min^{-1} in an air purge gas. Mass loss of the sample during heating was recorded.

Study of the lubricants of silver flakes using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

DRIFTS spectra of the silver flakes were collected using a Fourier Transform Infrared Spectrometer with a DRIFTS accessory from Nicolet, model Magna 560. Sample preparation and data collection procedure for the DRIFTS study were as follows: (a) prepared a mixture of an Ag flake and IR grade potassium bromide powder (KBr) (the mixture contained approximately 10 mass% of the silver flake), (b) collected a background using the KBr, (c) placed the mixture in a DRIFTS pan, and (d) collected a spectrum.

In this study, four samples of the mixture of the silver flake and KBr were heated separately at different temperatures (150, 190, 250 and 300°C) for 1 h in a Blue M convection oven. A small amount of KBr was also heated at the same temperature for 1 h. All the samples were cooled down to room temperature in a dissicator. The heated KBr powder was used to collect background and then the mixture of the Ag flake and KBr, which was heated under the same condition, was used to collect DRIFTS spectrum of the silver flake.

Results and discussion

DSC study of a silver flake

Because there is layer of organic lubricant on the silver flake surface, DSC can be used to detect the heat flow of the lubricant during heating. The silver flake was heated in the DSC cell from room temperature to 350°C in an air atmosphere. After cooled down to room temperature, the silver flake sample was heated for the second time in the DSC cell. The heat flow *vs.* temperature for the first run and second run is shown in Fig. 1.

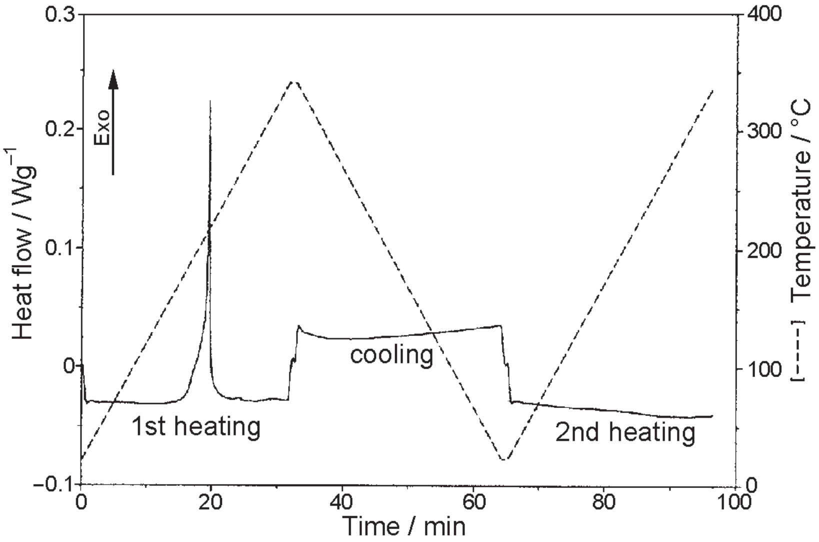

Fig. 1 Heat flow *vs.* temperature of a silver flake during the first and second heating

As can be seen from Fig. 1, in the first heating, there is an exothermic peak (ranges from 150 to 250°C) which was absent in the DSC curve of the blank silver powder (the silver powder before lubrication). This exothermic peak clearly indicated the presence of the organic lubricant on the silver flake surfaces. In the second heating, there was no peak. This result suggested that the organic lubricant probably decomposed /vaporized in the first heating cycle.

Thermogravimetric study of a silver flake

Mass loss of the silver flake was studied using thermogravimetry (TG) in an air atmosphere. The silver flake was heated in the furnace of a thermogravimetric analyzer (TG) from room temperature to 350°C. After cooling down to room temperature, the silver flake sample was heated for the second time in the TG. The mass loss *vs.* temperature of the silver flake for the first run and second run is shown in Fig. 2.

