Project no. COOP-CT-2006-031944

Acronym: **NaMaCo**

Project title: Nanostructured, Thermally Sprayed, Magnetic Coatings for Microwave Absorption Applications

Instrument: Co-operative Research Projects

Thematic Priority: Specific Research Projects for SMEs

Final Activity Report
(Months 1 - 27)

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Publishable executive summary

The main objective of the project entitled "*Nanostructured, thermally sprayed, magnetic coatings for microwave absorption applications*" ***(NAMACO)*** was the development of a new system for absorbing reflected high power microwave radiation in waveguide components used to protect sensitive microwave sources such as magnetrons, klystrons or semiconductor-based power amplifiers (PAs) from damaging reflections. The aim was to replace the current approach, which uses conventional NiZn spinel ferrite tiles. These are currently manufactured by ball milling the raw powder with an organic binder, pressing and firing/sintering to form tiles which are then bonded, for example, onto waveguide walls resulting in many problems with manufacture and performance as well as being expensive in labour and materials.

The use of these thin tiles of NiZn spinel ferrite material requires them to be ground to a precise thickness and adhesively bonded to metallic waveguide. The bonding layer has to be minimised to assure a minimum temperature gradient during high power operation. The lateral size (<30 mm) and thickness (< 2mm) of the ferrite tiles have to be limited in order to withstand the thermal stress induced by thermal gradients, the magnitude of which depend on the applied power density. In large-size devices, such as 3.5 MW peak power (3 kW average power) waveguide absorbers for frequencies of 2-3 GHz, this leads to the need for up to 3500 tiles in a high-performance absorber.

The main drawbacks of the present processing route are:

- costly and time consuming material processing and device fabrication;
- limited to flat and planar surfaces, not possible to produce "conformal" coatings on curved surfaces;
- detrimental effect of air gap at the interface on performance;
- maximum operating temperature and power density limited by choice of adhesive and not the Curie temperature of the NiZn ferrite (NZF).

The project objective was to develop an improved microwave absorption system based on the use of HVOF sprayed nanostructured NZF coatings deposited with specially tailored NZF feedstock powder. The methodology involved directly spraying NZF powders onto metallic waveguide walls or housing surfaces.

In the project, the types of microwave absorbing ferrite materials currently employed and the processes currently used to manufacture high power microwave absorbing components were critically reviewed. This led to an identification of the materials and powder types to be prepared and evaluated through thermal spraying in the work programme.

With regard to ferrite powder synthesis, a number of different powder feedstock materials with compositions based on the NZF spinel composition were evaluated. Two specific powder production routes termed (i) mechanical alloying and ferritization (MA+F) and (ii) mechanical alloying and self-propagating high-temperature synthesis (MA+SHS) were evaluated during the project. Both synthesis routes provided feedstock powder of the required chemical composition and spinel crystal structure. Powders were produced with a tailored composition so that after spraying coating compositions approximately matched those of the baseline ferrite tiles used at present. These powders were nano-crystalline with a typical crystallite size, defined as regions separated by high angle grain boundaries within a physically distinct crystal, of approximately 150 nm. The main advantage of the (MA+F) route was the homogeneity of the powder obtained but the (MA+SHS) route provided the important economic benefit of the elimination of the long and expensive furnace ferritization stage during powder production and powder was sufficiently homogeneous for a thermal spraying application. Powders were produced with a composition designed to match that of the baseline sintered tile material after spraying; i.e. the initial compositions of the powders were adjusted to allow for the loss of metallic elements during HVOF spraying (in particular Zn).

Laboratory HVOF spray trials showed that nanostructured NZF coatings could be sprayed by the Top Gun and DJ2600 HVOF systems; NZF is a ceramic material with a melting point/softening temperature in excess of 1500°C. The spinel crystal structure of NZF in the original feedstock powder was wholly or largely retained in the sprayed deposit. The spray parameters in both systems, specifically oxygen to fuel ratio, had a significant effect on the constitution of the deposit (i.e. phases present, composition of phases and microstructural scale of phases). Formation of undesirable secondary phases was favoured by the use of a higher temperature flame and creation of a higher temperature in the particles. The coating microstructure after HVOF spraying exhibited low porosity (<5%), less than that of the baseline sintered tiles. However, with the DJ2600 system only a low deposition efficiency of ferrite powder could be achieved. In the case of Top Gun spraying the deposition efficiency was satisfactory and good bond strength of coating to substrate was achieved (> 45 MPa) but it was difficult to control Zn loss from the powder during spraying. This is due to the fact that loss of Zn scales inversely with powder particle size. Indeed particle size is found to be a more critical factor affecting Zn loss than either residence time or particle temperature in the gas jet. It was calculated that Zn loss would be much lower with larger diameter particles (>60 μm). Whilst, powder particles of such sizes cannot be sprayed by HVOF, air plasma spraying (APS) is capable of depositing this size of ceramic powder. Consequently, APS trials were agreed by the consortium and, contrary to earlier expectations, promising results were obtained (with little Zn loss) using a suitable size range of relatively coarse (ie> 53 μm) powder. Although coatings were more porous there was reduced Zn loss, comparable degree of secondary phase formation (in this case FeO) and attainment of adequate bond strength.

In the project, the main interest was in developing high frequency microwave absorbers. This required the measurement of the complex magnetic permeability at frequencies in the range 2- 3 GHz. More specifically, good absorbers are required to possess high values of the imaginary part (μ''). Techniques were developed during the project to carry out low power measurements of μ'' for sprayed deposits and to compare the values with those of conventionally sintered powders including the baseline sintered tiles currently employed in commercial systems. Comparison of the magnetic loss factor, μ'', between pressed and sintered ferrite samples (the baseline material) and sprayed samples (both Top Gun HVOF and APS) showed that in the frequency range of interest (2-3 GHz) the sprayed coatings had μ” values approximately 45% and 90% of the baseline materials at 2 and 3 GHz respectively. These are acceptable for the microwave absorber application envisaged and on this basis scaled-up, industrial, thermal spraying trials were undertaken.

The industrial scale-up spraying trials were undertaken jointly by the appropriate SMEs and RTD providers. SMEs also conducted particle diagnostic measurements using SprayWatch in support of the scale up trials and to facilitate transfer of spray conditions from RTD providers to the industrial environment. The in-flight particle diagnostic measurements with SprayWatch were also used to establish the repeatability, reliability and limits of the processes. The main emphasis of the spraying trials was to optimise coating characteristics in relation to maximum deposition efficiency (DE), minimum coating porosity, adequate bond strength (~45 MPa), target composition (particularly Zn level), minimum quantity of secondary phases (e.g. FeO) present and maximum magnetic loss factor at 2 and 3 GHz. On the basis of the size of the industrial component to be sprayed, and the coating thickness required, powder was produced for HVOF spraying (6 kg of +5-53 μm) and APS spraying (6 kg of +53 -140 μm) to the previous specifications in terms of morphology, composition, grain size and crystal structure. The industrial development phase of TopGun HVOF and APS spray deposition was successfully completed. Procedures for the manufacture of case study demonstrator components were determined and documented. This resulted in a definition of powder characteristics, process parameters (including SprayWatch temperature and velocity measurements) and coating specification in terms of, for example, phases, microstructure and magnetic performance. The magnetic properties of the industrially deposited coatings (specifically μ'' in the 2-3 GHz range) were found to be comparable to the performance data for laboratory processed coatings and baseline material used to manufacture current sintered tiles. Hence the consortium proceeded with the manufacture and evaluation of full sized demonstrator components.

A total of five inner conductor waveguides (the demonstrator component referred to above) were sprayed up to 800 μm in thickness. A specific thickness profile was used to optimise the microwave absorption characteristics. Following the deposition of the coating, the inner conductor was assembled into its housing so that the microwave absorbing performance of each case study component could be evaluated. Before proceeding to evaluate the behaviour in a high power test, an initial low power screening experiment was performed using laboratory equipment to measure the complex reflection coefficient S_{11}. The absolute value of S_{11} is a measure of microwave absorption and it typically expressed on a log scale in decibels over the range of interest; in this case 2.6 to 3.9 GHz. Of the five components produced, three met the threshold performance standard of -23 dB in the low power screening test at room temperature. These three also showed little change in $|S_{11}|$ with temperature over the range 20 to 60 °C which indicates that in a high power test (where heating could occur) they were unlikely to breakdown catastrophically. Those that passed the low-power screening test were sent to an industrial end-user where high power tests could be performed. For comparison purposes, tests were also conducted on a conventional absorber manufactured using sintered tiles. The experimental arrangement comprised an RF power source operating at 2.856 GHz, an isolator device and a waveguide network attached to the device under test i.e. the ferrite absorber demonstrator. Tests were performed up to 4.5 MW peak power (corresponding average power of 3.8 kW). It was found that the reflection coefficients measured using the high-power test configuration at a low level of power were very similar to the precisely calibrated low-power test data. A degree of degradation of $|S_{11}|$ with increasing power was observed for all absorber components in the high power tests, mainly due to the heating of the ferrite during the test. Up to a power level of 3.5 MW peak power (3 kW average power) the drift of $|S_{11}|$ was comparable to the thermal drift observed at low power by varying the cooling water temperature. The observed power-induced drift of one of the APS-sprayed components was comparable to the tile absorber, while the other APS absorber and the HVOF-sprayed one varied slightly more as the power level was increased. Overall, the performance of the sprayed components was only slightly lower than that of an absorber with conventionally sintered ferrite tiles, even though the waveguide design (from a magnetic properties perspective) had not been optimized for thermally sprayed coatings.

A cost estimation that has been made suggests that a cost reduction of about 40% could be obtained compared to the conventional fabrication technology with sintered and bonded ferrite tiles. Even higher economic benefits could be expected for larger production lot quantities. Additionally, the development of this thermal spray approach provides scope for the design of new and improved absorber devices where coatings can be deposited on curved and complex surfaces. This has not hitherto been possible with current technology, involving the use of sintered and adhesively bonded ferrite tiles. The investigation of other ferrite powder compositions for thermal spraying could lead to more broadband devices or RF absorbers suited for other microwave frequency bands as well as conformal coatings for EMC-shielding in housings or walls of RF anechoic chambers.

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More information about the project can be found at:
http://www.nottingham.ac.uk/~emzjyel/NaMaCo

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1 Project objectives and major achievements

1.1 Overview

1.1.1 Introduction

The overall objective of the project was to develop a new system for absorbing reflected, high-frequency (microwave) radiation in high-power microwave isolator systems needed to protect sensitive microwave sources such as magnetrons. These are used in pulsed high-power microwave devices used in medical applications (e.g. X-ray tomography), industrial processes and scientific particle accelerators. The developed process is intended to replace the current approach which uses conventional pressed and sintered flat ferrite plates (bulk material) that are then glued on, for example, absorber walls resulting in problems with the following: air gaps which reduce effectiveness; the presence of an adhesive layer which limits the operating temperature; absorber substrate designs are constrained to have a flat surface; high cost in terms of labour and materials.

The approach set out in the proposal was to develop nanostructured ferrite powders which are thermally sprayed to form microwave absorbing coatings on the surfaces of absorber components. Such coatings must have low porosity, be well bonded to the substrate and have fine grain size – this combination was believed to be critical for optimum microwave absorbing performance. The work carried out during the project involved innovative developments in powder manufacture and thermal spray processing and led to the manufacture and evaluation of case study components. Whilst the deliverables from the work were products with electronic applications, the research also established an underpinning methodology for thermally spraying nanostructured coatings for functional applications.

