Note

THERMAL REACTIONS OF OCTADECANOL WITH SURFACES OF ALUMINUM, MAGNESIUM AND ALUMINUM/MAGNESIUM ALLOYS

ROBERT A. ROSS and JOAN WOODSIDE

Alcan International Limited, Kingston Laboratories, Box 8400, Kingston, Ontario, K7L 4Z4 (Canada)

The thermal reactions of metal and metal oxide surfaces with long chain acids, alcohols and related derivatives present a continuing interest to several areas of interfacial studies including adhesion and lubrication. This note describes an extension of our work on the reactions of octadecanoic acid with aluminum [1] and its principal alloying elements [1,2] to include the interactions of octadecanol with aluminum, magnesium and two alloys of magnesium in aluminum at nominally 1 and 4 wt% magnesium. Thermal measurements were supplemented by product identification mainly using Fourier transform infrared spectroscopy.

EXPERIMENTAL

Reagent grade octadecanol ($CH_3(CH_2)_{16}CH_2OH$) was obtained from Eastman Kodak; the purity was checked by an inductively coupled argon plasma spectrograph (ICP) and shown to contain traces of Zn (0.5 μg g^{-1}), and Pb (2.0 μg g^{-1}).

Alloys were cast from the highest purity metals available at nominally 1 and 4 wt% Mg. ICP analysis on the finished products showed 0.96 and 3.58 wt% Mg with Cu as the principal impurity at a maximum level of 0.01 wt% in both cases.

The various instruments and procedures employed in the experiments were described earlier [1]. A DuPont 900 instrument equipped with a range of thermogravimetric and calorimetric cells was used to obtain thermal data. The accuracy of the test procedure and computational method [1,3] for determining ΔH values was checked with three substances of established heats of fusion [4], Table 1.

TABLE 1

Comparison of ΔH_{fusion} measurements in air at 30 ml min^{-1} (NTP) with published values for heats of fusion [4]

Substance	ΔH_{fusion} (cal g^{-1})	Heat of fusion (cal g^{-1})
Octadecanoic acid	47.0	47.5
Dodecanoic acid	43.1	43.7
1-Hexadecanol	34.7	33.8

RESULTS AND DISCUSSION

Initial calorimetric measurements on octadecanol were carried out in AA1145 aluminum pans under dynamic conditions in both air and argon (Fig. 1).

The FTIR spectra were determined on several residues taken from the DSC cell at temperatures between 200 and 500°C. Samples were heated to each temperature at 10°C min^{-1} and then quenched to ambient.

Residues from the aluminum pans showed bands at 1735–1740 cm^{-1} and 1175–1180 cm^{-1} which are typical of ester C=O and C–O linkages. A band at 1720 cm^{-1} was attributed to acid C=O [5]. Spectra were consistent with ester formation probably through alcohol oxidation to acid, activated over
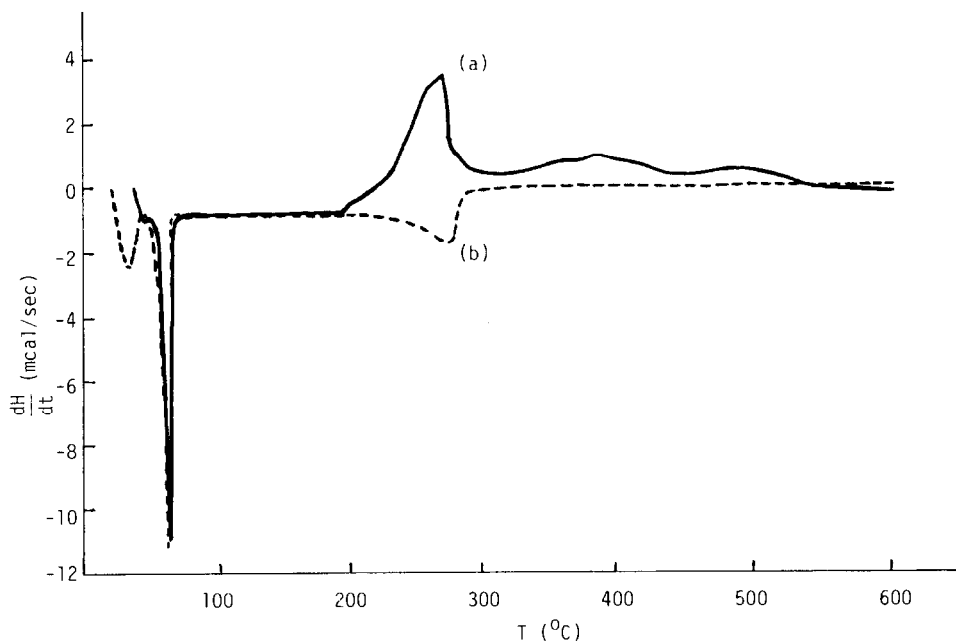

Fig. 1. Dynamic DSC scans of octadecanol in AA1145 aluminum alloy pans in (a) air and (b) argon. Flow rate 30 ml min^{-1} (NTP); heating rate 10°C min^{-1}.