From Fig. 2, it can be observed that the silver flake lost mass in the temperature range from 150 to 250°C in the first heating cycle. The mass loss probably corre-

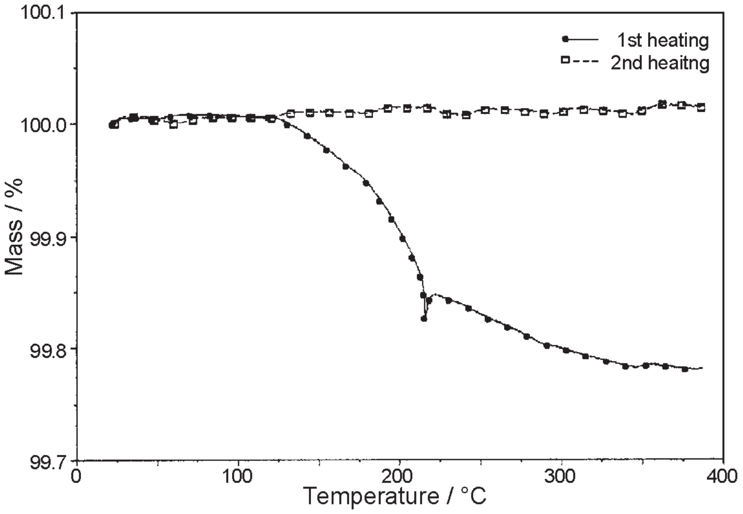

Fig. 2 Mass loss of a silver flake during the first and second heating

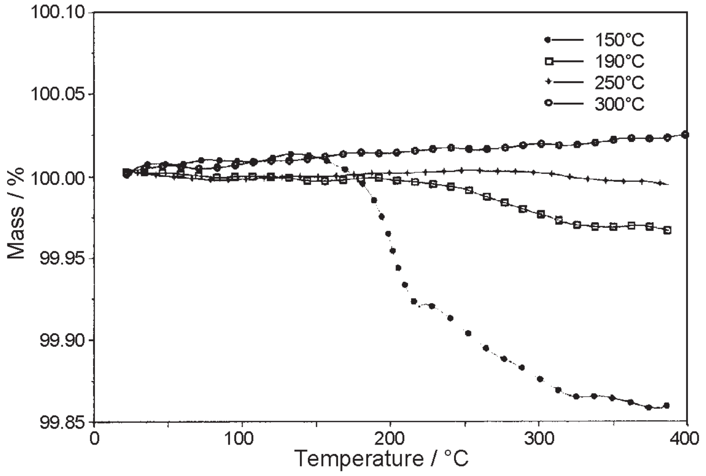

Fig. 3 Mass loss *vs.* temperature of a silver flake heated at different temperatures

sponds to the mass loss of organic lubricant of the silver flakes, i.e. 0.25%. However, in the second heating cycle, the mass loss was negligible. This result again indicated that the organic lubricant decomposed/vaporized in the temperature range from 150 to 250°C in the first heating cycle.

Four samples of the silver flake were heated at four different isothermal temperatures (150, 190, 250 and 300°C) for 1 h. Then these heated silver samples were studied using TG. Their mass losses *vs.* temperature results are shown in Fig. 3. It can be seen that silver flake sample heated at a higher temperature showed decreased mass loss (ca 0.14 to 0.035% from 150 to 190°C). The silver flake sample heated at 250 or 300°C had no appreciable mass loss (ca 0.02 to 0.00% from 250 to 300°C), which indicated that the lubricant of the silver flake decomposed/vaporized at these temperatures. The percentage of lubricant remained on a silver flake, which had been heated at a certain temperature, could be estimated by comparing the mass loss of the silver flake with the mass loss of the original silver flake (ca 0.25%). The percentages of lubricant remained on the silver flakes heated at four different isothermal temperatures are shown in Table 1. In addition, it was found that the silver flakes heated at 190, 250 and 300°C agglomerated together. This was another indication of the loss of lubricant of the silver flakes.