In this Overview, section 1.1.2 describes the strategic objectives and section 1.1.3 covers the scientific, technical and societal objectives; these are both as set out in the original proposal. Section 1.1.4 summarises the state-of-the-art at the outset of the project regarding: (i) the microwave absorber application; (ii) ferrite materials for magnetic applications; and (iii) their deposition by thermal spraying.

1.1.2 Strategic Objectives

To develop a microwave absorption system based on the use of nanostructured ferrite coatings suitable for use in high frequency applications, such as microwave waveguide absorbers.

To demonstrate that the coatings can be formed by thermally spraying ferrite powders to give high density deposits with nanostructures.

To demonstrate that these coatings give improved performance, at lower cost, than can be achieved in conventional microwave absorbing components.

To establish the commercial viability of the novel development by conducting at least one industrial case study evaluation.

To examine the potential benefits for wider frequency applications.

1.1.3 Scientific, Technical and Societal Objectives

The prime deliverable from this project will be a high performance, electromagnetic absorber system produced by thermally spraying ferrite powder to form a low porosity, nanostructured coating suitable for use in waveguides or coaxial lines operating at microwave frequencies. The proposed research will focus on powder development and spray process optimisation to achieve an innovative solution to a long-standing problem.

The scientific and technical objectives of the proposed project were:

- To produce Ni-Zn ferrite feedstock material that has a grain size of less than 1 µm within powder particles which are 10-50 µm in size.
- To develop the HVOF spraying technique so that ferrite coatings are deposited with the following target structures:
  - First level – 95% density, <1000 nm grain size
  - Second level – 97% density, <1000 nm grain size
  - Third level – 97% density, <500 nm grain size
- To measure spray particle velocities and temperatures and use this information to gain a scientific understanding of the factors that influence the HVOF process and the relationship between conditions in the spray and the structure/performance of deposited coatings.
- To determine the cost/performance benefits of the developed ferrite coating system by an industrial case study evaluation.
- To assess alternative materials such as Ba- or Li-ferrite for the given applications.

The societal objectives were:

- To increase the competitiveness of European SMEs in the thermal spraying and microwave equipment sectors.
- To increase employment in the sector by increasing the potential markets for thermal spraying powders, equipment and services.
- To improve the quality of life of European citizens by developing materials that can be used to improve the performance of medical equipment and contribute to reducing levels of electromagnetic radiation emitted by electronic devices.
- To improve working conditions, as the industrial coating process will be automated and grinding will not be necessary so exposure to dust is avoided.
- To reinforce the role of women in science, technology and research.

1.1.4 State-of-the-art

Microwave absorbers

Microwave absorbers are key components in high-power microwave isolator systems, needed to protect sensitive microwave sources such as magnetrons, klystrons or semiconductor-based power amplifiers (PAs) from damaging reflections.

At very high power levels of several kW of average power and peak powers up to the MW range, as in pulsed high-power microwave systems used in medical applications (X-ray tomography and oncology), industrial and scientific particle accelerators, only two absorber technologies have been established up until now:

(1) solid state ferrite loads (magnetic absorption due to high imaginary magnetic permeability component, μ''); and

(2) water loads (absorption due to dielectric polarisation in water or glycol mixtures).

Water loads suffer from reliability issues which increase with increasing power levels and, generally, ferrite loads exhibit several benefits which make them the current system of choice for this application. State-of-the-art ferrite absorbers in waveguide technology consist of thin plates (or tiles) of highly absorbing ferrite material, ground to a precise thickness (around 0.5 mm) and adhesively bonded to metallic absorber walls. Even in modest size waveguides the area to be covered is large, of the order of 400 cm^2. The main drawbacks of the solid-state ferrites are:

- costly and time consuming material processing by pressing and sintering of powder under carefully controlled conditions to achieve desired permeability values and dimensional tolerances in tiles;
- high cost finishing of plates and assembly due to manual fabrication procedures, overall the fabrication costs of precise ferrite tiles are 1.50€ to 3.00€/piece, depending on lot size,
- limited operating temperature < 150°C and limited (thermal) power density because of the presence of a polymeric adhesive;
- limitation to flat, planar surfaces due to the use of flat tiles which constrain component design.

Processing-structure-property relationships in ferrites

Ferrites are iron-containing, non-conducting ceramic materials which exhibit magnetic properties on the basis of the quantum mechanically-vested exchange force. Most ferrites possess a spinel crystal structure having the general chemical formula MO Fe_2O_3, they are thus electrical semiconductors or insulators. One of the most popular ferrite materials is $(Ni,Zn)_1Fe_2O_4$, commonly referred to as NiZn-ferrite, and this is widely used up to gigahertz (GHz) frequencies because of its particularly high resistivity ($\sim 10^5$ Ωm) and adjustable real and imaginary magnetic permeability values. The permeability values are matched to operating requirements by altering the precise composition and adding elements such Mn and Co to the basic $(Ni,Zn)_1Fe_2O_4$ formulation. Traditionally, ferrites have been manufactured by conventional ceramic powder processing routes which involve ball milling the component oxides (in the correct proportions) with an organic binder, compacting, drying, pre-firing to burn out the binder and then sintering to form the ferrite crystal structure. Typically, a ferrite absorber tile will have a composition chosen to optimise its imaginary permeability in the frequency range of interest and a sintering cycle optimised to reduce porosity and control dimensional changes.

The growing demand for improved magnetic properties, particularly high frequency performance, has led to renewed interest in the structure-property relationships in ferrite materials. First, porosity must also be minimized as pores also act to pin domain walls as well as exerting a demagnetizing effect on surrounding material. It is well established that magnetic properties in NiZn-ferrite depend on chemical composition, including the Ni:Zn ratio and oxygen stoichiometry, but more recent studies have addressed the influence of microstructure, especially grain size, on high frequency permeability and hysteresis loss. The magnetisation mechanisms contributing to the complex permeability in soft polycrystalline ferrites have been a controversial subject for many years and a full understanding has not yet been achieved. However, it is believed that the mechanisms which principally determine the complex permeability are the domain wall displacements and the spin rotations. It has been demonstrated that, by reducing the grain size of conventionally sintered NiZn-ferrite by one order of magnitude from 10 μm to 1 μm, high frequency (GHz) properties can be improved by enhancing spin rotation mechanisms to the detriment of domain wall motion mechanisms. It is argued that such improvements will accrue up to the limit at which the grain size is reduced to that of a single domain.

Manufacture of ferrite powders normally requires expensive high temperature sintering. However, recently, a new, convenient, inexpensive, single-step, route for the production of certain classes of ceramic materials has been reported, namely self-propagating high-temperature synthesis (SHS). SHS is a process in which an exothermic combustion wave propagates through a powder mixture to form a product. Typical reactions that can proceed in the SHS mode reach temperatures in the range 1200-4000 °C, and no energy input is required except to initiate the reaction. The exothermic nature of the reaction is captured and used to drive the process. SHS reactions are characterized by rapid heating and cooling, can produce metastable materials with smaller grain sizes than traditional ceramic methods and by adjusting the ratios of the starting materials in the powder then compositional variations can be readily manufactured in certain systems. However, to date, this method manufacture does not appear to have been investigated for the cost effective production of ferrite powders of specific compositions and grain structure. Primarily, this is because reaction of oxides normally lacks sufficient energy release to sustain a SHS reaction and is only possible if additional compounds, such as chlorates, which decompose exothermically are added to the mix and their by-products subsequently removed.

Thermal spray processing of ferrite powders

It is evident from the above that opportunities exist to significantly improve the high frequency electromagnetic properties of NiZn-ferrites through the production of material which has low porosity combined with nanosized (<100 nm) grains and a tailored chemical composition. However, manufacturing bulk material from nanograined powder is difficult to achieve in conventional sintering processes since the long time at high temperature (which is needed to attain good relative density) inevitably leads to grain growth and potentially loss of certain elements from surface regions by diffusion/oxidation. However, ferrites melt at moderate temperatures (< 2000 °C) and thus thick (>200 µm) NiZn-ferrite coatings having a nanograin size could, in principle, be produced from appropriate feedstock powder by the use of a thermal spray deposition process.

In general terms, thermal spraying utilises power from an electrical or chemical source to heat and soften micron-sized (10-150 µm) powders in a specially designed gun and propel them at high speed towards a substrate. High velocity oxy-fuel (HVOF) thermal spraying, in which thermal and kinetic energy is provided to powder particles by combustion of oxygen with a fuel, has emerged as a flexible technology for depositing low porosity metal, ceramic or cermet coatings well bonded to a substrate. In HVOF spraying, powder heating rates are rapid ($\sim 10^5$ Ks^{-1}) and dwell times at high temperature are very short ($\sim 1x10^{-3}$ s). The process is capable of generating high particle velocities (>500 ms^{-1}) without transferring excessive thermal energy to the powder and is potentially better suited to the deposition of NiZn-ferrite powder (where it is necessary to achieve a specific composition and crystal structure) than conventional air plasma spraying (APS) which involves higher thermal input and lower input of kinetic energy leading to greater likelihood of degradation and formation of higher porosity deposits. HVOF spraying thus has the potential to generate low porosity deposits in which the desired composition and spinel crystal structure are achieved under optimised processing conditions. Very little work has been published in the field of HVOF spraying of ferrite materials, although there is some evidence that under appropriate conditions it is possible to deposit them as low porosity coatings, with little chemical degradation and having promising high frequency magnetic properties. However, this was achieved with expensive sol-gel derived powder which would not be cost effective for coating the large areas involved in the present application.

Therefore, the successful industrial application of NiZn-ferrite coatings (by thermal spray technology) in microwave absorbing loads required extensive research to develop appropriate, low-cost feedstock powder and detailed understanding of the HVOF process in order to: minimize coating porosity; minimize chemical and structural degradation of the material; achieve good bond strength to the substrate; and maximise coating deposition efficiency.

1.2 Variations to the original work programme

The high power assessment of the demonstration parts was to be done by a company in the USA that had the necessary equipment. Extra time was required in order to prepare the demonstration parts and have them tested in the USA. It was for this reason the consortium submitted a request for a 3 month extension to the project so that this full evaluation of the results of case study trials could be undertaken. This was approved by the Commission and so the end date of the project changed from 30th September 2008 to 31st December 2008. The project Gantt Chart was updated accordingly and the revised version is shown in Table 1.

1.3 Summary of objectives for the reporting period, contractors involved, work performed and the main achievements in the period.

1.3.1 Objectives for the reporting period

The specific objectives of the workpackages undertaken during the reporting period and the associated deliverables are as follows:

- To identify the technical and commercial requirements of each industrial partner and to incorporate these within the project work programme. (**WP 1.1, D1**).
- To determine the most effective method of producing nanostructured ferrite powder, quantifying its structure and principal characteristics (**WP 1.2, D3, D7**).
- To carry out successful deposition of nanostructured ferrite powder by HVOF spraying under laboratory conditions. (**WP 1.3, D4**).
- Mid- term report preparation (**WP 4, D5**).
- To carry out successful deposition of nanostructured ferrite powder by HVOF spraying under laboratory conditions. (**WP 1.4, D6**).
- To optimise conditions for the HVOF deposition of ferrite coatings on an industrial scale (**WP 2.1, D8**).
- To document powder production and spraying procedures, and the characteristic structures and properties of the coatings deposited (**WP 2.2, D9**).
- To apply ferrite coatings, using the developed technology, for use as microwave absorber shields on at least one case study waveguide component (**WP 3.1, D10**)
- To document and transfer the developed technology from research providers to SMEs, to prepare information to assist in the future exploitation of the technology and to set up facilities to demonstrate the process to the wider industrial audience (**WP 3.2, D11**).
- Final report preparation (**WP 4, D12**).

