Surface & Coatings Technology 207 (2012) 89–95

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Cure kinetics of flame-sprayed thermoset coatings

Yuqing Bao [a], David T. Gawne [a,*], Tao Zhang [b]

[a] Department of Engineering and Design, Faculty of Engineering, Science and The Built Environment, London South Bank University, London, SE1 0AA, UK
[b] Faculty of Science, Engineering and Computing, Kingston University, London, SW15 3DW, UK

ARTICLE INFO

Article history:
Received 29 December 2011
Accepted in revised form 2 June 2012
Available online 9 June 2012

Keywords:
Flame spraying
Cure kinetics
Powder coatings
Curing of thermosets
Epoxy coatings
Thermal spraying

ABSTRACT

Thermoset powder coatings are traditionally cured by an isothermal heat treatment in an oven. This paper studies thermoset deposition by flame spraying, which is an alternative technology with potential for depositing these coatings. However, the flame-spray process is non-isothermal and the temperature of the coating oscillates greatly during deposition due to the scanning action of the spray gun. As a result, the process conditions needed to provide a satisfactory amount of cure cannot be defined simply by a given time at a specified temperature, as it is in conventional isothermal baking. The results in this study show that the rate of curing varies drastically during the spraying operation and that a mathematical model is needed for the prediction of the degree of cure. This research provides a model that can quantify the cure degree by determining the Arrhenius constants of the polymer and integrating over the temperature-time profile of the coating during deposition. The latter thermal profile may be obtained by real-time measurements or by theoretical calculations. The model is applied to a combined thermal spraying and infrared irradiance process and validated by differential scanning calorimetry. The work demonstrates that process parameters have a major influence and shows, for example, that very thick metal substrates can suppress curing due to a heat sink effect. The results also indicate that conventional epoxies cannot be fully cured during flame spraying and need additional thermal energy, as in infrared irradiation. The research develops a quantitative model to predict the degree of cure that takes into account the polymer formulation and flame-spraying conditions. It provides a methodology that could be used for the process control of flame-sprayed thermoset coatings in an industrial context.

1. Introduction

Powder coating is a generic family of processes in which coatings are deposited from powder. The most commonly used powder-coating process is electrostatic spraying in which the powder is fed into an electrostatic gun, the charged powder adheres to the earthed workpiece, which is then heated in an oven to fuse and cure the coating [1,2]. Powder-coating processes are solvent-free thereby avoiding the environmental problems and prolonged drying times of liquid paint. Their share of the polymer coating market has been growing strongly over the last decade. Thermosetting and thermoplastic powders are available but over 90% of the coatings market is for thermosets [1,3].

Flame spraying is within the powder-coating family of processes but is a radically different technology to electrostatic spraying. It involves injecting powder particles into a flame in which they are melted, accelerated and projected onto a substrate to form a coating [4–6]. In contrast to other powder-coating processes, flame spraying enables coatings (usually metallic) to be applied in the field, not just in the factory. Flame spraying is also more energy efficient as the powder particles are heated and melted in the flame so that there is no need to heat up the relatively massive substrate in an oven as in electrostatic spraying.

Despite the above considerable advantages, flame spraying of polymer coatings remains a relatively minor activity. An important reason for this is that the process has only been successfully used commercially for thermoplastics. Typical thermoplastics that are flame sprayed include polyamide and vinyl chloride copolymers [7–10]. Recent research has extended the range of possible thermoplastics that can be flame sprayed to include PMMA [11], UHMWPE [12], PVDF, ECTFE, PFA, FEP [10,13,14] and PEEK [15] as well as inorganic-thermoplastic composites [16–19].

Although thermoset coatings are much more important economically than thermoplastic coatings, little successful work has been undertaken on their deposition by flame spraying. This is largely because the formation of thermoset coatings is much more complex and demanding than that of thermoplastic coatings. Thermoplastic deposition only requires the particles to melt in the flame without degradation [20] and then flow on impact with the substrate to form a continuous coating.

Thermosets have the additional requirement of cross-linking or curing. As well as melting without degradation, thermoset particles must not cross-link in the flame, but must flow into a coherent deposit and then cross-link to produce a fully cured coating (cross-linking in the

---

* Corresponding author.
E-mail address: david.gawne@lsbu.ac.uk (D.T. Gawne).

0257-8972/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2012.06.007

flame increases the viscosity of the particles and prevents adequate flow on the substrate). Satisfying this need to control cross-linking and therefore temperature during the course of deposition is relatively easy in electrostatic spraying: the oven treatment is essentially isothermal (typically 170 °C for 20 min) and cure is controlled by adjusting the temperature at a fixed time or vice versa. The thermal characteristics of flame spraying, on the other hand, are more complex. The flame sweeps across and down the substrate surface depositing one or more layers until the required thickness of coating is built up. The hot gas jet from the spray gun impinges on and flows out laterally over the substrate or underlying layers of coating [21]. This imparts significant thermal energy into the coating, which can have a substantial effect on its properties, particularly for polymeric materials. The latter research [21] shows that the temperature of a polymer coating during thermal spraying varies widely: for example, from 100 °C to 180 °C in just one sweep of the flame across the width of the substrate. This is expected to have a major influence on the curing of thermosets.

