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THE EFFECT OF GAS ENVIRONMENT ON ROLLING OIL REMOVAL FROM COLD-ROLLED STEEL AS STUDIED BY TG

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This study investigates mechanisms of cold rolling oil removal from the surface of low-carbon steel. The removal process has been probed using thermogravimetric analysis techniques. A range of furnace atmospheres, from non-oxidising through to highly oxidising, have been used to simulate the oil removal conditions in the industrial process. The activation energies of oil removal under each gas atmosphere have been determined by MTG and the Flynn–Wall–Ozawa method. The results show that a reducing atmosphere is the optimal environment for effective oil removal. Steel-oil surface interactions have also been investigated to show that the steel substrate catalyses oil removal.

Keywords: *cold rolling, gas atmosphere, kinetics, MTG, oil, steel*

Introduction

Oil-based lubricants are commonly used in metal-forming processes. One such process is the cold rolling of sheet steel where a lubricating oil, a complex formulation of more than ten different ingredients, must be capable of satisfying several different, and often competing, requirements [1, 2]. One of these requirements is that the oil must be easily removed from the steel surface prior to the application of hot-dip metallic coatings. Common oil removal methods include alkaline, acid or electrolytic degreasing [3], however many metal coating lines elect to remove the rolling oil via treatment in a furnace. Furnace treatment enables simultaneous cleaning of the steel strip surface and modification of the physical properties of the steel. Two of the most common furnace set-ups used are 'batch annealing' and 'continuous annealing'. In the batch annealing process, cold rolled coils stacked within a furnace containing a mixture of hydrogen and nitrogen gases are heated at slow (1.7 K min^{-1}) heating rates to approximately 690°C [4]. Continuous annealing incorporates a dual furnace system. Removal of residual oil on the steel surface occurs within a furnace containing natural gas combustion products. The heating rates within this furnace are estimated to be approximately 6500 K min^{-1} and the final steel temperature is approximately 500°C. The steel then passes through a furnace containing a low dew point, hydrogen–nitrogen atmosphere under which steel surface oxides are reduced [5].

Effective removal of the rolling oil from the steel surface in both batch and continuous annealing is critical to the quality of subsequent surface treatments and coatings; the formation of thermally stable oil residues is highly detrimental to downstream processing [1, 3, 6–9]. Several different chemical processes have been identified as contributing to overall oil removal including evaporation, oxidation and decomposition resulting in the formation of volatile products [10–13]. The precise balance between each of these processes and the extent to which the equilibrium between them can be manipulated to optimise steel surface cleanliness in the metallic coatings industry is largely unknown. In addition, whilst much work has been undertaken to identify the different reactions that occur in the rolling oil removal process under batch annealing conditions [4, 7, 14], little has been done to investigate the reactions that occur under oxidising conditions. An improved understanding of the oil removal process and how the atmosphere in which oil removal occurs influences this process is of considerable interest and will aid in product development within the steel and lubricant industries.

Thermogravimetric analysis (TG) has long been used to evaluate the mechanism and kinetics of oil oxidation, decomposition and deposit formation. However, the majority of oils that have been analysed using

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this technique are used in automotive applications [11, 12, 15]. The application of TG to the analysis of cold rolling oils has been limited to studies of deposit formation, the effect of additives on oil residue and the effect of cold rolled coil ‘aging’ on oil volatility [7, 16–18]. In this study TG has been employed to investigate how cold rolling oil is removed from the surface of low-carbon steel. A range of industrial furnace conditions, from non-oxidising through to highly oxidising, have been simulated by performing the TG tests under argon, 5% hydrogen–95% nitrogen gas mixture, nitrogen and oxygen. The activation energies of oil removal, E_a, under each of these gas atmospheres have been determined by both modulated thermogravimetry (MTG) [19, 20] and the Flynn–Wall–Ozawa [21–23] method to establish an optimal furnace atmosphere for rolling oil removal.

Experimental

Materials

A commercial cold rolling oil, consisting of a bulk amount of base ester blended with various lubrication, viscosity boosting and emulsification additives, was used in all experiments as supplied by Quaker Chemical (Australasia). A low-carbon steel, with properties as described in Table 1 below, was supplied by Bluescope Steel®. The steel was cut into 6 mm diameter (conventional TG) and 8 mm diameter (MTG) pucks. The pucks were solvent-cleaned using an ultrasonic bath (10 min each solvent) in hexane, followed by acetone, followed by toluene. Immediately prior to TG analysis, the steel was ‘pickled’ in a 10% HCl solution at 75°C for ~1 min, rinsed in de-ionised water and then acetone and finally dried under a stream of nitrogen. An even film of rolling oil was placed onto the steel sample for TG analysis.