The contractors participating in these workpackages are listed in Table 2.

Tasks		Partners Involved	Period (months)														
			2	4	6	8	10	12	14	16	18	20	22	24	26	27	
WP 1	**LABORATORY DEVELOPMENT OF POWDER & HVOF PROCESS**																
1.1	Definition of Industrial Requirements	ALL		**D1**													
1.2	Ferrite Powder Synthesis and Characterisation	1,6,9,10							**D3**			**D7**					
1.3	Preliminary HVOF Spraying Trials	1,2,3,5,6,7, 8,9,10							**D4** **M**								
1.4	Thermal Spraying Trials Using Nanostructured Ferrite Powders	ALL									**D6** **M**						
WP 2	**INDUSTRIAL VALIDATION OF PROCESS**																
2.1	Industrial Thermal Spraying Trials	1,2,3,5,6,7, 8,9,10													**D8**		
2.2	Definition of Process Parameters	1,2,3,6,7,8,9 ,10													**D9** **M**		
WP 3	**INDUSTRIAL EVALUATION & TECHNOLOGY TRANSFER**																
3.1	Manufacture and Evaluation of Case Study Components	1,2,3,4,5,7, 9,10															**D10** **M**
3.2	Technology Transfer and Dissemination	ALL															**D11**
WP 4	**PROJECT MANAGEMENT & REPORT PREPARATION**	ALL				**D2** **R**		**D5** **MTA**									**D12** **FR**

Table 1: Project Gantt Chart

Table 2: Details of Contractors involved in workpackages

Partic. Role	Partic. Type	Partic. no.	Participant name	Participant short name	Country
CO	RTD	1	The University of Nottingham	UNOTT	UK
CR	SMEP	2	AFT Microwave GmbH	AFT	DE
CR	SMEP	3	Rybak & Höschele GmbH	RHV	DE
CR	SMEP	4	Rasceur BV	Rasceur	NL
CR	SMEP	5	Oseir Ltd	Oseir	Fin
CR	SMEP	6	Phoenix Scientific Industries Ltd	PSI	UK
CR	SMEP	7	PyroGenesis SA	Pyro	GR
CR	SMEP	8	Metallisation Ltd	Met	UK
CR	RTD	9	Surface Engineering Institute, Aachen University of Technology	SEI(IOT)	DE
CR	RTD	10	National Academy of Sciences of Belarus	PMI	Belarus

1.3.2 Amendments to workpackages

Because of the 3 month extension to the project the finish dates for Worpackages 2.1, 2.2, 3.1, 3.2 and 4 were pushed back by 3 months along with the associated milestones and deliverables. The end date of the project changed from 30th September 2008 to 31st December 2008. The project Gantt Chart was updated accordingly and the revised version is shown in Table 1. These changes were approved by the Commission at the time.

The main achievements for the first 12 month period were reviewed at the Mid-term meeting and in the periodic activity report and it was concluded that the 12 month milestone associated with Work Package 1.3 (Preliminary HVOF spraying trials) had been successfully met. In other words, the feasibility of thermally spraying ferrite powders to form coatings with retained feedstock powder structure was demonstrated. However, it was noted in the mid-term report that the Met-Jet liquid-fuel HVOF system did not have sufficient heat input to successfully spray ferrite. However, the HVOF Top Gun system at UNOTT and the DJ2600 at SEI were both capable of depositing coatings over a range of operating conditions. In accordance with the contingency plan, the project Steering Group approved a recommendation to proceed with the use of the TopGun system and the Diamond Jet system.

It was also noted in the mid-term report (WP 1.4, Thermal spray trials using nanostructured ferrite powders, months 6 to 18) that Zn loss was occurring during HVOF spraying with the TopGun and DJ2600 systems. It was found that by adjusting the starting Zn level of the powder, its loss could be allowed for. Further work within WP 1.4 established that Zn loss increases as the surface to volume ratio of a powder particle increases. In other words it scales as 1/d where d is the particle diameter. This scaling with 1/d is much more important than residence time or temperature in the spray gun. It was also found that Zn loss varied greatly in different batches of HVOF coatings because of the difficulties in precisely controlling the distribution of particle diameters within the size range suitable for HVOF spraying (nominally 5-63 µm). With larger diameter particles (such as would be suitable for air plasma spraying (APS)), Zn loss was calculated to be much lower, even if the particles are subjected to higher temperatures and longer residence times.

On the basis of these considerations the Steering Group approved a short study within WP1.4 on the use of APS spraying to deposit coatings with the nanostructured powder. The results obtained (reported in **Deliverable 6** Report) demonstrate that APS can, surprisingly, produce good quality ferrite coatings with relatively low Zn loss. As a consequence of this unexpected result, the Steering Group confirmed that APS trials should take place in parallel with HVOF trials in workpackages 2 and 3. The consortium was able to undertake this work within the original partnership because RTD performer SEI has a long track record in APS work and is well equipped to carry out the research. Furthermore, the SMEs, Pyro and Met, both had the industrial capability to perform APS spraying. The introduction of APS into the project, in parallel with HVOF, also enabled better use to be made of the powders being supplied by PMI. This is because the HVOF processes use the powder in the size range approx 5 - 63 µm whereas APS employs the powder in the approx range 90 - 120 µm. Therefore, more cost effective use was made of the powder batches that were being manufactured.

In summary, the overall objectives for workpackages 1.4, 2.1, 2.2 and 3.1 remained the same but the means of achieving the coated components was broadened to include the use of APS as well as HVOF and the magnetic properties of the two coating types were compared in parallel studies. Demonstration parts were successfully produced by both spray methods and tested.

1.3.3 Work performed and the main achievements

<u>Definition of Industrial Requirements (WP1.1)</u>

Initially, the types of microwave absorbing ferrite materials currently employed and the processes currently used to manufacture high power microwave absorbing components were critically reviewed. This led to an identification of the materials and powder types to be incorporated into the work programme, based on industrial needs. It was established that the baseline material for setting property and performance comparisons was that currently employed by partner AFT for the manufacture of their current absorbing tiles. This is referred to as AFT tile material. It was clearly established that the main applications for the thermally sprayed ferrite coatings to be developed in the project are in high-power loads for microwave isolators where the ferrite coatings or layers act to absorb microwaves efficiently and so protect highly sensitive equipment from potential damage. Through discussions involving the industrial partners a wedge-type microwave absorbing load was identified as the demonstrator component to be produced as an outcome of the project.

<u>Powder synthesis (WP 1.2)</u>

Having established the materials and compositions required, three separate routes were investigated for the production of nickel-zinc ferrite (NZF) powder with a spinel crystal structure namely chemical co-precipitation, self-propagating-high-temperature-synthesis (SHS) and mechanical alloying with ferritization (MA+F). From preliminary experiments the chemical co-precipitation route was found to be unsuitable due to difficulties with control of composition. Thus SHS and MA+F routes were further studied through production of larger batch sizes.

The SHS route has been shown to be suitable for the production of powders with the required composition and nano-grain size. The use of mechanical alloying prior to the SHS stage improved the product homogeneity. The initial problem of residual Na and Cl impurities following the SHS reaction was corrected by improved cleaning. SHS of a pressed compact gave the best results and with the optimization of the post-SHS powder milling procedure to achieve the desired particle size distribution proved to be a successful method of producing kilogram quantities for the spraying of demonstration parts.

A MA+F route has also been established as suitable for the processing of mixed oxides so that they can be converted to the ferrite crystal structure with the desired nano-grain size and uniform composition. The particle size post-ferritization was found to be largely independent of ferritization temperature if loose powder was sintered. If, however, the powder was pressed prior to the sintering/ferritization stage then this significantly affected particle size without loss of the nano-scale grain size within the particles. Further work was conducted to examine the ferritization stage in order to optimize the morphology and size distribution of the powders for thermal spraying. The MA+F route was successful in varying the ferrite composition especially with respect to Zn content to allow for losses during spray deposition.

Ferrite powder synthesis then continued on a larger scale for industrial spraying trials. It had been shown that work performed showed that two of the technological routes selected for ferrite powder production could provide materials of the required chemical composition and spinel crystal structure. These powders were nano-crystalline with a typical crystallite size, defined as regions separated by high angle grain boundaries within a physically distinct crystal, of approximately 150 nm. The main advantage of the mechanical alloying and ferritization (MA+F) route was the homogeneity of the powder obtained, but the mechanical alloying and self-propagating high-temperature synthesis (MA+SHS) route provided the important economic benefit of the elimination of the long and expensive furnace ferritization stage. Thus the latter route was chosen by the consortium for the supply of powder for thermal spray trials and manufacture of case study components.

Preliminary HVOF Spraying Trials (WP 1.3)

The high velocity oxy-fuel MetJet, Top Gun and the DJ2600 systems are known to exhibit different characteristics in terms of the balance between powder heating and powder acceleration towards the substrate. It was found that both the TopGun and DJ2600 were suitable for spraying NZF which is a ceramic material with a melting point/softening temperature in excess of 1500°C. Within the range of powder sizes currently investigate (5- 100 µm), process parameters could not be established which enabled the MetJet system to spray this material successfully. The results show that, when using conventional, commercially available ferrite powder, both the TopGun and DJ2600 systems were capable of spraying NZF coatings in which the ferrite crystal structure of the original feedstock powder was wholly or largely retained in the sprayed deposit. The spray parameters in both systems, specifically oxygen to fuel ratio, had a significant effect on the constitution of the deposit (i.e. phases present, composition of phases and microstructural scale of phases). Formation of undesirable secondary phases was favoured by the use of a higher temperature flame and creation of a higher temperature in the particles. Thus process operating windows exist for both spray systems that allow the successful deposition of NZF.

A range of conventional feedstock powders were employed in the studies to explore the effect of powder morphology, powder size and powder size range on factors such as deposition rate and thermal degradation of the powder during spraying. It was found that powder particles greater than around 45 µm could not be heated sufficiently during spraying to deposit on the substrate. Conversely, particles less than around 10 µm appear to be overheated and suffer thermal decomposition during spraying which leads to loss of Zn and the formation of undesirable FeO in the coating as a secondary phase.

The best deposition rate obtained was around 4-5 µm per pass and the best deposition efficiency around 35% for the powders investigated. It was thought that the deposition efficiency and deposition rate can be improved by having (i) a narrower particle size distribution and (ii) powder particles which are less angular. The optimum size distribution is expected to be one with powder particle diameters between 5 and 45μm and a D_{50} value of around 30 μm. These parameters were specified for further batches of ferrite power.

XRD analysis has confirmed that the major phase in the sprayed coatings was ferrite with the spinel crystal structure and a lattice parameter close to that of both the original AFT tile material (the baseline material for this project) and the powder feedstock material. The XRD peaks of the coatings show considerable broadening which can be taken to be an indication of fine scale coherent diffracting domain size. In some of the coatings, FeO was identified as a secondary phase and it is found that the DJ2600 system produced somewhat less thermal decomposition of powders than the TopGun system within the range of parameters currently investigated.