The above results indicate a need for a fuller understanding of the interaction of a scanning flame with the coating and its effect on the cross-linking of thermosets. This paper specifically studies epoxies but the methodology is valid for all thermosetting polymers. The research is directed at developing a quantitative model to predict the degree of cure that takes into account the flame-spraying conditions and polymer formulation. It provides a computational methodology that could be used for the process control of flame-sprayed thermoset coatings in an industrial context.

2. Experimental procedure

2.1. Materials

The substrate materials for the coatings were flat plates of low-carbon steel. The feedstock materials investigated for the coatings were epoxy powders supplied by Akzo Nobel Ltd (Gateshead, UK). The details of the relevant properties are given in Table 1.

The Q and A values in Table 1 are the characteristic constants in the Arrhenius Equation (the activation energy and pre-exponential constant as described more fully in Section 3.2) determined using the Kissinger method (which does not need a precise knowledge of the reaction mechanism [22] and assumes a first order reaction: n = 1):

$$\ln\frac{\beta}{T_p^2} = \ln\frac{AR}{Q} - \frac{Q}{RT_p} \tag{1}$$

where β is the heating rate, T_p is the peak temperature of the exothermal peak from differential scanning calorimetry (DSC) measurements running at different heating rates and R is the gas constant.

2.2. Thermal spray deposition

The steel substrates were degreased with acetone, grit-blasted with alumina grit and air-blasted. The epoxy coatings were then deposited on the substrates by flame spraying with acetylene as the fuel gas and compressed air as both the oxidant and powder-carrier gas. The deposition parameters were chosen to avoid decomposition of the epoxy particles in the flame but to provide them with sufficient flow on impact with the substrate. Fuel-gas flow rates were selected and specified in the range 3 to 10 standard litres per minute. The scanning speed of the torch over the substrate surface was set at 200 mm s^{-1} and the torch nozzle-to-substrate distance at 200 mm. An infrared (IR) scan was applied in selected trials as a post-deposition treatment immediately after spray deposition using an IR device mounted close to the flame gun.

Table 1
Properties of feedstock materials.

Powder	T_p/°C	Reaction on set/°C	T_g/°C	Q/kJ/mol	A/mol^{-1} s^{-1}
Epoxy-1	180	130	65	59.3	5.90×10^4
Epoxy-2	160	128	58	52.7	2.72×10^4

2.3. In-situ temperature measurements

The temperatures at the coating surface, T_s, at the coating-substrate interface, T_i and at the back of the substrate, T_b were measured in-situ during different stages in the process: pre-heating, deposition and post-deposition irradiation in order to obtain a complete heating history of the deposit. T_s and T_b were measured using an infrared thermometer (MX4 CF Infrared Thermometer, Raytek, UK), which has a response time of 0.1 s. The data collection was set at 0.1 s so that 10 readings were recorded in computer each second. The interface temperature T_i was measured using type K thermocouples attached to the steel–coating interface before deposition. The infrared thermometer was calibrated using the type K thermometer to define the emissivity for the measurements.

2.4. Differential scanning calorimetry

DSC was used to quantify the extent of cure or the cross-linking reaction of thermally sprayed coatings. The DSC measurements were undertaken with a Mettler Toledo differential scanning calorimeter, model DSC822e. Most DSC tests were carried out at a 20 °C/min heating rate within a temperature range of 40–300 °C during which nitrogen with a flow rate of 15 ml/min was used as protective gas. A range of heating rates was used in the determination of the activation energy Q and pre-exponential constant A in Eq. (1).

3. Results and discussion

3.1. Characteristics of flame-spray deposition

A flame-sprayed coating is built up from the stream of incoming molten particles from the flame, which flow into splats on impact with the substrate and form a dense deposit. The spray gun moves across the width of the substrate, drops down a step and moves back across the width at a lower level, drops down another step and so on. This rastering action ensures that the substrate surface is effectively covered with the coating material. The hot gas jet carrying the particles impinges on the substrate, spreads out sideways and thereby heats the substrate or underlying splats [21]. The temperature increases markedly as the flame approaches a given elemental area on the surface of the substrate, reaches a maximum as it passes over the top and falls just as rapidly as the flame moves away. This moving heat source will inevitably produce a series of oscillations in temperature, as shown by the

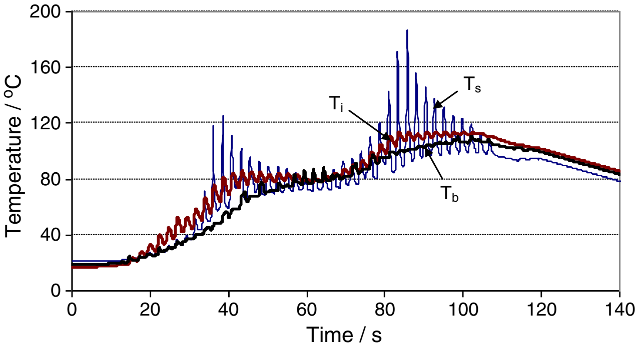

Fig. 1. Experimentally measured thermal history of an epoxy coating during flame spraying deposition. The coating of thickness 210 μm was deposited on a 150 mm × 100 mm × 3 mm steel plate.