Table 1 Percentages of lubricant remained on the silver flakes

	Original Ag flake	Ag flake heated for 1 h at/°C			
		150	190	250	300
TG mass loss (%)	0.25	0.14	0.035	0.02	0.00
Percentage of lubricant remained on the silver flake/ (%)	100	56	14	10	0.00

Investigation of mechanism of decomposition of the silver flake lubricant

DSC and TG study indicated that the lubricant layer decomposed/vaporized in the temperature range from 150 to 250°C. In order to study the mechanism of thermal decmposition of the lubricant in this temperature range, four samples of the mixture of the silver flake and KBr were heated at 150, 190, 250 and 300°C for 1 h in an air atmosphere. DRIFTS spectra of these heated silver flake samples and the silver flake before heating were collected. The spectra of stearic acid, the unheated silver flake, the silver flake heated at 150, 190, 250 and 300°C are shown in Figs 4–9, respectively.

Figure 4 is the DRIFTS spectrum of stearic acid, $CH_3(CH_2)_{16}COOH$. Three peaks at 2952, 2914 and 2849 cm^{-1} correspond to the C–H stretching vibration of carbon-hydrogen long chain of stearic acid. Due to the long C and H chain of stearic acid, the C–H stretching peaks are very intense. The strong absorption at 1698 cm^{-1} is the stretching of C=O bond in carboxylic acid group (–COOH) of stearic acid. For a short chain acid, there is usually a strong and broad absorption band in the range from 2500 to 3300 cm^{-1}, which is the stretching vibration of hydroxyl (–OH) in –COOH