The coating microstructure after HVOF spraying using conventional powder exhibited low porosity (<5%) which is much less than that of the AFT sintered tiles. SEM/EDX analysis showed that individual splats appeared to be well bonded and were of relatively uniform composition. During thermal spraying the only element which was lost in significant amounts was Zn. The Zn loss was lower with the DJ2600 than with the TopGun, as expected from the lower heat input of the former system. Typically, in a coating produced with the TopGun the Zn content fell to around 0.4 of its original value whereas with the DJ2600 the Zn was in the range 0.4 to 0.6 of the content of the original powder, depending on spray parameters.

Particle diagnostic measurements with the SprayWatch system showed that particle velocity, temperature and flux could be measured and the effect of parameter changes on particle properties quantified. This facilitated proper selection of parameters with the thermal spray equipment used by the industrial partners.

The adhesion of the coating to the substrate, as measured in standard bond strength test, was found to be in excess of 45 MPa. This is typical of values obtained for thermally sprayed coatings and is expected to be sufficient for the AFT application (currently tiles are adhesively bonded to a substrate).

Using conventional, commercially available powder, ferrite coatings were successfully deposited on both Al rings and a stainless steel tube to permit measurement of the complex magnetic permeability of the material by two different methods. At 3 GHz frequency it was found that the loss (imaginary part of the permeability) of the HVOF-coated ferrite layers using commercial powder was nearly comparable to that of the sintered AFT ferrite material (baseline material). There was good agreement between the two measurement methods, one using ferrite coated ring in a shorted coaxial line configuration and the other a ferrite-coated stainless steel tube in the coaxial transmission line method. The results were therefore encouraging, since the 3-GHz band is a typical operation frequency for commercial high-power microwave devices, one of the main motivations for this project. It was thought possible to increase the losses of HVOF ferrite coatings (i.e. increase the imaginary part of the complex permeability) in this frequency range by using a powder which will give a coating composition similar to that of the AFT tile material, and by optimizing the conditions in the HVOF spray process. (The commercial powder used in the trials was of different composition to that of the AFT tile and the resultant coating was particularly low in Zn content).

<u>Thermal spraying trials using nanostructured powder (WP 1.4)</u>

Work on the deposition of nano-structured powder showed that spray deposition efficiencies with both the TopGun and DJ2600 were lower than with the commercially conventional powder. To overcome this, work was done to improve the powder flowability and to achieve a particle size distribution for the nanostructured powders which is more suited to the HVOF spray systems. XRD analysis of the coatings produced from nano-grained powder confirmed that they comprised principally the NZF spinel crystal structure.

Microanalysis on the SEM confirmed that Zn was the main element lost during spray deposition of nanograined powders and the percentage loss of Zn was somewhat less than the losses measured for the conventional materials. This was a promising result as it indicates that modified powder compositions could be employed to take account of the Zn losses during spraying to arrive at a coating composition close to that of the AFT tile material which is the baseline.

This laboratory HVOF spray trials showed that, although nanostructured coatings could be sprayed by the Top Gun and DJ2600 HVOF systems, the feedstock powder and spray parameters required further optimisation. Thermal spray deposition with the DJ2600 system gave low deposition efficiency of ferrite powder. In the case of Top Gun spraying the deposition efficiency was satisfactory but it was difficult to control Zn loss. This was due to the fact that loss of Zn increases with a decrease in powder particle diameter and, surprisingly, particle size was a more critical factor in affecting Zn loss than either residence time or particle temperature in the gas jet. With larger diameter particles (>60 μm) Zn loss was calculated to be much lower. Whilst, powder particles of such sizes cannot be sprayed by HVOF, air plasma spraying (APS) is capable of depositing this size powder. Thus APS trials were agreed by the consortium and promising results were obtained using a suitable size range of relatively coarse (ie> 53 μm) powder. A number of coatings were produced by APS and characterized alongside TopGun HVOF coatings. Overall, a range of coating structures was produced, all with nanostructured grains (crystallite sizes in the range 20 – 50 nm). Comparison of the magnetic loss factor, μ'', between pressed and sintered ferrite samples (the baseline material) and sprayed samples (both Top Gun HVOF and APS) showed that in the frequency range of interest (2-3 GHz) the sprayed coatings had μ″ values approximately 45% and 90% of the baseline materials at 2 and 3 GHz respectively. These are acceptable for the microwave absorber application envisaged by AFT. Thus, the magnetic properties of the sprayed Ni-Zn-ferrite coatings were sufficiently promising to warrant industrial thermal spraying trials being conducted by Top Gun HVOF and APS spraying leading to the definition of process parameters for the manufacture of a demonstrator component. It was also recommended by the Steering Group to conduct a trial with the DJ2600 HVOF system of an SME as this employed propane as a fuel as opposed to the hydrogen based system of the laboratory trials. It was believed that better results might be obtained as a result of the different flame characteristics.

Industrial Thermal Spraying Trials and Definition of Parameters (WP 2.1 and 2.2)

The industrial scale-up spraying trials were undertaken jointly by the appropriate SMEs and RTD providers. SMEs also conducted particle diagnostic measurements using SprayWatch in support of the scale up trials and to facilitate transfer of spray conditions from RTD providers to the industrial environment. The in-flight particle diagnostic measurements with SprayWatch were also used to establish the repeatability, reliability and limits of the processes. The main emphasis of the spraying trials was to optimise coating characteristics in relation to maximum deposition efficiency (DE), minimum coating porosity, adequate bond strength (~40 MPa), target composition (particularly Zn level), minimum quantity of secondary phases (eg FeO) present and maximum magnetic loss factor (imaginary part of the magnetic permeability, μ'', and 2 and 3 Gz). In determining how the scale up trials were to be conducted, it was necessary to design the case study component as this affects, for example, the quantity of powder required and the procedures which had to be put in place for holding and handling the component and manipulating the torch/component during spray deposition. The demonstrator part was designed by AFT. An inner conductor, in the form of a hollow plate ~ 250 mm x 70 mm, was to be coated by spraying on both sides and then assembled into an outer casing. On the basis of the size of the component and the coating thickness required (up to 0.8 mm), powder was produced for HVOF spraying (6 kg of +5-53 μm) and APS spraying (6 kg of +53 -90 μm) to the previous specifications in terms of morphology, composition, grain size and crystal structure. The industrial development phase of TopGun HVOF and APS spray deposition was successfully completed. In the case of the DJ2600 system, it was found that the deposition rate was still low at around 2 μm per pass even with propane fuel. A coating ~ 250 μm in thickness was built up but the residual stresses developed in this coating caused it to spall off during handling prior to testing. Consequently the Steering Group agreed that further evaluation of the HVOF DJ2600 deposition process should be discontinued in order to concentrate project resources on the more promising Top Gun HVOF and APS processes. Therefore procedures for the manufacture of case study demonstrator components by TopGun HVOF and APS were determined and documented. This resulted in a definition of powder characteristics, process parameters (including SprayWatch temperature and velocity measurements) and coating specification in terms of phases, microstructure and magnetic performance. The magnetic properties of these industrially deposited coatings (specifically μ'' in the 2-3 GHz range) were found to be comparable to the performance data for baseline material used by AFT to manufacture their current sintered tiles. Hence the consortium agreed to proceed with the manufacture and evaluation of full sized case study components.

<u>Manufacture and Evaluation of Case Study Component</u>

A total of five inner conductor waveguides (the demonstrator component referred to above) were sprayed on both sides using a stepped coating profile ranging from 400 to 800 μm in thickness. The stepped profile was used to optimise the microwave absorption characteristics of the assembled demonstrator component. Powder was supplied in different size ranges for APS and HVOF spraying and spraying parameters were selected on the basis of the work undertaken earlier in the project. The inner conductor had to appropriately cooled during spraying. Following the deposition of the coatings the inner conductor was assembled into its housing so that the microwave absorbing performance of each case study component could be evaluated. Before proceeding to evaluate the behaviour in a high power test, an initial low power screening experiment was performed using laboratory equipment to measure the complex reflection coefficient S_{11}. The absolute value of S_{11} is a measure of microwave absorption and it typically expressed on a log scale in decibels over the range of interest; in this case 2.6 to 3.9 GHz. Of the five components produced, three met the threshold performance standard of -23 dB in the low power screening test at room temperature. These three also showed little change in $|S_{11}|$ with temperature over the range 20 to 60 °C which indicates that in a high power test (where heating could occur) they were unlikely to breakdown catastrophically. All three thermally sprayed components that passed the low power screening test were sent to an industrial customer of AFT where high power tests could be performed. For comparison purposes, tests were also conducted on a conventional absorber manufactured using sintered tiles. The experimental arrangement comprised an RF power source operating at 2.856GHz (generated by a klystron microwave tube). The microwaves were fed through an isolator device and a waveguide network to the device under test i.e. the ferrite absorber demonstrator. Tests were performed up to 4.5 MW peak power (corresponding average power of 3.8 kW). It was found that the reflection coefficients measured during the high-power test at a low power level were very similar to the precisely calibrated low-power data. A degree of degradation of $|S_{11}|$ with increasing power was observed for all absorber components in the high power tests, mainly due to the heating of the ferrite during the test. Up to a power level of 3.5 MW peak power (2.96 kW average power) the drift of $|S_{11}|$ was comparable to the thermal drift observed at low power by varying the cooling water temperature. The observed power-induced drift of one of the APS-sprayed components was comparable to the tile absorber, while the other APS absorber and the HVOF-sprayed one varied slightly more as the power level was increased. Overall, the performance of the sprayed components was only slightly lower than that of an absorber with conventionally sintered ferrite tiles, even though the waveguide design (from a magnetic properties perspective) had not been optimized for thermally sprayed coatings. A cost estimation made suggests that a cost reduction of about 40% could be obtained compared to the conventional fabrication technology with sintered and bonded ferrites. Even higher economical benefits could be expected for larger production lot quantities. Beyond this, it provides scope for the design of new and improved absorber devices where coatings can be deposited on curved and complex surfaces which was not hitherto possible with current technology involving the use of sintered and adhesively bonded ferrite tiles. The investigation of other ferrite powder compositions for thermal spraying could lead to more broadband devices or RF absorbers suited for other microwave frequency bands as well as conformal coatings for EMC-shielding in housings or walls of RF anechoic chambers.

2 Section 2 – Workpackage progress of the period

Workpackage number 1.1 Start date: Month 0 End date: Month 2

Title: Definition of Industrial Requirements

Contractors Involved: AFT, RHV, Rasceur, Oseir, PSI, Pyro, Met, UNOTT, SEI and PMI

Objective

To identify the technical and commercial requirements of each industrial partner and to incorporate these within the project work programme.

Deliverable

Specification of performance requirements of coatings for microwave applications; definition of target structural and compositional ranges of coatings; equipment availability; initial identification of other application areas.

Progress

Each partner provided information relating to their current and future interests in the fields of nanostructured powders, thermally sprayed coatings and microwave absorbing materials. The types of microwave absorbing materials currently employed and the identification of materials and powder types to be incorporated into the work programme, based on industrial needs were reviewed. Facilities available for the manufacture of powder, HVOF spraying and testing, design and manufacture of microwave systems were assessed and the range of applications in which ferrite materials and microwave absorbers are currently used reviewed. Also considered were the potential future applications. As part of this assessment a preliminary identification was made of case study components that will be used later in the work programme. This information was collated into Deliverable report **D1**.

This deliverable report contained a summary statement of the work which would be undertaken during the project. For convenience, an extract from this deliverable report is set out below.

The general goal of the project is to transfer the magnetic and mechanical properties of pressed and sintered solid state NiZn ferrites to thermally sprayed NiZn thick-film coatings on metallic substrates or ceramics. The performance of conventionally sintered absorber ferrites will be improved with respect to an extension of the operating temperature and power range for microwave absorbers and loads.