Table 1 Properties of the low-carbon steel used

Element	Nominal percentage
iron	99.7
carbon	0.06
aluminium	0.04
manganese	0.2
yield strength=550 MPa	

Methods

A TA Instruments TGA 2950 Thermogravimetric Analyzer was used for all TG analyses. The instrumental temperature calibration was performed using the Curie temperatures of nickel and alumel. Oil-on-steel samples were analysed under various high purity purge gases supplied by BOC Gases Australia including 5% hydrogen–95% nitrogen (HNX), nitrogen, argon and oxygen. A flow rate of 50 mL min^{-1} was used. The samples were suspended from the TG balance using platinum crucibles.

1.0±0.1 mg of rolling oil was placed on a 6 mm steel puck for use in conventional TG analysis. Runs were performed in triplicate under each gas atmosphere between room temperature and 500°C at heating rates of 5, 10 and 20 K min^{-1}. Control runs were also performed using a steel puck with no rolling oil to assess the contribution of substrate oxidation to the oil-steel curve. TA Instruments Thermal Speciality Library Software v1.00F was used to calculate kinetic parameters.

MTG runs were initially carried out using a range of different oil masses, modulation periods and modulation amplitudes to determine the optimal conditions for sample analysis. Ultimately, 10±0.5 mg of rolling oil was selected as this was the minimum oil mass that could be used whilst providing an adequate mass% signal-to-noise ratio. The oil was spread onto an 8 mm diameter steel puck for analysis with a steel substrate, or directly onto the platinum crucible for analyses without a steel substrate. A linear heating rate of 2 K min^{-1} was used together with a modulation period of 150 s and a modulated temperature amplitude of ±4 K min^{-1}. The sample was equilibrated at 70°C and then heated using this profile to 500°C. Runs were performed in duplicate.

Results and discussion

Conventional TG

Initially, the process of rolling oil removal from steel was studied by conventional TG under each of the four gas atmospheres (argon, HNX, nitrogen and oxygen). Figure 1 shows the results obtained under nitrogen. The onset point of oil mass loss occurs at 240°C, indicating that the oil is thermally stable under nitrogen in the temperature region used during the cold rolling process. The removal of the oil from the steel occurs in a single, continuous step containing two different regions; the primary region and the secondary region. The primary region maximum occurs at a temperature of 301°C and the majority of the oil mass (93%) is converted to volatile products over this region. The secondary region occurs at a peak temperature of 410°C. Only 4.2% of the oil mass is lost over this region and a residue of 5.1% remains on the steel surface at 490°C. The steel substrate contribution to this residue measurement is negligible; 0.04% mass increase is evident from the steel control curves. The results obtained under the other gas atmospheres follow this trend and a summary of the onset points of mass loss, primary and secondary region temperatures, mass losses and % residue at 490°C is given in Table 2.

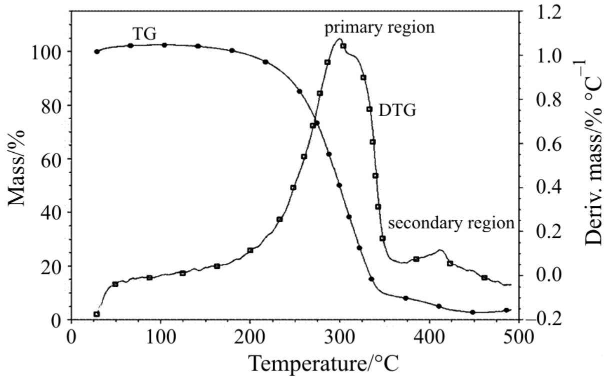

Fig. 1 Conventional TG results obtained with a steel substrate under nitrogen. The mass loss and first derivative of mass loss signals are shown and the primary and secondary regions within the mass loss peak are highlighted

The onset temperature for oil removal under oxygen was 203°C, which is approximately 60°C lower than under any of the other gases. This temperature is comparable with that reported for semi-synthetic automotive lubricants [15]. The primary region temperature and primary mass loss were also lower under oxygen, indicating that whilst the oil removal process begins at lower temperature in a highly oxidising atmosphere, less volatile matter is produced during the primary oil removal stage compared with the other gas environments. The secondary region temperature and mass loss under oxygen were much higher than those recorded under the other gases. This indicates that more oil is left on the steel surface under oxygen after the primary removal process than under the other gases. The oil left over after the primary process is also more thermally stable under oxygen than under the other gases. Despite the large percentage of oil mass lost over the secondary region, oxygen produced the second largest amount of oil residue (7.4%) at 490°C. Only under argon was the amount of residue higher. This is most likely to be caused by the production of less volatile matter due to non-reactivity of argon with the oil.