TABLE 2

ΔH data for the octadecanol reaction with magnesium in air flowing at 30 ml min^{-1} (NTP) (heating rate 10°C min^{-1})

Amount of magnesium (wt%)	Total sample mass (mg)	Temperature range (°C)	ΔH (cal g^{-1})
4.3	5.8		−507
8.6	4.4	190–550	−516
19.9	5.8		−554
Pan	–		−422

the oxide film on the pan, and the subsequent reaction of the acid with the residual alcohol. Residues from reactions above 300°C showed no such bands although a signal at 1060 cm^{-1} could be attributed to Al–O. No evidence of metal soap formation was obtained.

Gas chromatographic analysis of the gaseous products formed between octadecanol and aluminum in air at 300°C showed carbon monoxide, carbon dioxide, methane, ethane, propane, butane, water and traces of hydrogen; products which are indicative of dehydrogenation and degradation reactions in addition to esterification.

Experiments with mixtures of 70–80 mesh magnesium powder and octadecanol were completed in air only at metal concentrations of about 4, 8 and 20 wt% (Table 2).

Spectra of samples from the experiments with 8.6 wt% magnesium gave bands at 1735 and 1180 cm^{-1} attributable to ester formation, and at 1720 cm^{-1} possibly indicative of the presence of acid. A broad band at 1590–1620 cm^{-1} together with a shoulder at 1420 cm^{-1} suggested some possibility of metal soap formation at 200°C. The C=O stretch lies at 1577 cm^{-1} in magnesium stearate and at 1588 cm^{-1} in aluminum stearate [1,2].

Table 3 shows ΔH data obtained in the magnesium alloy experiments at 190–550°C. Each value is the average of two determinations with a maxi-

TABLE 3

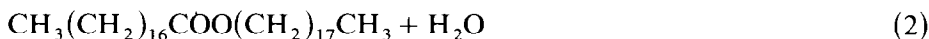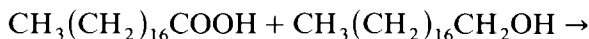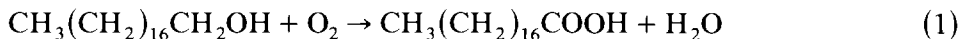Octadecanol reactions with the magnesium alloys in air flowing at 30 ml min^{-1} (NTP) (heating rate 10°C min^{-1})

Alloy (nominal wt% Mg)	Amount of alloy in mixture (wt%)	Average sample mass (mg)	ΔH (cal g^{-1})
4	4.0	5.9	−430
4	16.0	8.2	−435
4	20.0	7.1	−460
1	4.0	6.6	−478

mum spread of $\pm 1.5\%$ in the measurements.
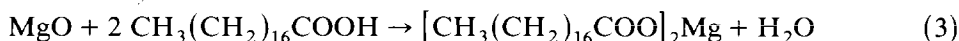
Infrared spectra of the residues were consistent with ester formation while the bands at 1720 cm^{-1} were attributed to acid C=O. No evidence of metal soap formation was found in contrast to the results with magnesium metal.

In separate but similar experiments with the 4 wt% magnesium alloy and octadecanoic acid, residues from 300 to 350°C gave unequivocal spectral evidence of metal soap formation and a ΔH value of -800 cal g^{-1} at 20 wt% alloy.

Generally the results suggest an initial surface reaction sequence

$$CH_3(CH_2)_{16}CH_2OH + O_2 \rightarrow CH_3(CH_2)_{16}COOH + H_2O \tag{1}$$

$$CH_3(CH_2)_{16}COOH + CH_3(CH_2)_{16}CH_2OH \rightarrow$$

$$CH_3(CH_2)_{16}COO(CH_2)_{17}CH_3 + H_2O \tag{2}$$

and at 200°C with magnesium powder, probably

$$MgO + 2\,CH_3(CH_2)_{16}COOH \rightarrow [CH_3(CH_2)_{16}COO]_2Mg + H_2O \tag{3}$$

These reactions are not exclusive and both homogeneous and heterogeneous octadecanol decomposition mechanisms can be invoked and most extensively at the highest temperatures examined.

The thickness of the oxide film on the magnesium powder was between 200 and 400 Å as estimated by ion etching with argon in an XPS instrument. The oxide film was close to an average of 60 Å thick on the alloys with magnesium, detected at 1.1 and 2.7 atomic% on the outermost oxide skin of the 1 and 4 wt% alloys, respectively. Thus the ΔH values show a trend towards increased exothermicity with an increase in the magnesium oxide content of the surface with the exception of the 1 wt% alloy. Further investigations on the detailed stoichiometries of the surface oxides by Auger analysis should lead to a more specific interpretation of these phenomena.

REFERENCES

1 R.A. Ross and A.M. Takacs, Ind. Eng. Chem., Prod. Res. Dev., 22 (1983) 280.
2 R.A. Ross and A.M. Takacs, Surf. Technol., 20 (1983) 219.
3 S.L. Boersma, J. Am. Ceram. Soc., 38 (1955) 281.
4 Handbook of Chemistry and Physics, 62nd edn., Chemical Rubber Publishing Co., Cleveland, OH, 1981–1982, p. C693.
5 L.J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen, London, 1954.