Specified performance characteristics to be assessed will be:

- *high magnetic absorption at microwave frequencies*
- *broadband absorption or adjustable absorption band by varying material composition or thermal spraying deposition techniques,*
- *temperature stable electrical and magnetic properties,*
- *high temperature operation with a Curie temperature $T_{Curie} \geq 450°C$,*
- *high thermal conductivity ≥ 3 W/mK,*
- *high relative mechanical density ≥ 95%, the density of NiZn ferrites is typical 4.5 g/cm^3*
- *low porosity,*
- *low surface roughness,*
- *the deposited thick films should exhibit low thermally induced stress,*
- *good adhesion on metallic (stainless steel, Al or Cu) surfaces or ceramics (e.g. Al_2O_3),*
- *high mechanical and chemical robustness,*
- *high reliability.*

The project will focus on the (Ni,Zn)Fe_2O_4 material system. The Ni:Zn ratio and other components will be chosen equal to a ferrite powder, that is currently already used for the production of solid state ferrites and optimised for high-power microwave absorber devices and thermal spray processing.

Powders will need to be prepared with different grain sizes and the agglomerate size of the powders will be optimised for the selected thermal spray techniques.

Powders will be manufactured by a number of routes to examine the most appropriate for manufacture of the ferrite and the requirements of the spray systems used in the project. Typical powder manufacture routes to be investigated will include:

- *SHS synthesis*
- *mechanical alloying*
- *chemical synthesis*

The principal HVOF spray processes to be evaluated will be the HVOF capabilities of the industrial partners and RTD performers which are as follows:

DJ2700 gas-fuel HVOF system from Sulzer Metco

TopGun gas fuel HVOF system

MetJet liquid fuel HVOF system

These systems provide between them a range of operating conditions in terms of heat and momentum input to the particles which will allow spray conditions to be varied widely in order to achieve the optimum for the deposition of the chosen NiZn ferrite powders.

To support the thermal spray work the SprayWatch 2i (Oseir) spray diagnostics system for monitoring temperature and velocity of particles in HVOF spraying will be employed to monitor effect of process changes on particle characteristics and to ensure effective transition of RTD trials to industrial partners.

The main applications identified for the developed thermally sprayed ferrite coatings are in high-power loads for microwave isolators. Hence, a high-power WR284 waveguide load for the frequency band from 2.6 to 3.9 GHz (S-Band) will be considered as a valuable demonstrator case-study component. The WR284 waveguide offers a reasonable device size (ca. 80mm x 40mm x 320mm) and reasonable fabrication costs within the project. Ferrite coatings will be thermally sprayed on the planar metallic plates that serve as waveguide walls and include a water cooling structure. After the ferrite coating, the parts will be joined by screwing, brazing or welding.

Possible additional microwave application areas will be in:

- *analog and digital broadcast (88MHz to 900MHz, broadband),*
- *medical and industrial particle accelerators (3GHz to 10GHz, narrowband),*
- *scientific particle accelerators (50MHz to 3GHz, narrowband),*
- *industrial microwave heating (e.g. 433MHz, 915MHz, 1300MHz, narrowband),*
- *civil radar, space and defence applications (e.g. 4-6GHz, 7-9GHz, 8-11GHz, 11-13GHz).*

Besides microwave load devices, further application potential could be expected in the field of electromagnetic capability (EMC) that involves issues as shielding of electronic components or installations with low-cost ferrite absorber coatings in communications, automotive and military (30 MHz to 100 GHz, broadband) applications.

Workpackage 1.2 **Start date:** Month 3 **End date:** Month 18

Title: Ferrite Powder Synthesis and Characterisation

Contractors Involved: PSI, UNOTT, SEI and PMI

Objective

To determine the most effective method of producing nanostructured ferrite powder, quantifying its structure and principal characteristics.

The main ferrite powder to be employed was identified as a deliverable in WP1.1. This material was synthesized by **PMI** working with the powder-producer SME, **PSI,** and the other two RTD Performers. Commercially available chemicals and metals were used as the starting materials in the processes for manufacture of the nanostructured ferrite feedstock required for thermal spraying. Three separate routes were investigated for the production of ferrite powder namely chemical co-precipitation, self propagating high temperature synthesis (SHS) and mechanical alloying with ferritization (MA+F).

Samples prepared by different routes were examined to determine the optimum route. The overall purpose of the work was to determine the process and conditions needed to obtain ferrite powder in a form suitable for HVOF spraying and with a chemistry and nanostructured grain size that would enhance the magnetic properties of the deposited coatings.

The main achievements, as set out in the Deliverable reports **D3** & **D7,** are summarised below.

From preliminary experiments the chemical co-precipitation route was found to be unsuitable due to difficulties with control of composition. This route was not pursued further. Thus SHS and MA+F routes formed the basis of the bulk of the work on the production of batch sizes of powder which could be used in thermal spray trials (typically 1-2 kg is needed for such trials).

The SHS route was shown to be suitable for the production of powders with the required composition (Table 3), particle size, nanograin size (Table 4) and ferrite crystal structure. Furthermore, the use of mechanical alloying prior to the SHS stage improved the product homogeneity. Selected images of nanostructured SHS powder are shown below in Figure 1.

A MA+F route was also established as suitable for the processing of mixed oxide starting powders so that they can be converted to the ferrite crystal structure with the desired nanograin size and uniform composition in a subsequent heat treatment known as the ferritization stage (see tables below). The particle size post-ferritization was found to be largely independent of ferritization temperature if loose powder was sintered. If however, the powder was pressed prior to the sintering/ferritization stage then this significantly affected particle size without loss of the nano-scale grain size within the particles. Further work was required to optimize the ferritization stage to improve the size distribution of powder for the thermal spray guns that were being employed in the project. A specific particle size range (5 to 45 μm) was identified as being the most suitable for successful HVOF spraying.

Another relevant feature for these powders is their external morphology. An angular one is usually regarded as difficult to handle in thermal spray operations. Therefore work in this workpackage examined routes to improve the powder morphology for spray deposition.

Both MA+SHS and MA+F routes were shown to have the capability to vary the ferrite composition especially with respect to Zn content to allow for losses during spray deposition and an optimised composition was achieved. The table below shows target AFT tile composition, composition of originally produced powder (close to that of the tile) and composition of a revised powder composition which was produced to take account of Zn losses that were found to occur in the thermal spray trials.

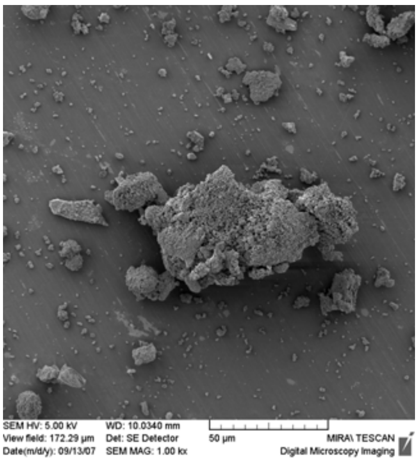
Details of processing conditions, powder morphology, size range, crystal structure, composition analysis and so on are set out in the Deliverable 3 report **D3**.

Table 3 Selected powder compositions as determined by EDX analyses on particle cross-sections along with the composition of the AFT tile.

	wt%O at%	wt%Fe at%	wt%Ni at%	wt%Zn at%	wt%Mn at%	wt%Co at%
Polished MA+F powder (1)	24.9 ± 0.4 54.1 ± 0.5	52.8 ± 1.4 33.0 ± 1.1	14.7 ± 3.7 7.5 ± 2.2	5.3 ± 2.8 3.5± 1.5	1.4 ± 0.2 0.9 ± 0.1	1.0 ± 0.3 0.9 ± 0.2
Polished MA+F powder (2)	21.9 ± 4.2 49.1 ± 6.5	49.0 ± 3.0 32.1 ± 4.4	16.2 ± 0.7 10.9 ± 1.2	10.4 ± 0.6 5.8 ± 0.7	1.6 ± 0.2 1.0 ± 0.2	1.4 ± 0.2 1.0 ± 0.2
EDX analysis on sintered AFT tiles	25.5 ± 0.67 55.0 ± 0.90	50.7 ± 1.14 31.3 ± 0.99	16.0 ± 0.35 9.4 ± 0.24	5.4 ± 0.69 2.8 ± 0.35	1.5 ± 0.06 0.9 ± 0.04	1.0 ± 0.23 0.6 ± 0.14

Table 4 Effective size of coherent-scattering areas of ferrite powders for selected different production modes

Production mode		Effective size of coherent-scattering domains/ nm
MA + F	1150°C, powder	50 ± 1.5
	1200°C, powder	58 ± 1.5
	1250°C, powder	56 ± 1.5
	1250°C, pressed sample	58 ± 1.5
SHS	*SHS1 Loose Powder*	*31 ± 1.5*
	SHS1c Pressed Compact	*31 ± 1.5*
	SHS2	*28*
	SHS3	*37*



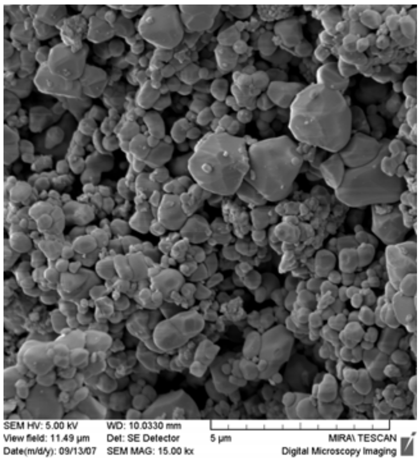


Figure 1 SEM images of nanostructured powder produced by the SHS method showing agglomerates of nanoscale grains

Samples prepared by the (MA+F) and (MA+SHS) routes during the second phase of the work were evaluated by the RTD performers to determine which was the optimum. This included a study of phases present, composition, microstructure of the individual powder particles and particle size distribution. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed to identify phases, crystal structure and grain size within the powder particles. Bulk X-ray fluorescence analysis and energy dispersive X-ray analysis on an SEM were used for bulk and microanalysis of the composition. SEM and automated optical image analysis were used to determine particle size distribution.

Once the optimum synthesis routes had been established on small batches, work was undertaken to scale up the processes (to kg size batches) and determine the set of process parameters which gave the best yield of powder. The optimised routes are thus summarized below.

MA+F route

The MA+F route involved mechanical milling of the starting oxide mixture (for homogenization of the powder mixture, acceleration of the reaction and reducing the ferrite synthesis temperature) with a subsequent solid-phase sintering (termed ferritization) for the formation of the ferrite phase. Commercial powders of Fe_2O_3, NiO, ZnO, CoO (Co_3O_4), MnO_2 were used as source materials for the work. The duration of MA was typically 8 hours and ferritization involved heating to 1250°C for around 2 hours. After ferritization the material was ground in a ball mill, passed through sieves and then classified in a classifier to remove the fines. Using optimized parameters two batches each of around 2 kg were produced. These were characterized in terms of grain size, crystal structure, chemical composition and microchemical homogeneity. See **D7**, section 3.2 for XRD patterns, SEM images, powder size distributions and EDXA of compositions. Typical results obtained are given below. The powder morphology is shown in Figure 2 for PMI(6) following sieving and classification. The size distribution is shown in Figure 3.