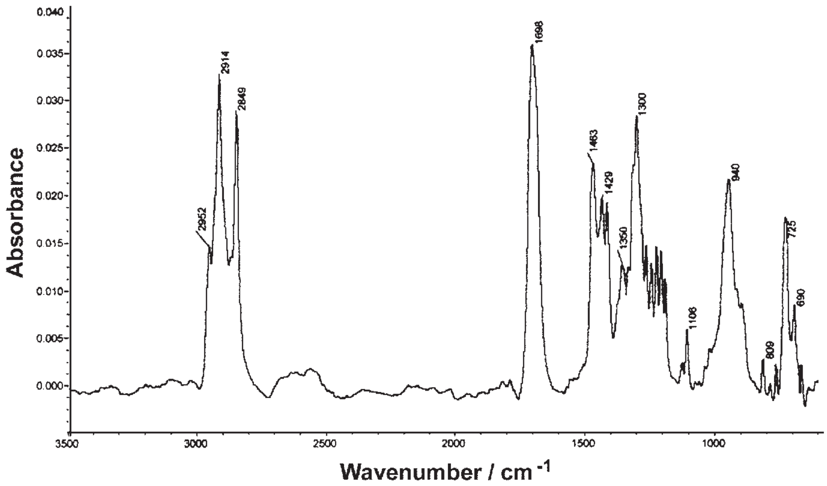

Fig. 4 DRIFTS spectrum of stearic acid

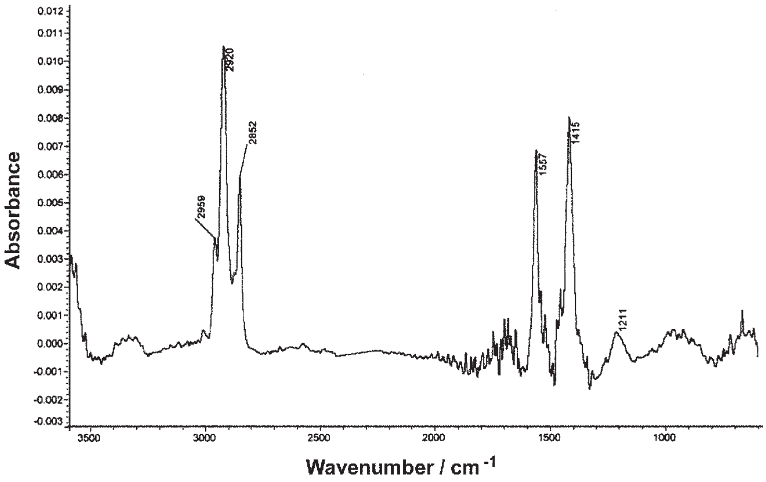

Fig. 5 DRIFTS spectrum of the silver flake before heating

group. However, this peak did not appear in the spectrum of stearic acid because the –OH concentration is very low in stearic acid molecule which has a long hydrocarbon chain [12].

Figure 5 shows the spectrum of the silver flake lubricated with stearic acid. Previous study already proved that the lubricant of the silver flake surfaces was not free stearic acid but a salt, silver stearate, formed between stearic acid and the silver surfaces [10]. The assignments of the peaks can also be found in that paper. Because the lubricant on the silver flake surfaces is silver stearate, the thermal decomposition of this salt rather than stearic acid was the investigated here. The DSC and TG study in-

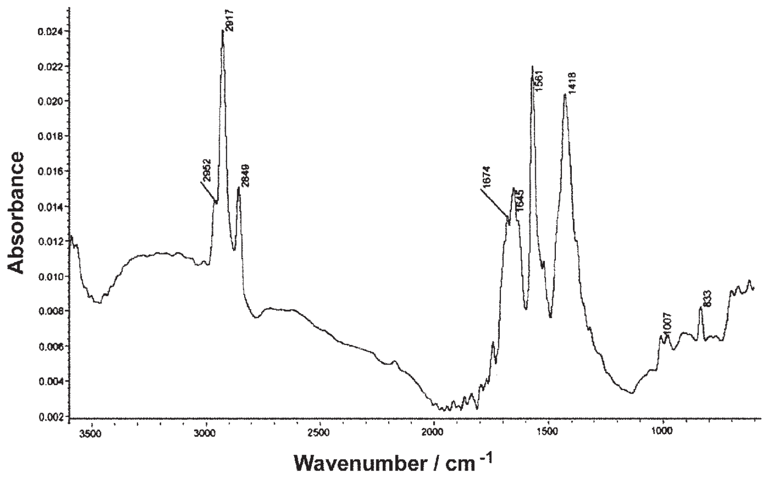

Fig. 6 DRIFTS spectrum of the silver flake heated at 150°C for 1 hour

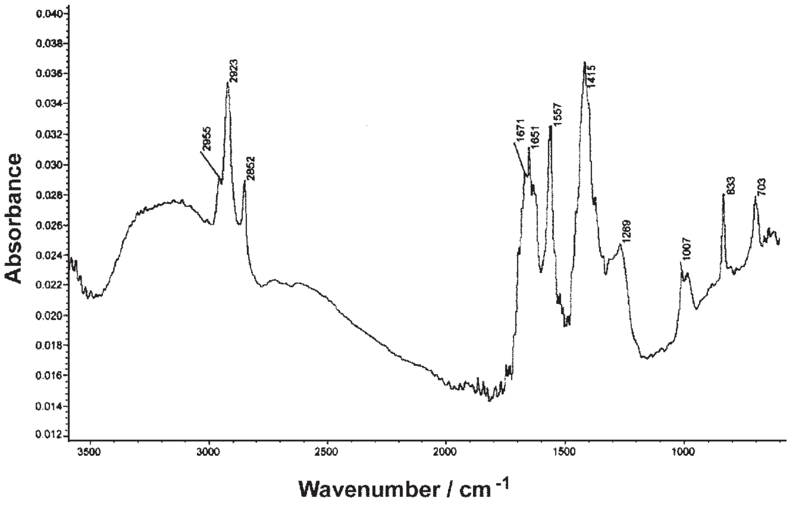

Fig. 7 DRIFTS spectrum of the silver flake heated at 190°C for 1 h

dicated that this lubricant layer underwent decomposition at the temperature range from 150 to 250°C. In order to investigate the thermal behavior of this lubricant layer at the temperature range, the mixture of the silver flake and KBr was heated at four different temperatures.

