Project no. 505451-1

Project acronym: GLASCOAT

Project title: HIGH-PERFORMANCE GLASS-BASED COATINGS

Instrument: SPECIFIC TARGETED RESEARCH ON INNOVATION PROJECT

Thematic Priority: NMP-PROPRITY 3

Publishable Final Activity Report

Period covered: 1 January 2007 **to** 30 September 2007

Date of preparation: 14 December 2007

Start date of project: 1 January 2004 **Duration**: 45 months

Project coordinator: Professor D.T. Gawne

Project coordinator organisation: London South Bank University

Table of contents

EXECUTIVE SUMMARY

Glasses are a unique and versatile class of materials, whose properties are greatly under-exploited in coatings due to the limitations of existing materials and available processes. Glasses do not have the same compositional restrictions of ceramics and metals and this enables more opportunities of tailoring their properties to suit specific applications. Their amorphous structure contains no grain boundaries and enables low-permeabilities. Their low softening/fusing temperatures allow them to flow at much lower temperatures than ceramics to the benefit of formability and surface finish. The metastability of glasses provides the ability for crystallization into strong glass-ceramics and sol-gel processing has the potential of introducing nanostructures into glass-based materials.

The available industrial process for the deposition of thick glass coatings on engineering components is enamelling. However, enamelling has drawbacks in materials performance and process capability. The coatings contain large-scale flaws and possess a low fracture toughness, which results in limited performance. Enamelling involves melting glass particles at high temperatures (800-900^{o}C) in a furnace. This severely restricts the substrate materials that can be coated, as many materials suffer degradation, softening or distortion at such temperatures. It also restricts the application of high-strength glass systems as coating materials, since the latter require even higher fusing temperatures, which unavoidably causes damage to the metal substrate. Furthermore, the need for a furnace in enamelling means that large components or outside structures cannot be treated. Enamelling is thus a not suitable platform from which to exploit glasses as coatings for high-performance applications.

This project has developed a new integrated process based on a thermal-spray technique coupled with infrared crystallization. The partners have synthesized new glass compositions and developed tailor-made feedstock powders. Computational modelling and process simulation of the deposition and post-treatment processes with associated experimental validation has been undertaken. This has enabled the thermal history of the feedstock materials to be predicted throughout the deposition process. This has also saved considerable time on experimental trials and, in combination with nano/microstructural characterization, has allowed an understanding of the critical process mechanisms to be developed. Over seventy tailor-made glass compositions have been developed on basis of science and experience, enabling dense, well-bonded coatings with smooth surface finishes to be produced. The characteristics necessary for successful deposition in terms of composition, process parameters, particle size distribution and additives have been determined and successful equipment designs have been developed. Cooperative work between the end-user partners has enabled common test procedures to be established so that effective evaluation took place. Materials modelling defined the relationships between composition and properties and promoted the development of new glasses. Work was undertaken in sol-gel processing and crystallization in order to produce nanostructured glass-ceramic coatings. The sol-gel method enables mixing on a molecular level in the liquid state, which gives greatly improved homogeneity, control of purity and composition, and the synthesis of hybrid systems. The sol-gel-derived nanostructured powders have been transformed to coatings by heating to high temperatures in the spray-jet, cooling rapidly on impact with the substrate surface and subjecting the resulting deposit to high-energy infrared radiation.

Once the principles of materials synthesis, feedstock powder preparation and deposition had been established and generally sound, adherent coatings produced, the end-user partners

provided performance specifications for four selected potential proof-of-principle applications. The latter partners carried out laboratory testing on the glass coatings, while the raw materials and processing partners developed new coatings iteratively with the aim of satisfying each of the potential applications. The results showed that the coatings satisfied the end-user specifications for three out of the four potential applications. The specifications were not met for concrete, although sound, adherent coatings were deposited, and more work is required. However, the flame-sprayed coatings on burner caps for domestic cookers, chemical reactor vessels and injection moulding components did meet the test requirements.

