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Thermal behaviour of oil contaminated residues from metal cutting

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Abstract

The thermal behaviour of oil contaminated residues from metal cutting is studied using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Reaction energy, peak shift and formal activation energy were determined. It was found that the combustion of oil is increased because of tribomechanical activation at the metal surface. To avoid uncontrolled ignitions during transport or storage of these sludges, guidelines for their save handling were established. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Thermogravimetric analysis; Metal cutting; Tribomechanical changes; Combustion; Grinding oil

1. Introduction

In metal cutting processes like grinding and honing, a sludge is obtained consisting of very fine metal chips, abrasives, metal working fluids and various impurities. The majority of these materials arise in machining of medium- and high-alloyed steels or non-ferrous materials. As grinding and cutting oils are used in these operations as cooling lubricants in the resulting metal sludges, the solute is present in amounts of up to 50 wt.% of the material. Due to the variety of the metals, the machining process and the oils, many sludges with different physical and chemical properties result [1,2]. According to the German Federal Environmental Office, about 200 000 t of these residues are produced each year. Before October 1996 when the German Kreislaufwirtschafts- and Abfallgesetz came into law, a great part of the residues with high oil content was disposed by combustion with the oil acting as fuel. Materials with an oil content of <4% were stored at a hazardous waste site [3]. A direct recycling in metallurgical plants was not possible, because the high organic contents cause off-gas problems. Therefore, different reprocessing techniques were developed for recycling the oils and the metal matrix [3,4]. At present, the EMSIC (*E*xtraction of *m*etal *s*ludges *i*n *c*arbon dioxide) process [5], which was developed at the Forschungszentrum Karlsruhe is in commercial use. The thermal behaviour of the sludge is very important as in the past several uncontrolled ignitions during transport or storage were reported. Keeping in mind that fact, the aim of this work was to study a representative sludge in order to establish guidelines for their safe handling.

2. Experimental

Four original sludges from different productions as well as the separated oils (EMSIC) and the pure metals

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were subjected to thermal analysis using a NETZSCH STA409 thermal analysis station under air and nitrogen atmosphere (flow rate 120 ml/min). As the sample mass used for analysis was very small (about 100 mg), all charges of waste were homogenised very carefully and analysed twice. The heating rate was optimised in a sequence of previous experiments. The best performance was found for a heating rate of 1 K/min. For isothermal storage experiments, the samples were kept for 25 h at 130, 140, 150, 180 and 200°C, respectively. For studying the dependence of DTA peaks on the heating rate, different heating rates of 10, 8, 5, 3 and 0.5 K/min were used as complementary.

The analysis of the hydrocarbons of the oils was performed with a Hewlett–Packard GC/MS station (model 5988) using an HP5-MS capillary column. The chromatographic oven temperature was held at 40°C during the first 3 min, ramped up to 300°C within 20 min and kept constant for 5 min.

Solid residues were analysed using a wavelength-dispersive X-ray fluorescence spectrometer (Siemens SRS2000). The surface of the metal was examined by a scanning electron microscope (Leo DSM-982).

3. Results and discussion

The metals mainly consist of iron (about 97%) and traces of chromium and manganese. Sample number four additionally contains some silica- and alumina-based additives for filtration. The detailed compositions are given in Table 1. The GC-MS analysis of the oils show different hydrocarbons with 8 up to 32 carbon atoms, as well as several methyl esters of the corresponding acids. A typical thermoanalytical curve of sample No. 1 is shown in Fig. 1. Under the given standard conditions, the samples are stable up to 150°C. The oxidation process of the oil occurs in the temperature range from 150 up to 400°C and is registered on the DTA curve as several large exothermic signals (Table 2, line 2). The temperature of the first DTA signal is very close to the flash point (160°C) given in the safety date sheet of the pure oils. The mass

Table 1
Metal composition (mass in %)