Table 2 Summary of TG results under each of the gas atmospheres investigated

	Argon	Nitrogen	Oxygen	HNX
onset point/°C	222	240	203	221
primary region *T*/°C	290	301	233	283
primary mass loss/%	86	93	83	91
secondary region *T*/°C	412	410	433	398
secondary mass loss/%	3.6	4.2	11	5.6
residue/%	14	5.1	7.4	4.9

The reducing HNX atmosphere produced the lowest secondary region temperature (398°C) for oil removal. The oil left after the primary removal process under reducing conditions is therefore less thermally stable than under oxidising conditions. Removal of the oil under HNX also produced the least amount of residue at 490°C (4.9%). This is likely to be due to the formation of volatile products in the secondary region under HNX that are not formed under oxidising conditions. CO and CO_2 production can occur under both reducing (decarboxylation of esters and fatty acids as shown in Scheme 1) and oxidising (decarboxylation together with hydrocarbon combustion) conditions.

$$RCH_2COOH_{(l)} \rightarrow CO_{2(g)} + RCH_{3(l)}$$

Scheme 1 Decarboxylation of a fatty acid to produce carbon dioxide and residual hydrocarbon

However, the reactions of hydrocarbons with hydrogen to produce CH_4 are more likely to occur under HNX than under oxygen or nitrogen (Schemes 2a and b) [4].

$$H_2O_{(g)} + C_{(s)} \rightarrow CO_{(g)} + H_{2(g)}$$

Scheme 2a Oxidation of carbonaceous deposits to form volatile products

$$CO_{(g)} + 3H_{2(g)} \rightarrow CH_{4(g)} + H_2O_{(g)}$$

Scheme 2b Consumption of hydrogen by a Fischer–Tropsch reaction of carbon monoxide

Achieving a lower secondary removal temperature and lesser amount of residue after the oil removal process would be highly beneficial in the industrial process [7].

The highest onset point (240°C) and primary region temperature (301°C) together with the greatest amount of primary mass loss (93%) occurred under nitrogen. This is of considerable interest as it shows that a neutral (neither oxidising nor reducing) environment promotes the removal of the rolling oil in the primary region via the production of volatile matter, whilst a highly oxidising atmosphere favours the formation of residue on the steel surface. Similar results were obtained under argon, although the onset point and primary region temperature values were shifted to lower temperature. This is most likely to be due to the higher thermal conductivity of argon. The lesser amount of mass loss over both the primary and secondary regions under argon could result from a variation in the kinetics of the oil removal reactions together with unavailability of gaseous reactants such as O_2 and H_2. Heating the oil more rapidly in the absence of these gaseous reactants is likely to favour deposit formation via hydrocarbon cracking reactions as outlined in Schemes 3a and b [4].

$$RCH_2CH_{3(l)} \rightarrow RCH^*_{2(g)} + CH^*_{3(g)}$$

Scheme 3a Catalytic cracking of a typical hydrocarbon producing hydrocarbon radicals

$$2RCH^*_{2(g)} \rightarrow RCH_2CH_2R_{(s)}$$

Scheme 3b Reaction of a hydrocarbon radical produced via Scheme 3b to form hydrocarbon residue

Effect of gas atmosphere and steel substrate on activation energy of oil removal

The kinetics of the rolling oil removal from steel were analysed using both Flynn–Wall–Ozawa (non-isothermal) [21–23] and MTG [19, 20] techniques. Flynn and Wall and Ozawa, developed a method whereby the activation energy for a mass loss process could be determined from Eq. (1)

$$\log\beta = -0.457\frac{E_a}{RT} + \left(\log\frac{AE_a}{RT} - \log F(\alpha) - 2.315\right) \qquad (1)$$

where β is the heating rate, T is the temperature, R is the gas constant, α is the sample conversion, A is the pre-exponential factor and E_a is the activation energy.