1. PROJECT EXECUTION

1.1 THE OBJECTIVES OF THE PROJECT:

1. A new family of glass coatings with superior properties to enamel
2. A new integrated spray-deposition infrared-irradiation process
3. A process for coating temperature-sensitive materials, such as concrete and cast iron
4. A process that can deposit glass-based coatings on large components
5. Computational models simulating the process
6. Computer model for glass composition selection
7. Designs for the integrated spray-deposition infrared-irradiation equipment
8. End-user evaluation of coatings

1.2 PARTICIPANTS

There are nine participants in the project:

London South Bank University
Ircon AB
Pfaudler Werke GmbH
Escol Products Limited
Bouygues TP
Pramar SRL
Ege Kimya & Ticaret AS
Fundacion Tekniker
Engineering Surfaces Limited

The coordinator organization is London South Bank University and the coordinator is Professor David Gawne (david.gawne@lsbu.ac.uk, fax +44 207 815 7688).

1.3 SUMMARY OF WORK PERFORMED AND MAJOR ACHIEVEMENTS

The project has for the first time developed a flame-spray and infrared process with new nanostructured materials for engineering glass coatings. In the initial stages of the project, experimental trials showed that the glass compositions used for many years in conventional enamelling were unsatisfactory for thermal spraying. Serious problems were incurred in flame spraying due to residual stresses, cracking, adhesion, colour stability and coating performance. A further difficulty was that the glass compositions used in the previous and very limited amount of research on plasma spraying were also found to be unsuitable. As a result, a new family of materials and new spray-gun designs needed to be developed in this project.

Figure 1. Glass smelting at Ege

A series of tailor-made glass compositions were developed for the new process based on experimental trials, property measurements, materials characterization, materials modelling and the resulting framework of knowledge built up throughout the project. Many of the problems in thermal-spray deposition were found to be caused by its short thermal cycles, rapid heating and cooling conditions. Flame spraying was particularly problematic owing to its much lower gas temperatures and velocities than those of plasma spraying. New glass compositions were synthesized by melting or by sol-gel processing. A range of new glass compositions were produced by smelting (Figure 1) in pilot furnaces in order to provide experimental glasses with characteristics tailored for flame spraying including expansion coefficient, viscosity, permeability, mechanical and chemical properties. Initially, the grinding of the glass powders was generally unsatisfactory. This was solved by using liquid additives as encapsulents to prevent the particles from agglomerating. This enabled the grinding process to proceed efficiently and produce feedstock powders with controlled particle size distributions and flowability. The coatings were optimized by control of composition, powder processing, flame-spray parameters and post-heating (Figure 2). Modelling and iterative experimental trials played an important role. Sol-gel processing was also used as an important synthesis technique. Glass-alumina nanocomposite coatings, for example, were made by synthesizing the precursor material by sol gel, processing to powder, depositing by flame spraying and, if required, post-treating with high-energy infrared radiation. These materials cannot be made by traditional processing owing to their very high fuse temperatures, which cannot be reached in conventional smelting furnaces with their operating temperatures of 1200-1250^{o}C. The coatings were smooth and glossy and the presence of nano-particles increased the hardness of the glass coatings by approximately 40% with further increases possible by control of the uniformity of the particle dispersion. Other glass compositions were developed that could be flame sprayed and the coatings crystallized to give glass-ceramics by infrared post-treatment (Figure 3).

Figure 2. Depositing a glass coating by flame spraying

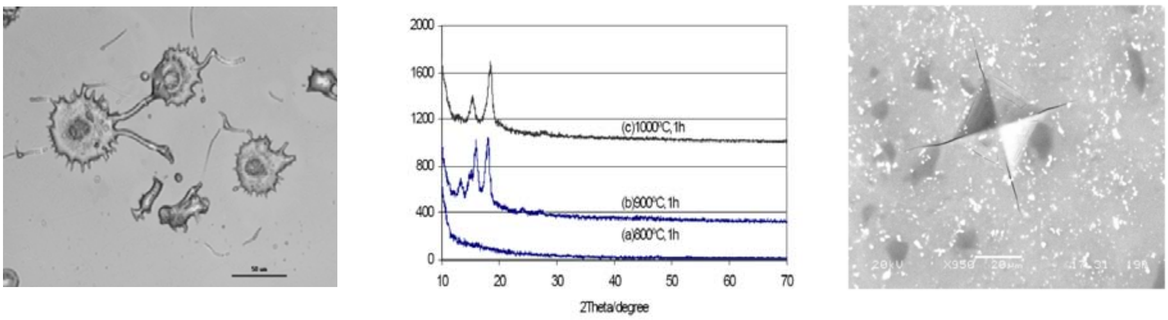

Figure 3. (a) Individual splats of sol-gel glass; (b) Infrared crystallization of glass ceramic; (c) Indentation fracture of glass-based coating.