Sample No.			
1	2	3	4
Fe 96.8	Fe 96.7	Fe 97.8	Fe 58.7
Cr 1.3	Cr 1.0	Cr 0.2	Cr 2.8
Mn 1.2	Mn 0.4	Mn 0.7	Mn 0.2
	C 1.4	C 1.0	C 2.5
	Si 0.1	Si 0.1	SiO_2 20.7
Ni 0.1	Ni 0.1		Mo 2.6
Cu 0.1	V 0.1		V 0.1
			Co 0.8
			Al_2O_3 4.1
			WO_3 6.0

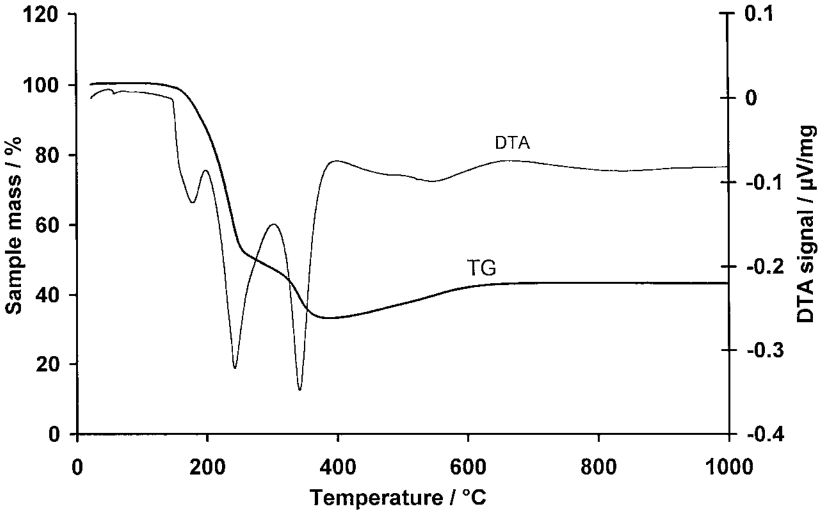

Fig. 1. TG and DTA curve of sample No.1; atmosphere: air 120 ml/min; heating rate 1 K/min; sample mass: 120 mg.

Table 2
Thermal behaviour of four samples

	Sample No.			
	1	2	3	4
Mass decrease (%)	50.6	9.1	67.2	18.3
Temperatures of exothermic DTA maxima (°C)	162, 247, 280, 359	150, 257, 325	179, 243, 342	169;274;338
T_{onset} (°C)	151	129	149	163
Mass increase (%)	3.3	35.5	10.1	24.6
Temperatures of exothermic DTA maxima (°C)	494	520	545	590, 650

loss calculated from the TG curve varies depending on the different oil contents of the samples from 10 up to 67% (Table 2, line 1). In accordance with the composition of the oil, the process starts with the evaporation of the hydrocarbons with the lowest boiling-points. In contact with oxygen ignition occurs at the surface of the iron-containing compact mass. The total energy release is about 10 kJ/g oil. The weight increase at temperatures above 490°C is caused by the exothermic oxidation of the metal (Table 2, lines 4,5). No DTA signals appear when the oil–metal mixtures are heated up under nitrogen atmosphere. Supplementary experiments with the pure oils show in the same temperature range a smaller exothermic DTA signal involving a lower energy release (Table 3). The problem whether metals or their salts influence exothermic decomposition reactions was first studied with some nitro compounds [6]. Further experiments with synthetic mixtures of oil only show one large exothermic stage resulting in a much lower energy release, however (Table 3). Only in the presence of oxidising agents like $Fe(NO_3)_3$ a higher energy release is found. In general, the metals of the examined four samples consist of small fibres with a rugged surface due to the preceding processes (Fig. 2). It is well known that mechanical processes like grinding, honing, sandblasting and even hammering and pressing may cause tribomechanical changes at the surface — like structural interferences, finally resulting in an increased catalytical activity of the materials [7–9]. These changes disappear when the sample is annealed at higher temperatures. Corresponding experiments were done tempering the pure metal for 10 h in air. The cool samples mixed with oil were heated up under standard conditions afterwards. For the evaluation, the total energy release is printed vs. the tempering temperature in Fig. 3. Already, at 100°C the initial energy of 9 kJ/g oil decreases slightly. The whole process is finished after tempering at about 600°C. The final energy release of 4.2 kJ/g oil corresponds very well with the result of pure iron–oil mixtures (Table 3).