It was found that this batch of powder was single phase spinel ferrite crystal structure, that following sieving and classification a good size distribution for thermal spraying could be achieved with most particles in the size range 5 – 100 µm, that the crystal size was ~ 154 nm and the composition was very close to that required, as shown in Table 5. (The powder composition was chosen so that following spraying, the composition of the coating would approximately match that of the AFT tile material, i.e. allowance was made for Zn loss during spraying.

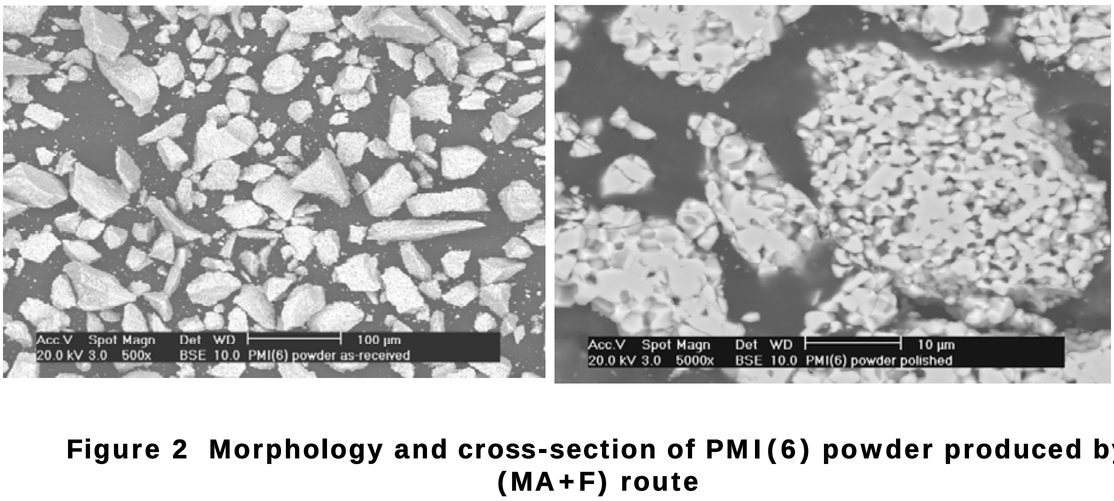


Figure 2 Morphology and cross-section of PMI(6) powder produced by (MA+F) route

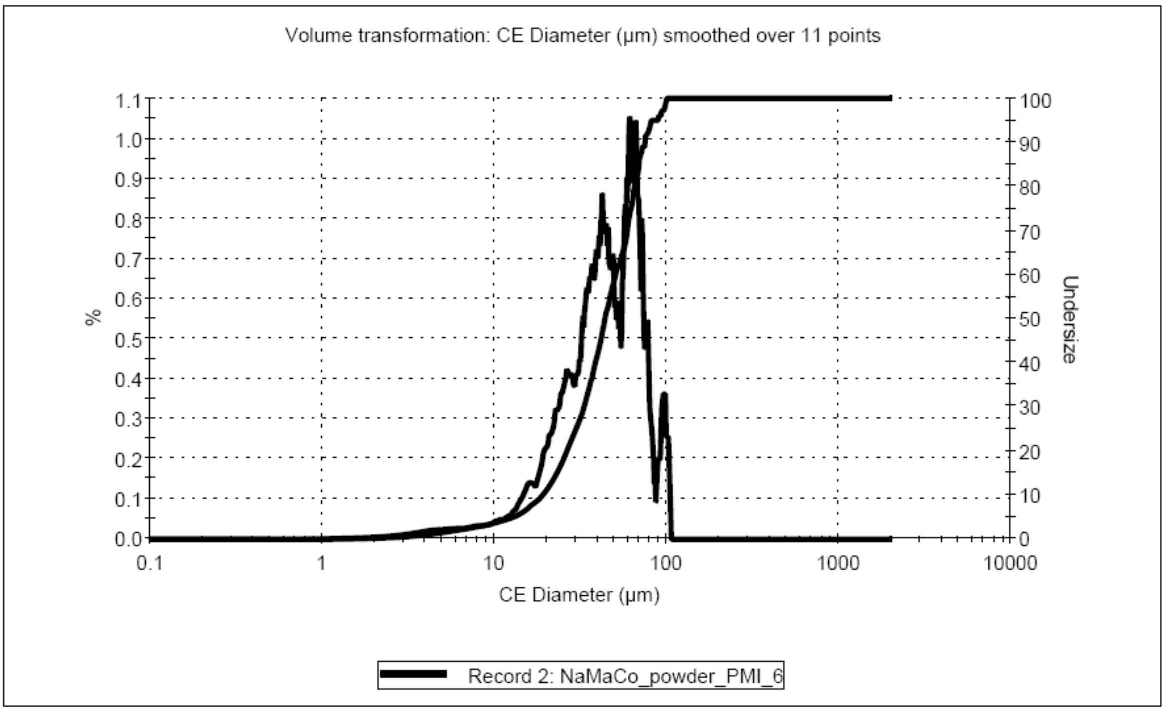


Figure 3 Powder size distribution of PMI(6) powder

MA+SHS route

For the target composition, the reactive mixture comprises 22.4 wt% Fe, 39.4 wt% Fe_2O_3, 13.3 wt% ZnO, 1.95 wt% MnO_2, 1.15 wt% Co_3O_4 with an addition of the reactive component 18.4 wt% $NaClO_4$. The MA+SHS route involves a milling stage in alcohol for 6 hours after the initial powder mixing stage to give good homogeneity prior to ignition. The SHS reaction was carried out in an experimental reactor at constant pressure equipped with a tungsten coil through which a current is passed to heat the coil and initiate the process. The synthesis was performed in the open air. In this reaction Fe is a combustible and sodium perchlorate is an oxidant and the remaining oxides, corresponding to the required composition, act as diluents. The general chemical equation of the reaction can be written as follows:

$$Fe + NaClO_4 + Me_xO_y \rightarrow MeFe_2O_4 + NaCl.$$

The batch size for producing spray powder feedstock was 1.7 kg and after completion of the SHS cycle the batch was milled, wet cleaned in distilled water to remove the NaCl by-product and then sieved and classified. Details of this process are in section 2.4 of **D7**.

The SHS product was characterized in terms of grain size, crystal structure, chemical composition and microchemical homogeneity. See **D7**, section 3.3 for XRD patterns, SEM images, powder size distributions and EDXA of compositions. A typical powder morphology is shown in Figure 4 for PMI(7)-SHS4 following sieving and classification. The corresponding size distribution is shown in Figure 5. It was found that this SHS powder was single phase spinel ferrite crystal structure, that following sieving and classification a good size distribution for thermal spraying could be achieved with most particles in the size range 5 – 100 µm, that the crystal size was ~ 145 nm, the lattice parameter was 0.83987 nm and the composition was close to that required, as shown in Table 5.

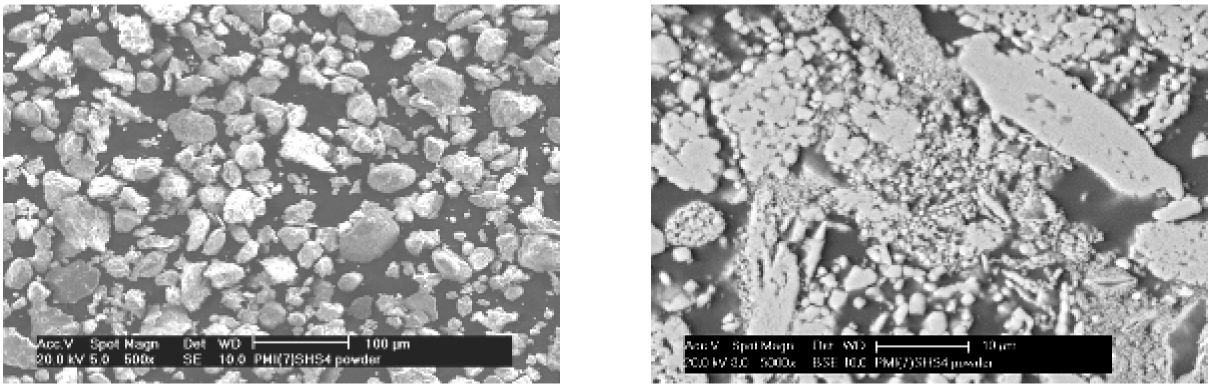


Figure 4 Surface morphology and polished cross section of the PMI(7)-SHS4 powder

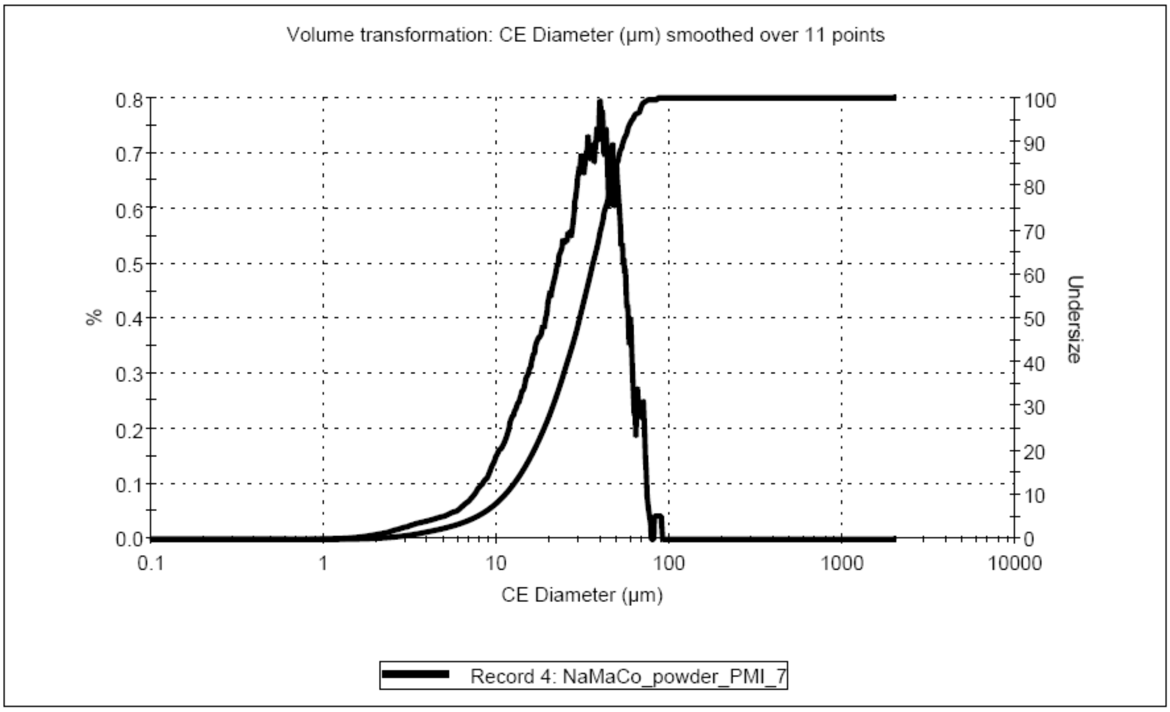


Figure 5 Particle size distribution of PMI(7)-SHS4 powder

Table 5: Compositions of powders and AFT reference tile.

	wt%O	wt%Fe	wt%Ni	wt%Zn	wt%Co	wt%Mn
Target composition for powder	26.7	44.5	16.5	10.4	0.79	1.2
AFT tile compositon	25.5 ± 0.62	50.7 ± 1.16	16.0 ± 0.35	5.4 ± 0.69	1.0 ± 0.23	1.5 ± 0.06
PMI(6)-MA+F	22.1 ± 0.60	47.2 ± 0.62	17.1 ± 0.36	10.5 ± 0.23	1.7 ± 0.36	1.4 ± 0.09
PMI(8)-SHS5	27.7	45.3	13.9	9.5	0.6	1.1

	at%O	at%Fe	at%Ni	at%Zn	at%Co	at%Mn
Target composition for powder	56.7	27.1	9.6	5.4	0.45	0.7
AFT tile compositon	55.0	31.3	9.4	2.8	0.6	0.9
PMI(6)-MA+F	50.6	31.0	10.6	5.9	1.0	0.9
PMI(8)-SHS5	57.6	27.6	7.9	4.8	0.4	0.7

Conclusions

Both MA+SHS and MA+F routes can produce ferrite powders of the required chemical composition and spinel crystal structure.