Computational modelling using fluid mechanics and heat transfer analysis was applied to predict the time-temperature profiles and thermal history of the materials throughout processing (Figure 4). This, in conjunction with experimental trials, enabled the materials compositions to be developed and processing conditions to be optimized. Modelling also played an important role the development of gun designs necessary for the new process.

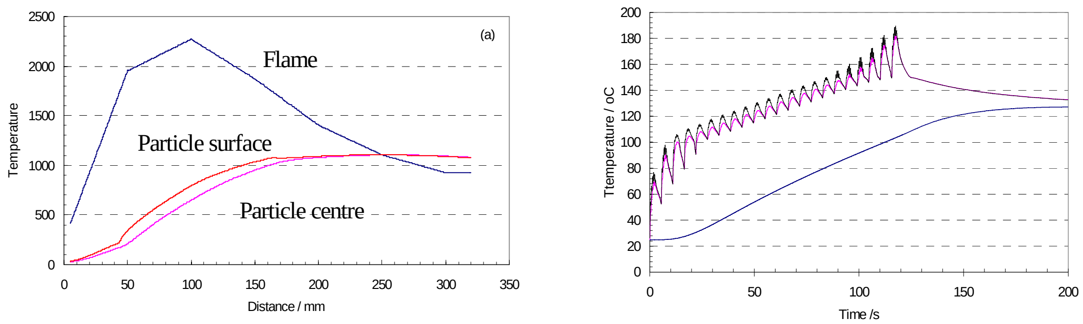

Figure 4. Modelling of (a) particle temperature and (b) coating surface and substrate during spray deposition

Important elements in the project included: synthesis of glass compositions by smelting and sol-gel processing, spray gun design, process and materials modelling, characterization of the materials structure to provide an understanding of the important mechanisms and evaluation in an industrial context. The last of these, evaluation, was directed at showing whether or not the process could produce coatings capable of satisfying the laboratory test specifications for four proof-of-principle potential applications: (i) domestic burner caps; (ii) chemical reactors; (iii) injection moulding machines manufactured from aluminium; (iv) concrete construction components. If the specifications made on test pieces for each potential application could be met, then this would indicate that the new process/materials had real promise for the future. These potential applications were demanding and quite different from one another: each potential application needed a unique glass composition and set of process parameters. A total of 72 glass compositions were synthesized by the partners throughout the project.

Regarding the domestic burner cap potential application, the industrial requirements for the coatings were severe and challenging. The glass compositions of conventional enamel were unsuitable for flame spraying. The industrial requirements involved mechanical impact resistance to a dropping weight, thermal shock resistance to quenching three times from 400^{o}C into water, chemical resistance to exposure to citric acid and discoloration after heating to 600^{o}C. The latter temperature, for example, was particularly severe, as many manufacturers only specify a test temperature of 520-550^{o}C. After systematic development of glass compositions and the deposition process, the required specifications were finally satisfied and successful coatings were produced. The advantages of flame spraying include

Figure 5. Current burner cap production at Pramar using (from left to right) wet spray enamelling, electric radiation drying and gas-oven enamelling at 850^{o}C.

enhanced properties and the ability to apply glass coatings on burner caps in a one-step process instead of the three used at present (Figure 5). More work is required after the completion of the project to develop an efficient deposition system for real industrial-scale application.

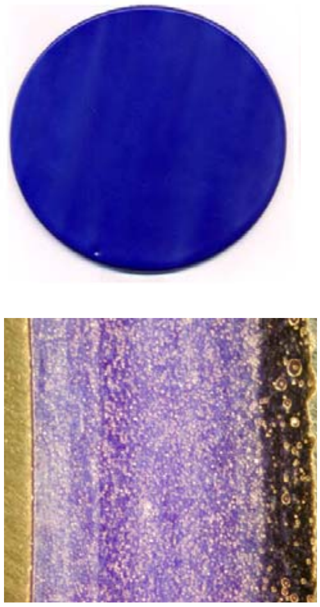

Figure 6. Flame-sprayed glass lining on reactor steel substrate showing (a) surface; (b) cross-section .