The slope of the straight line obtained by plotting logβ *vs.* $1/T$ at any level of sample conversion can be used to calculate the activation energy for the mass loss process. A typical logβ *vs.* $1/T$ plot calculated for the rolling oil removal from steel under nitrogen is shown in Fig. 2. The straight lines are parallel between 20 and 50% conversion, however at conversion levels above 50% the slope of the lines changes and the fit of the line to the data is not as good. The change in the slope of the line at 50% conversion indicates a change in the kinetic process of oil removal in the latter stages of the primary oil removal region (the primary region covers 0–75% conversion and the secondary region is ≥75% conversion) [15, 24]. The slope of the straight lines in plots obtained under the other gas atmospheres also varied, indicating changes in the activation energy and mechanism of oil removal. A summary of the activation energies between 20 and 90% conversion is given in Table 3.

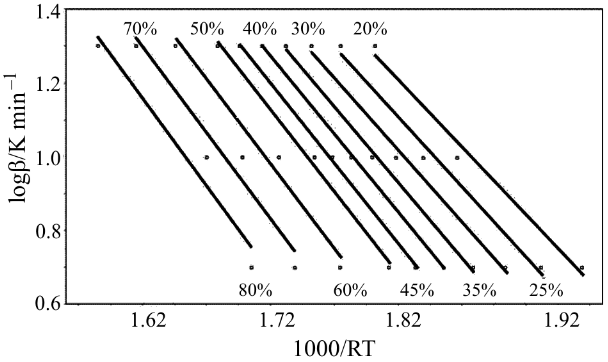

Fig. 2 Logβ *vs.* $1/T$ plot obtained for rolling oil removal from steel under nitrogen

The activation energies for the oil removal calculated by the Flynn–Wall–Ozawa method increase as the oil removal proceeds under every gas atmosphere except for nitrogen. This shows that the oil left on the steel surface becomes more thermally stable as the oil removal process advances. This lower activation energy corresponds with both the higher onset point of mass loss and the higher primary region temperature under nitrogen compared with the other gases. The fact that the activation energy under nitrogen at low conversion is greater than at higher conversion enables the large proportion of oil mass to be converted to volatile products over the primary region.

Table 3 Summary of activation energies obtained between 20 and 90% conversion under each gas atmosphere

	Conversion level/%	Activation energy, E_a/kJ mol^{-1}			
		argon	nitrogen	oxygen	HNX
primary region	20	100	78	65	140
	30	102	79	66	145
	40	104	77	68	148
	50	119	74	72	153
	60	131	72	82	157
	70	142	71	90	160
secondary region	80	154	71	104	164
	82	154	71	96	161
	84	154	71	89	157
	86	152	71	79	155
	88	149	70	75	155
	90	146	69	78	159

Under oxygen, HNX and argon, the maximum activation energy occurs at a conversion level of 80%. This conversion level corresponds to the secondary mass loss region where a greater amount of energy is required to initiate the removal of the oil. At conversion levels above 80%, the activation energy under each of the gases gradually decreases as the secondary phase of oil removal reactions concludes.

The rolling oil removal process was also studied by MTG both with and without a steel substrate. Figure 3 illustrates the MTG results obtained for the removal of rolling oil from platinum under argon. The modulated temperature profile, mass loss and rate of mass loss signals are shown and it can be seen that the oil removal proceeds via the same two-region process as was observed by conventional TG. A typical plot of activation energy (calculated from the oscillatory rate of mass loss) as a function of conversion under argon is shown in Fig. 4 for MTG tests with and without steel and as calculated by the Flynn–Wall–Ozawa method. Similar plots were obtained under the other gas atmospheres.

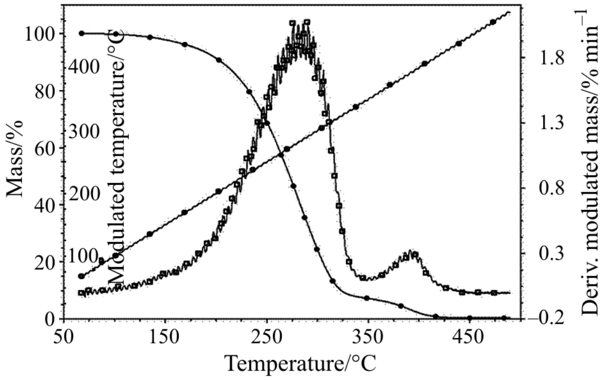

Fig. 3 MTG results obtained without a steel substrate under argon. The modulated temperature profile, mass loss and rate of mass loss are shown