Typical crystallite size in the powders, defined as regions separated by high angle grain boundaries within a physically distinct crystal, is approximately 150 nm. Some inhomogeneity occurs in the powder produced by the MA+SHS route.

The main advantage of the MA+F route is the homogeneity of the powder obtained. However, the MA+SHS route provides the important economic benefit connected with the substitution of the long and expensive furnace ferritization stage with the fast and energy efficient SHS process.

As reported elsewhere, magnetic measurements on thermally sprayed coatings do not reveal a significant effect of powder type on microwave absorption (imaginary part, μ”, of the complex magnetic permeability) in the frequency range of interest. Thus, in view of the economic benefits, powder produced by the MA+SHS route was selected by the consortium for thermal spraying trials under workpackages 1.4, 2.1, 2.2 and the manufacture of the case study component in 3.1.

Workpackage number 1.3 **Start date:** Month 2 **End date:** Month 12

Title: Preliminary HVOF Spraying Trials

Contractors Involved: AFT, RHV, Oseir, PSI, Pyro, Met, UNOTT, SEI and PMI

Objective

To assess the capability of the HVOF process to deposit ferrite coatings using conventional powder feedstock

Progress

The overall aim was to determine process operating conditions and the process windows for achieving dense, coherent and well bonded ferrite deposits on metallic substrates. A principal objective was to determine the thermal spray parameters required to minimize powder degradation during deposition whilst achieving good deposition efficiency.

The HVOF guns operated by the partners are representative of those available in the wider industrial sector. These guns exhibit different characteristics in terms of the balance between powder heating and powder acceleration towards the substrate. Therefore, parallel investigations were needed to establish process operating conditions which would enable ferrite powders to be deposited successfully and with optimised characteristics. The preliminary trials were based around the use of conventional, coarse-grained ferrite powder which is commercially available in a range of size distributions as well as initial batches of powder from PMI as developed under WP 1.2. **UNOTT** carried out studies to examine deposition characteristics of Met-Jet and TopGun systems (see D1 report) whereas **SEI** established the coating characteristics using the DJ 2600 system.

The coatings were examined and coating compositions and microstructures were characterised by SEM and XRD and compared with those of the feedstock powders. Data were obtained on bond strength (a standard ASTM pull-off test was used) and level of porosity (metallographic methods were employed). Deposition efficiency was assessed as a function of process parameters. **AFT** undertook measurements of magnetic properties specifically the frequency dependent permeability and a comparison was made with existing sintered ferrite materials as a benchmark. In-flight particle diagnostics were used, in collaboration with **Oseir**, to measure powder particle temperatures and velocities so that the impact of process parameter changes on these fundamental particle characteristics can be clearly understood, and the potential for degradation during spraying minimized.

The main achievements over the period months 2 to 12 are set out in the **Deliverable report D4** and are summarised below.

Nickel-zinc ferrite (NZF) is a ceramic material with a melting point/softening temperature in excess of 1500°C and it was found that the Met-Jet system did not have sufficient heat input to successfully spray this type of material. However, the high velocity oxy-fuel Top Gun system at UNOTT and the DJ2600 at SEI were both capable of depositing coatings over a range of operating conditions. (This possibility was foreseen in the project proposal (see description of work p32) and a contingency plan set up. As indicated in the contingency plan, the need to diverge from the use of a liquid fuel gun and concentrate on the use of two types of gas-fuel gun were presented to the Steering Group and the recommendations to proceed with the use of the TopGun system and UNOTT and the Diamond Jet system at SEI were approved.) The results show that both systems are capable of spraying NZF coatings in which the ferrite crystal structure of the original feedstock powder is wholly or largely retained in the sprayed deposit. The spray parameters in both systems, specifically oxygen to fuel ratio, have a significant effect on the constitution of the deposit (i.e. phases present, composition of phases and microstructural scale of phases). Formation of undesirable secondary phases is favoured by the use of a higher temperature flame and creation of a higher temperature in the particles as measured by the SprayWatch system. Thus process operating windows exist for both spray systems that allow the successful deposition of NZF. Examples of powder morphologies and coating structures are shown in Figure 6 and Figure 7.

A range of feedstock powders were employed in the studies to explore the effect of powder morphology, powder size and powder size range on factors such as deposition rate and thermal degradation of the powder during spraying. It was found that powder particles greater than around 45 µm cannot be heated sufficiently during spraying to deposit on the substrate. Conversely, particles less than around 10 µm were overheated and suffer thermal decomposition during spraying which led to loss of Zn and the formation of undesirable FeO in the coating as a secondary phase.

The best deposition rate obtained was around 4-5 µm per pass and the best deposition efficiency around 35% for the powders investigated. The deposition efficiency and deposition rate can be improved by having (i) a narrower particle size distribution and (ii) powder particles which are less angular. The optimum size distribution is expected to be one with powder particle diameters between 5 and 45 µm and a D_{50} value of around 30 µm.

XRD analysis confirmed that the major phase in the sprayed coatings was ferrite with the spinel crystal structure and a lattice parameter close to that of both the original AFT tile and the powder feedstock material. The XRD peaks show broadening compared with XRD patterns from the original coarse grained powder which can be taken to be an indication of nano-scale coherent diffracting domain size. In some of the coatings, FeO was identified as a secondary phase and it was found that the DJ2600 system produces somewhat less thermal decomposition of powders than the TopGun system. This is shown by the higher intensity FeO peaks in the TopGun coatings compared with those produced by the DJ2600. The XRD patterns obtained from the coatings are shown in **Fig. 21 of the D4** report.

The coating microstructure after HVOF spraying exhibits low porosity (<5%) which is less than that of the AFT sintered tiles. SEM/EDX analysis showed that individual splats appear to be well bonded and are of relatively uniform composition. During thermal spraying the only element which is lost in significant amounts is Zn. The Zn loss is lower with the DJ2600 than with the TopGun, as expected from the lower heat input of the former system. Typically, in a coating produced with the TopGun the Zn content falls to around 0.4 of its original value whereas with the DJ2600 the Zn is in the range 0.4 to 0.6 of the content of the original powder, depending on spray parameters. The Zn loss is reproducible and by using a powder with higher Zn content (as is being produced in workpackage 1.2) it will be possible to achieve, approximately, the desired final composition in the coating.

Preliminary particle diagnostic measurements with the SprayWatch system showed that particle velocity, temperature and flux can be measured and the effect of parameter changes on particle properties quantified. This will facilitate proper selection of parameters with the thermal spray equipment used by the industrial partners.

The adhesion of the coating to the substrate, as measured in standard bond strength test, was found to be in excess of 45 MPa. This is typical of values obtained for thermally sprayed coatings and is expected to be sufficient for the AFT application (currently tiles are adhesively bonded to a substrate).

Ferrite coatings were successfully deposited on both Al rings (UNOTT) and a stainless steel tube (R&H) to permit measurement (by AFT) of the complex magnetic permeability of the deposit by two different methods. (Note that these experiments used commercial powder and so the final deposit had a composition different from that of the AFT tile material.) At 3 GHz (a typical operation frequency of commercial high-power microwave devices) it was found that the loss (imaginary part of the permeability) of the HVOF-sprayed ferrite layers using the commercial FP350 coarse grained powder was comparable to that of the sintered AFT ferrite material. There was good agreement between the two measurement methods employed, one using ferrite sprayed on an Al ring and the other a ferrite coated stainless steel tube. The results are therefore encouraging because a non-optimised powder composition was used to make the coatings. As a consequence the coatings had a different composition to the AFT tile. It should be possible to increase the imaginary part of the permeability of HVOF ferrite coatings in this frequency range by using a powder which will give a coating composition similar to that of the AFT tile material, and by optimizing the conditions in the HVOF spray process. High values for the imaginary part of the permeability are desirable as they indicate good microwave absorbing capability.