Regarding the chemical reactor potential application, the glass coatings on alloy steel substrates were required to withstand severe corrosion conditions, mechanical impact and colour stability. As with the burner caps, the conventional glasses were found to be unsuitable for flame spraying the reactors owing to the stringent requirements of the flame-spray process. Edge cracking was initially a serious problem owing to thermal expansion mismatch and the high viscosity of the conventional powder. This was solved by synthesizing new glass compositions, refining the particle size distribution and spray gun design. The corrosion requirements were severe and were initially not satisfied. The specifications included a seven-day exposure to 20% HCl vapour and a one-day exposure to 1N sodium hydroxide; the latter being particularly difficult in view of the high silica content of the conventional reactor vessel frits. Development of the glass composition through synthesis was eventually successful in providing a corrosion resistance similar to that of conventional coatings. The colour of the flame-sprayed coatings was initially significantly different from that of conventional coatings. It was already known that high cobalt-bearing glasses are generally the least colour-stable, especially when there are little or no other transition metal oxides present. The problem was solved by the use of additives and processing parameters. In summary, the project has been able to produce flame-sprayed coatings that satisfy the requirements of reactor vessels. Conventional processing involves heating the massive reactors to 950^{o}C and the smallest defect means the reactor has to be stripped and re-processed at 950^{o}C. Flame spraying offers enhanced properties, the use of much lower substrate heating temperatures and the possibility of local repair. Further work is required after the project to apply and upscale this knowledge to real industrial applications.

Figure 7. (a) Flame-sprayed glass coating on aluminium alloy substrate; (b) equipment for simulative wear testing of glass coated aluminium

Regarding the injection moulding machine potential application, the glass coatings were aimed at providing wear-resistant coatings on the aluminium-magnesium substrate. At the outset, it was recognized that the presence of magnesium in the aluminium generally caused serious problems in conventional enamelling. In the event, the initial trials revealed that flame spraying caused coarsening of precipitates and unacceptable softening of the aluminium alloy substrate. Other serious problems were encountered: cracking, delamination and colour instability of the glass coatings. These problems were overcome by the adjustment of glass compositions, equipment modification and control of process parameters. The flame-sprayed glass coatings showed excellent abrasive wear resistance compared with uncoated aluminium alloy and high adhesion to the aluminium alloy substrate. Trials also showed that the coatings had the ability to withstand the machining necessary to achieve precision size tolerances during manufacture. The potential advantages of aluminium injection moulding machines over steel are shorter injection times due to its higher thermal conductivity, shorter mould production time due to ease of manufacturing and low weight, which has positive effect of handling. The drawback is the poor wear resistance of aluminium during the processing of glass-fibre composites; the present project has shown that flame-sprayed coatings have major potential in overcoming this problem.

The final proof-of-principle potential application was concrete used in construction. Glass coatings have potential in protecting concrete containing embedded reinforcing steel from degradation by restricting the ingress of water, chlorine ions, carbonation, etc. Major challenges were encountered throughout the course of the project but considerable improvements in coating quality on concrete were achieved. The alkali resistance improved from an initial 240 g/m^2 to 50 g/m^2, optimised coatings survived three days immersion in water without de-bonding and satisfactory adhesion strengths were obtained. Experimental work and modelling indicated that there was a possibility of damage to the concrete by the

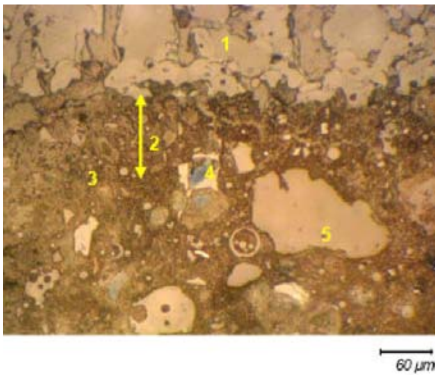

Figure 8. (a) Cross section through concrete showing its multiphase structure; (b) flame-sprayed glass coating on concrete substrate.

flame during deposition. The effect of this on the long-term properties of concrete was not clear and would need substantial further work for clarification. In general, further research is required before the practical requirements for glass coatings on concrete can be satisfied. Nevertheless, major impovements in properties have been obtained and an important framework of knowledge has been established.