The spectrum of the silver flake heated at 150°C for 1 h is shown in Fig. 6. When compared Fig. 5, it is found that this spectrum is similar to the one in Fig. 5 except that a new peak at approximately 1667 cm^{-1} appeared. This new peak is due to the stretching vibration of C=O in the carboxylic acid group. The result suggested that the lubricant (silver stearate) released free long chain acids, probably stearic acid or other long chain acids, at 150°C. This result was consistent with that of another study [11].

Figure 7 is the DRIFTS spectrum of the silver flake heated at 190°C for 1 h. Similar to the spectrum in Fig. 6, the new peak at 1674 cm^{-1} in Fig. 7 was even stronger. Also, a shallow and broad peak appears in the frequency range from 3000 to 3400 cm^{-1}. This peak suggested that acids with shorter chains were formed. These results indicated that, at 190°C, the long chain acids which had been formed at lower temperature decomposed into shorter chain acids by the decomposition of hydrocarbon moiety of the long chain acids.

The DRIFTS spectrum of the silver flake treated at 250°C for 1 h is shown in Fig. 8. It can be seen from this figure that there is significant difference between Fig. 8 and Figs 6 and 7. The especially intense absorption band at the wavenumber range from 2700 to 3500 cm^{-1} corresponds to strong O–H stretching vibration in –COOH of some short chain acids. The peak at 1670 cm^{-1} is again the stretching of C=O in –COOH. The results again strongly suggested that the long chain free acids released from the lubricant turned into carboxylic acids of even shorter carbon-hydrogen chains.

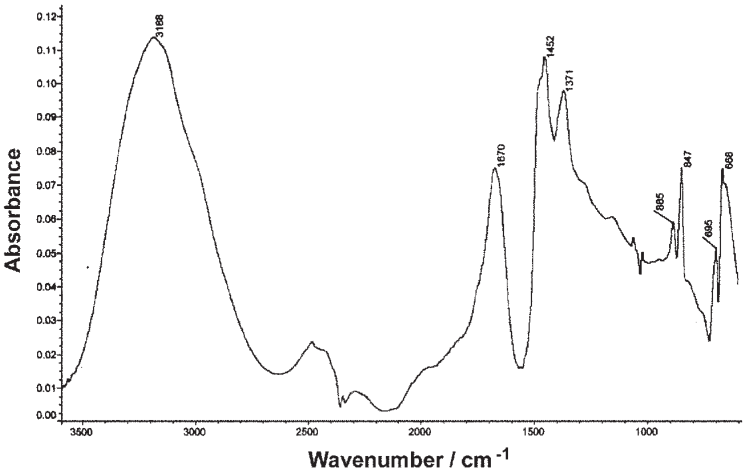

Fig. 8 DRIFTS spectrum of the silver flake heated at 250°C for 1 h

Figure 9 shows the DRIFTS spectrum of the silver flake which was heated at 300°C for one h. This spectrum was different from the other spectra. The strong peak in the wavenumber around 3000 cm^{-1} is still the stretching of O–H. However, the absorption peak at approximately 1670 cm^{-1} was absent in this spectrum, which indicated the compound here is an alcohol not a carboxylic acid. The result indicated that the short chain acids formed from the lubricant turned into alcohols through the decarbonation process [13].