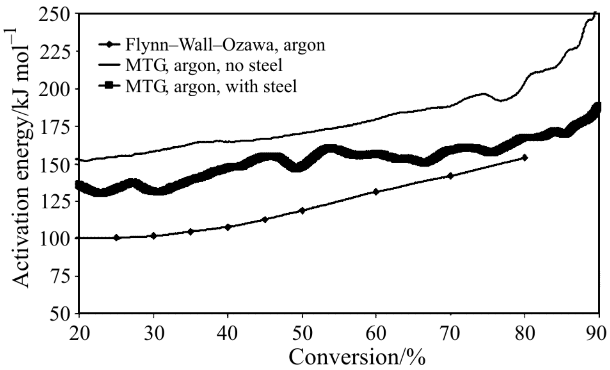

Fig. 4 Activation energies calculated as a function of conversion from MTG and Flynn–Wall–Ozawa results under argon

The activation energy of the mass loss process is calculated by Eq. (2) [20]

$$E_{\mathrm{a}} = \frac{R(T^2 - A^2)L}{2A} \qquad (2)$$

where T is the average temperature, A is the temperature amplitude and L is the ratio of the natural logarithm of the maximum and minimum rate mass loss taken at adjacent half cycles of the sine wave.

Figure 5 shows the activation energies of oil removal as determined by MTG and the Flynn–Wall–Ozawa method under each of the gas atmospheres calculated at the 50% conversion level. A comparison of the activation energies obtained by MTG with and without a steel substrate shows that the steel catalyses the oil removal process under each of the gas atmospheres by lowering the activation energy by ~20 kJ mol^{-1}. This is consistent with the reactions outlined in Schemes 1–3 as iron is a well-known catalyst for the cracking of hydrocarbons. The MTG data supported findings from the Flynn–Wall–Ozawa analysis that there was an increase in activation energy with increasing conversion under all gas atmospheres. This confirms that more energy is required to initiate the removal of oil left over after the primary process.

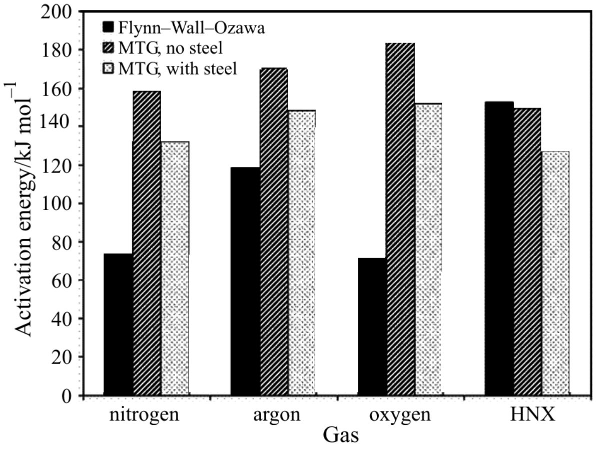

Fig. 5 Activation energies under each gas atmosphere calculated at 50% conversion from MTG results with and without steel and using the Flynn–Wall–Ozawa method

Under every gas atmosphere except for HNX, the activation energy for oil removal obtained by Flynn–Wall–Ozawa analysis was at least 35 kJ mol^{-1} lower than that obtained by MTG. This is consistent with what has been found for engine oils [15] and suggests that the oil removal process under gases except for HNX evolves significant amounts of heat [20]. Thus, a higher average temperature value is measured under oxygen and nitrogen in particular as there is a greater contribution to the heating part of the sinusoidal temperature cycle from the heat evolved by the sample. The activation energy is therefore greater than that measured using the Flynn–Wall–Ozawa procedure. A comparison of the activation energies calculated by the Flynn–Wall–Ozawa and MTG techniques therefore provides significant information on the nature of mass loss processes.

Conclusions

The process of removal of commercial cold rolling oil from low-carbon steel has been studied under a range of gas atmospheres by TG. The results of the study have shown that a reducing atmosphere of 5% hydrogen–95% nitrogen appears to be the optimal gas environment for effective removal of rolling oil from steel because a greater amount of oil mass is lost at lower temperatures and less thermally stable products are formed. This increased oil removal efficiency corresponds to higher activation energy as measured by the Flynn–Wall–Ozawa technique. A highly oxidising atmosphere has detrimental effects on the oil removal process as it causes the formation of thermally stable products and high amounts of residue within the maximum temperature range employed in the industrial oil removal process. The steel substrate has also been shown to catalyse the process of oil removal (relative to platinum). Variation between the activation energies determined by the Flynn–Wall–Ozawa method and by MTG is indicative of the exothermic or endothermic nature of the oil removal reactions.

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