2. FINAL PLAN FOR USING AND DISSEMINATING THE KNOWLEDGE

2.1 EXPLOITABLE KNOWLEDGE AND ITS USE

The Consortium identified four potential applications: burner caps for domestic cookers, chemical reactor vessels, an injection-moulding machine and a concrete construction component. The test specifications for these potential applications were obtained and the experimental coatings developed with the aim of meeting these requirements. The results showed that the coatings satisfied three out of the four potential applications and promising results were obtained for the fourth. Nevertheless, the coatings produced in the laboratory with research equipment and the evaluation was carried out on simple test pieces. In order to exploit the results and use them in a real industrial context, the equipment needs to be adapted and integrated for production, the materials upscaled and the process conditions adjusted for production throughputs, environment, health and safety. This involves substantial effort and resources and will require a follow-on project. The table below provides an overview of the exploitation of the results.

Exploitable Knowledge (description)	**Exploitable product(s) or measure(s)**	**Sector(s)** of application	Timetable for commercial use	Patents or other IPR protection	**Owner** & Other Partner(s) involved
1. New precursor materials for glass coatings on burner caps.	*Domestic cookers*	*Domestic appliance industry*	*Needs a follow-on project to upscale synthesis and materials for real industrial application.* *4 years.*	*Depends on outcome of follow-on project.*	*EGE, ESCOL, PRAMAR, ESL, LSBU*
2. New powder-making process for glass coatings on burner caps.	*Domestic cookers*	*Domestic appliance industry*	*Needs a follow-on project to upscale powder making and additives for real industrial application.* *4 years.*	*Depends on outcome of follow-on project.*	*EGE, ESCOL, PRAMAR.*
3. New process parameters for deposition of coatings on burner caps.	*Domestic cookers*	*Domestic appliance industry*	*Needs a follow-on project to modify equipment set-up for production and determine process conditions for real industrial application.* *4 years.*	*Depends on outcome of follow-on project.*	*ESL, LSBU, PRAMAR.*
4. New precursor materials for glass coatings on chemical reactors	*Chemical/ pharmaceutical reaction vessels*	*Chemical, pharmaceutical industries*	*Needs a follow-on project to upscale synthesis and materials for real industrial application.* *4 years.*	*Depends on outcome of follow-on project.*	*PFAUDLER, ESCOL, LSBU*
5. New powder-making process for glass	*Chemical/ pharmaceutical reaction*	*Chemical, pharmaceutical industries*	*Needs a follow-on project to upscale powder making and additives for real*	*Depends on outcome of follow-*	*PFAUDLER, ESCOL.*

Exploitable Knowledge (description)	**Exploitable product(s) or measure(s)**	**Sector(s)** of application	Timetable for commercial use	Patents or other IPR protection	**Owner** & Other Partner(s) involved
coatings on chemical reactors	*vessels*		*industrial application. 4 years.*	*on project.*	
6. New process parameters for deposition of coatings on chemical reactors	*Chemical/ pharmaceutical reaction vessels*	*Chemical, pharmaceutical industries*	*Needs a follow-on project to modify equipment set-up for production and determine process conditions for real industrial application.* *4 years.*	*Depends on outcome of follow-on project.*	*ESL, LSBU, PFAUDLER.*
7. New precursor materials for glass coatings on injection moulding machines.	*Injection moulding machines*	*Polymer processing industry*	*Needs a follow-on project to upscale synthesis and materials for real industrial application. 4 years.*	*Depends on outcome of follow-on project.*	*EGE, ESCOL, TEKNIKER, ESL, LSBU.*
8. New powder-making process for glass coatings on injection moulding machines.	*Injection moulding machines*	*Polymer processing industry*	*Needs a follow-on project to upscale powder making and additives for real industrial application. 4 years.*	*Depends on outcome of follow-on project.*	*EGE, ESCOL, TEKNIKER.*
9. New process parameters for deposition of coatings on injection moulding machines.	*Injection moulding machines*	*Polymer processing industry*	*Needs a follow-on project to modify equipment set-up for production and determine process conditions for real industrial application.* *4 years.*	*Depends on outcome of follow-on project.*	*ESL, LSBU, TEKNIKER.*
10. New precursor materials for glass coatings on concrete	*Reinforced concrete components*	*Construction industry*	*Needs a follow-on project to tailor both concrete and glass for flame spraying, upscale synthesis and materials for real industrial application. 6 years.*	*Depends on outcome of follow-on project.*	*ESCOL, LSBU, ESL, BOUYGUES.*