TG results in Fig. 3 showed that the silver flake lost lubricant at high temperatures such as 250 or 300°C. However, DRIFTS results indicated that the silver flake and KBr mixture which were heated at these temperature for the same period of time

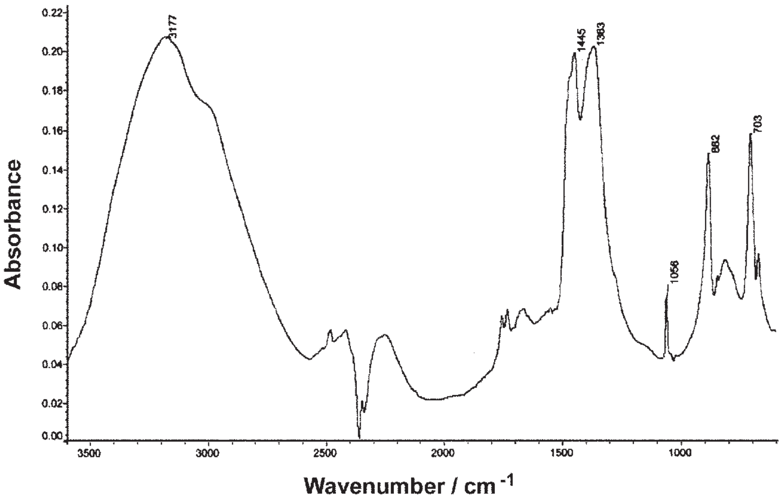

Fig. 9 DRIFTS spectrum of the silver flake heated at 300°C for 1 h

still contained the decomposed compounds. This was probably because the decomposed compounds absorbed on the surfaces of KBr powders. To confirm this idea, another experiment was conducted. A mixture of silver stearate and KBr (the mixture contained 1 mass% of the silver flake) was also heated at 250°C for 1 h. After cooling down to room temperature, the mixture was studied using DRIFTS. The spectrum is shown in Fig. 10; it can be seen that the decomposed compounds of silver stearate was similar to that of the silver flake. Even though the silver stearate should have de-

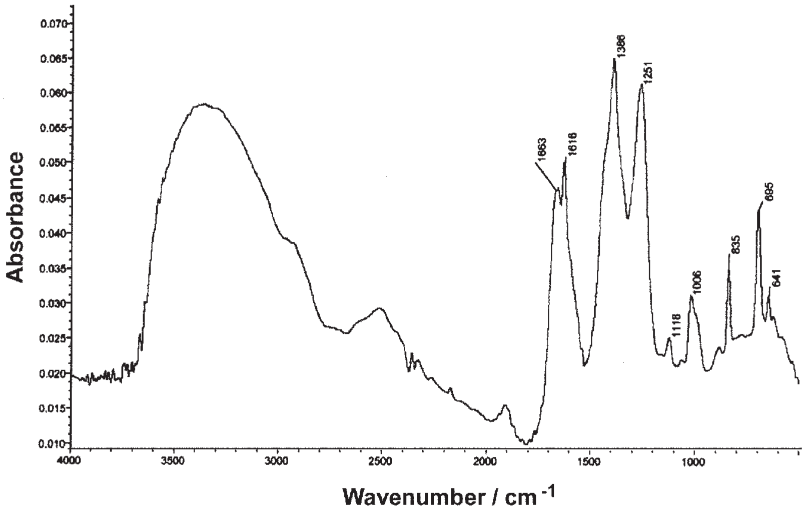

Fig. 10 DRIFTS spectrum of the silver stearate heated at 250°C for 1 h

composed and vaporized according to the TG results, it remained on the surface of the KBr and gave the observed DRIFTS spectrum.

Summarizing the above results, it can be concluded the decomposition of the lubricant of the silver flake included release of long chain acids from the silver salt, formation of shorter chain acids from the long chain acids by decomposition of the hydrocarbon chain of the long acids, and formation of alcohols from the short chain acids by decarbonation of the COOH group.

Conclusions

The silver flake lubricant decomposes in the temperature range from 150 to 250°C. The mechanism of decomposition of the silver flake lubricant includes release of long chain acids from the silver salt, formation of shorter chain acids by decomposition of the hydrocarbon moiety of the long chain acids, and formation of alcohols by decarbonation of the carboxyl group of the acids.

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