For the safe handling of the sludge reaction energy, peak temperatures, peak shift, formal activation energy and isothermal induction time were determined from the DTA curves [10]. Because of the different oil content of the sludges, the reaction energy varies from 1 to 6 kJ/g sludge. Referring to the pure oil, the total decomposition energy is about 10 kJ/g oil +10% for all the samples.

If the stability of a substance is investigated, the dependence of DTA peaks on the heating rate is important [11]. For the evaluation, the peak temperature of the first peak was plotted in the familiar way vs. heating rate in an Arrhenius-type diagram. From the slope of the straight lines, the temperature shift ($d \ln w/dT$) of the first exothermic DTA signal and an apparent activation energy were determined (Table 4) [12–14]. The mean formal activation energy of about 68 kJ/mol is in the normal region of exother-

Table 3
Thermal behaviour of pure oil and different mixtures[a]

	Reaction energy (kJ/g oil)	Temperatures of exothermic DTA maxima (°C)
Oil alone	1.4	*217*, 292, 450
Oil on glass wool	1.4	*199*, 290
Oil in steel crucible	–	*207*, 286, 440
Oil and iron powder	3.9	*274*, 370
Oil and $FeSO_4$	2.1	292
Oil and $Fe(NO_3)_3$	11	373

[a] Very small DTA signals in italics.