Exploitable Knowledge (description)	**Exploitable product(s) or measure(s)**	**Sector(s)** of application	Timetable for commercial use	Patents or other IPR protection	**Owner** & Other Partner(s) involved
11. New powder-making process for glass coatings on concrete.	*Reinforced concrete components.*	*Construction industry*	*Needs a follow-on project to upscale powder making and additives for real industrial application. 6 years.*	*Depends on outcome of follow-on project.*	*ESCOL, BOUYGUES.*
12. New process parameters for deposition of coatings on concrete.	*Reinforced concrete components.*	*Construction industry*	*Needs a follow-on project to modify equipment set-up for production and determine process conditions for real industrial application.* *6 years.*	*Depends on outcome of follow-on project.*	*ESL, LSBU, BOUYGUES.*
13. Spray system modifications for low-temperature substrates.	*Coating deposition on low-temperature substrates*	*Thermal-spray industry*	*Needs a follow-on project on flame spraying concrete and aluminium substrates in production.*	*Depends on outcome of follow-on project.*	*ESL, LSBU.*
14.Demonstration of processes in university courses.	*MSc and BEng courses.*	*Higher Education*	*6 months*		*LSBU*
15. Inclusion of non-sensitive knowledge in case studies and lecture content of university courses.	*MSc and BEng courses.*	*Higher Education*	*6 months*		*LSBU*

Exploitable Knowledge (description)	**Exploitable product(s) or measure(s)**	**Sector(s)** of application	Timetable for commercial use	Patents or other IPR protection	**Owner** & Other Partner(s) involved
16. Application of knowledge to preparing new research proposals and PhD studentships.	*Research grants*	*Higher Education*	*6 months*		*LSBU*

2.2 DISSEMINATION OF KNOWLEDGE

Technology transfer between the partners took place throughout the project. This has involved knowledge of glass smelting technology between Escol and Ege, residual stress control from Pfaudler, thermal spray technology and sol-gel processing from LSBU, infrared technology from Ircon, computational modelling and equipment design from ESL, civil engineering from Bouygues, injection moulding manufacture from Tekniker and domestic appliance manufacture from Pramar.

The partners have agreed that suitable scientific findings can be disseminated through papers in refereed journals, trade/professional journals and presentations at conferences. However, this will only take place after screening by the partners to ensure that potential patent property is secured.

There are well-established links between enamellers across the EU, including an International Enamellers Association. The Consortium presented papers at two congresses of the International Enamellers Association. Papers for publication of the non-confidential findings from the project are being prepared for publication and presentation.

An important vehicles for exploitation are the follow-on projects described in the previous section. All partners have agreed to participate in such projects. These projects are needed to put the new knowledge into practice and to convince other potential manufacturers and end-users to take up the new technology.

Planned /actual Dates	**Type**	**Type of audience**	**Countries addressed**	**Size of audience**	**Partner responsible /involved**
2008/9	*Publication in refereed journals*	*Manufacturers, end users, researchers.*	*EU*	*Readership of journals and citations. Hundreds.*	*LSBU and other partners*
2009/10	*Conferences*	*Manufacturers, end users, researchers.*	*EU*	*Hundreds.*	*LSBU and other partners*
2009/10	*Publication in trade /*	*Manufacturers and*	*EU*	*Hundreds.*	*LSBU and*

Planned /actual Dates	Type	Type of audience	Countries addressed	Size of audience	Partner responsible /involved
	professional journals	*end users,*			*other partners.*
2008 onwards	*Communication between partners and customers. The partners have wide customer networks throughout the EU.*	*Manufacturers and end users.*	*EU*	*Relatively small but key personnel*	*Escol, Ege, Pfaudler, Bouygues, ESL, Pramar.*
2009	*Follow-on project to upscale the process and materials for production*	*Manufacturers and end users.*	*EU*	*Small but key personnel*	*Escol, Ege, Pfaudler, Bouygues, ESL, Tekniker, Pramar. LSBU.*