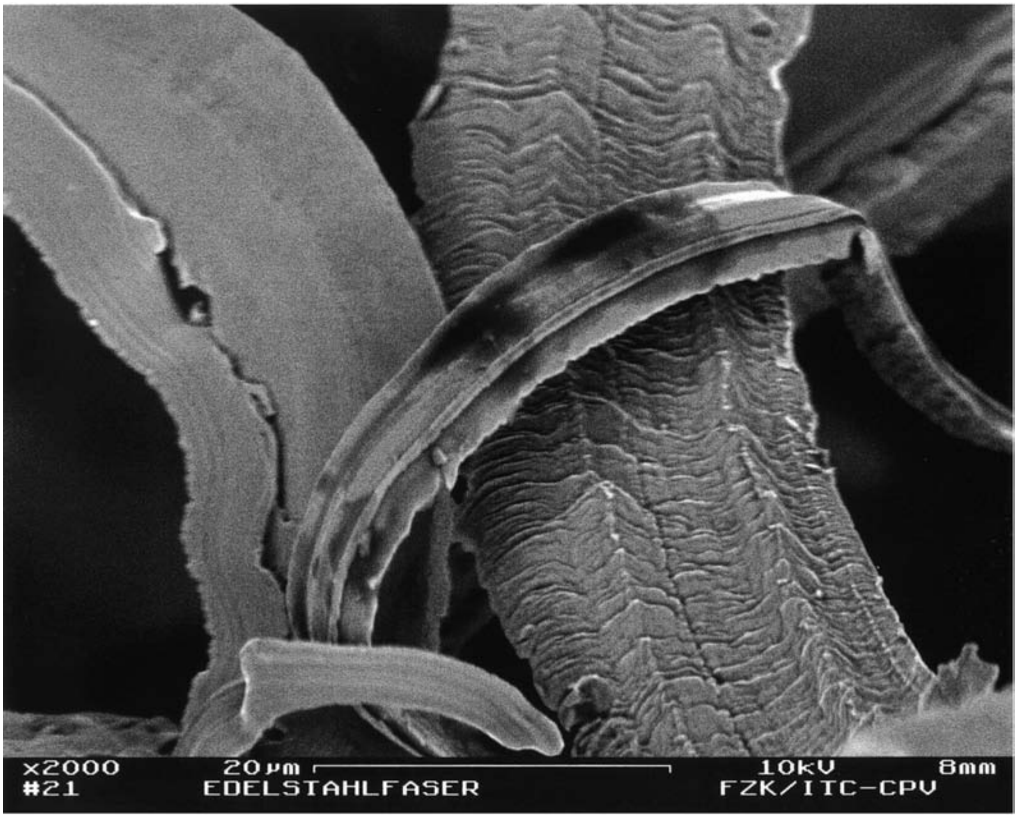

Fig. 2. Surface of the pure metal of sample No.1; scanning electron microscope, enlargement 1:2000.

mic decomposition reactions [9]. The mean slope of the temperature shift is about 0.037 K^{-1}; hence, an increase of the heating rate by a factor of 10 raises the peak temperature by 60 K. Consequently, the examined process seems to have still a normal temperature dependence reaction rate, as 'unusual' reactions are found to have a shift of 85°C or more [11].

For the determination of the isothermal induction time the samples were kept at 120, 130, 140, 180 and 200°C. The time to the maximum of the DTA curve (isothermal induction time) was plotted in a logarithmic scale vs. the reciprocal absolute storage temperature. For an induction time of 24 h, the reaction temperature of 100°C was determined by extrapolation.

An often used rule of thumb for the interpretation of thermal hazards of a substance is the '100-degree rule' [10,11]. This rule states that there will be no risk, if the operating temperature of a process is 100°C away from the nearest detectable exothermic signal in a DTA experiment and if its temperature dependence is normal. Based on that rule our results show that, for a safe transport or storage, the uncontrolled

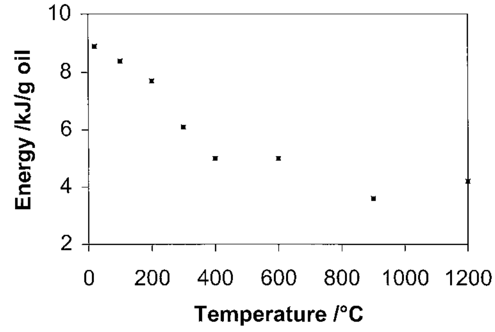

Fig. 3. Energy release as a function of tempering temperature.

Table 4
Characteristic data calculated from TG – DTA curves

	Sample No.			
	1	2	3	4
Reaction energy (kJ/g sludge)	−5.5	−1.0	−2.3	−5.9
Reaction energy (kJ/g oil)	−10.8	−10.4	−8.8	−12
Peak shift (K^{-1})[a]	0.035	0.034	0.040	0.039
Formal activation energy (kJ/mol)[a]	63	59	76	68
24 h Induction temperature (°C)[a]	95	103	–[b]	105

[a] First exothermic decomposition reaction in the low-temperature region.

[b] Not determined because of overlapping signals.

rise of temperature above 60°C should be strictly avoided.

4. Summary

Neither the composition of the metal nor different oil amounts show an influence onto the thermal behaviour of four different iron-based metal–oil sludges. In the presence of oxygen, the combustion of the oil starts at about 150°C in three exothermic stages. Because of the tribomechanical changes at the surface of the metal, the observed energy release is much higher when compared to normal iron oil mixtures. At temperatures above 150°C, these influences are lost gradually. As the formal activation energy and the temperature dependence of the first exothermic DTA signal are in the 'normal' range, the '100-degree rule' can be used. Consequently, the temperature during the storage and transport should not exceed 60°C. Temperatures up to 90°C may be acceptable for a short period. Ignition sources have to be excluded. The untempered pure metal was not found to be phyrophoric. Therefore, it can be stored without safety measures against deflagration.

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