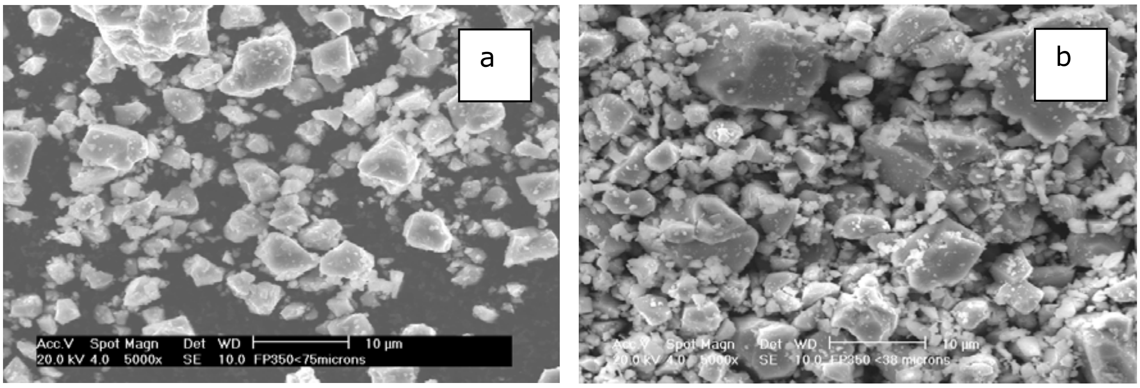


Figure 6 Examples of conventional powder used in thermal spray trials

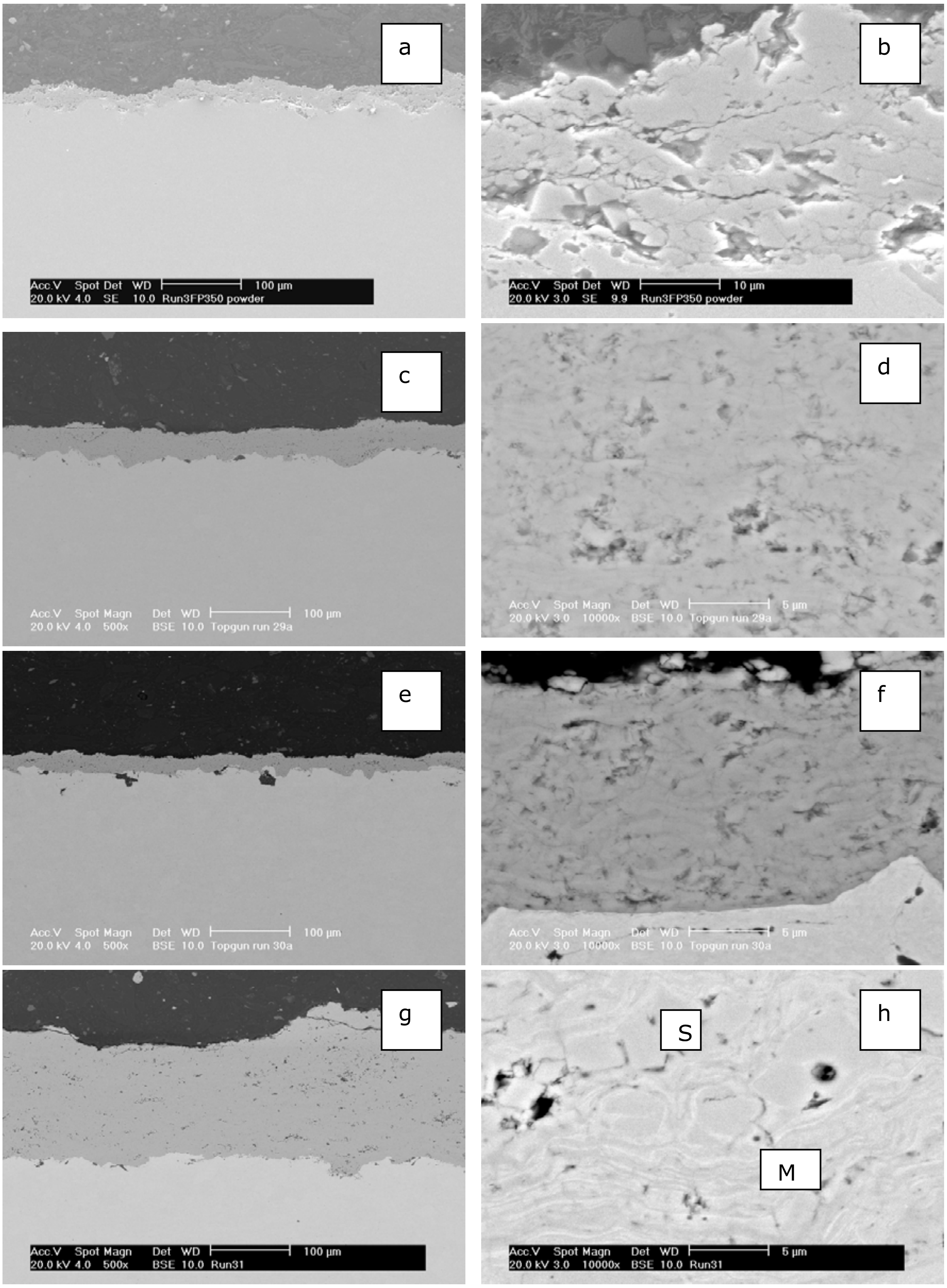


Figure 7 Examples of the HVOF coating microstructures obtained at low (a,c,e,g) and high (b,d,f,h) magnifications. Coatings deposited in initial trials (a,c,e). Coating shown in (g) was produced under optimised conditions.

Workpackage 1.4 **Start date:** Month 7 **End date:** Month 16

Title: Thermal Spraying Trials Using Nanostructured Ferrite Powders

Contractors Involved: AFT, RHV, Rasceur, Oseir, PSI, Pyro, Met, UNOTT, SEI and PMI

Objective

To carry out successful deposition of nanostructured ferrite powder by HVOF spraying under laboratory conditions.

The overall aim of the work was to successfully deposit nanostructured ferrite coatings and to achieve coating compositions which match those desired for the microwave absorbing applications i.e. similar to that of AFT tile material.

A number of different powder feedstock materials have been manufactured by PMI and PSI with a nanoscale grain structure using both the SHS route and the MA+F routes described earlier in this report and also in the deliverable report **D3**. As indicated in the report **D3** fine grain size has been confirmed by XRD peak broadening analysis.

The external powder particle morphologies and size distributions of the nanostructured powders were assessed with regard to their suitability for thermal spraying. Examples of feedstock powder size distributions are shown in Figure 8.

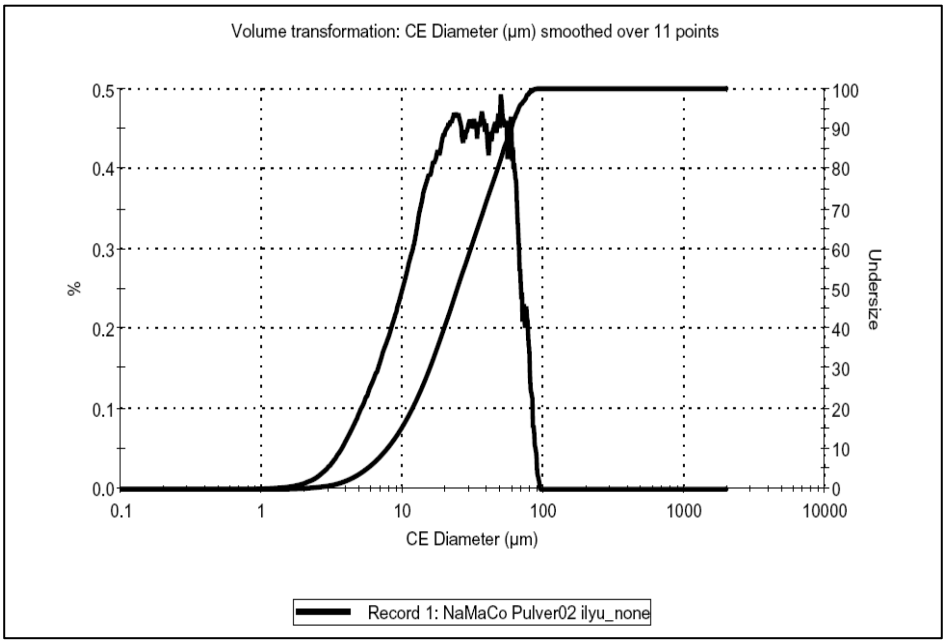
Spray deposition efficiencies with both the TopGun and DJ2600 were examined for the initial nanostructured powders supplied and it was found that the deposition efficiencies are lower than with the commercially available FP350 conventional powder. This was identified as due to poor flowability and the wide size range of the powder available. Poor flowability leads to pulsing of the feedstock and irregular deposition. The presence of particles that are too large means that these are not heated sufficiently and do not deposit. Small powder particles are heated in the gun but cool quickly once they leave the gun and also do not deposit. Work was thus undertaken to improve the flowability of the powder, to modify the feeding characteristics of the powder feeders used in the thermal spray systems and to produce a narrower particle size range to overcome these problems and greatly improve the deposition efficiency.

XRD analysis of the coatings produced from nano-grained powder confirmed that they comprise principally the NZF spinel crystal structure. Depending on the spray parameters employed some FeO was also found to form but the quantity can be reduced by appropriate selection of process conditions on both the TopGun and the DJ2600. Samples were supplied to RTD partner PMI for measurement of grain size using the XRD methods employed with the feedstock powder (detailed method is described in **D3** report). Qualitatively, significant peak broadening was noted in the XRD patterns obtained from the coatings, which is indicative of coherent diffracting domain size below 100 nm.

SEM EDX analyses of coating compositions were undertaken and compared with the compositions of the original feedstock powders used. This work confirmed that Zn is the main element lost during spray deposition of nanograined powders (as was found for conventional materials which had lower starting Zn levels anyhow) and the percentage loss of Zn is somewhat less than the losses measured for the conventional materials. Thus modified powder compositions were employed to take account of the Zn losses during spraying and hence arrive at the desired coating composition (i.e. close to that of the AFT tile material). Selected results are shown in Table 6 below.

Table 6 Average composition in weight % of selected powders, coatings and AFT tile material

Element	O/ wt.%	Fe/ wt.%	Ni/ wt.%	Zn/ wt.%	Mn/ wt.%	Co/ wt.%
Conventional powder	24.4	53.9	7.4	11.5	1.4	0.0
Coating from conventional powder	23.8	63.2	7.8	4.1	1.6	0.0
Nanostructured PMI powder (1) (close to AFT tile material)	24.9	52.8	14.7	5.3	1.4	1.0
Nanostructured PMI powder (2) (extra Zn to allow for losses)	21.9	49.0	16.2	10.4	1.6	1.4
Coating from nanostructured powder (2)	23.5	52.1	14.1	7.3	1.6	1.5
AFT Tile	25.5	50.7	16.0	5.4	1.4	0.9



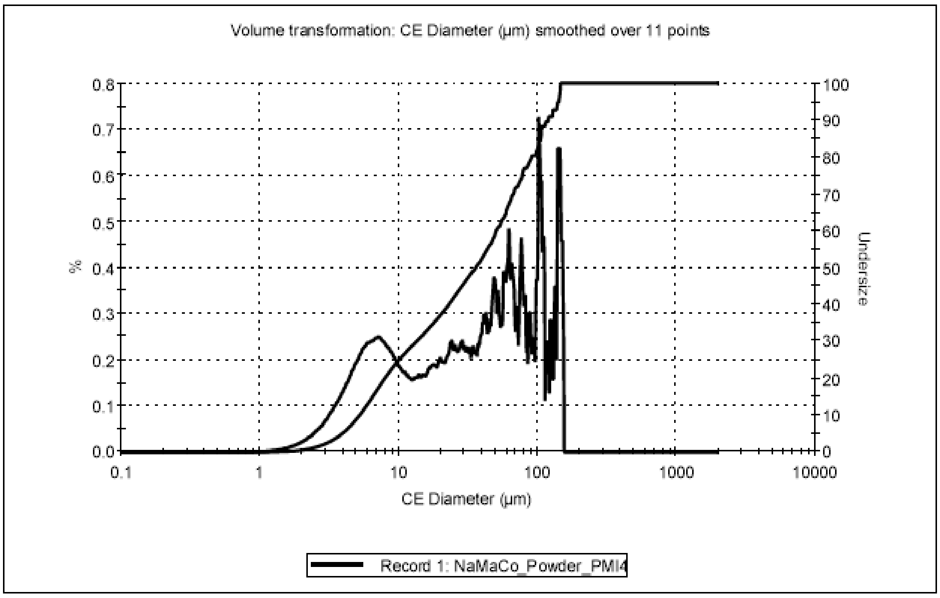


Figure 8 Selected examples of particle size distributions for nanostructured powder.

PMI powders were produced by MA+F and MA+SHS routes and sieved to produce various different size fractions in order to establish through the spray trials the most suitable ones for spraying. Table 7 lists the powder characteristics. Typically crystallite size was ~ 150 nm (as determined by XRD peak broadening analysis), particle aspect ratio was around 0.75 and the Zn content was ~ 9.5 wt% to allow for losses of this element whilst achieving a coating composition close to that of the target AFT tile material. Several different batches were produced in kg quantities to allow the spray trials to proceed

This powder was used to carry out successful deposition of nanostructured ferrite powder by HVOF spraying. This deliverable covered the determination of process characteristics and the previously mentioned coating. It also covered the determination of the frequency dependence of the complex magnetic permeability of test samples, with specific interest in the imaginary component (µ′′) which quantifies absorption effects. As explained earlier in this report, the Steering Group approved the inclusion of a parallel APS study alongside the HVOF work because of the unforeseen difficulties concerning significant Zn loss during spraying; the loss scales with the inverse of the powder diameter. Thus loss is minimized with large diameter powder but this cannot be sprayed by HVOF due to insufficient heating. APS spraying is capable depositing much larger particles but it does involve higher particle temperatures and longer residence times. However, this seems to be a less significant factor in Zn loss.

The spray systems used for the trials were as follows:

- HVOF systems
  - Hydrogen fuelled Top Gun system at UNOTT
  - Hydrogen fuelled Sulzer Metco DJ2600 at SEI
  - Ethene (C_2H_4) fuelled Top Gun system at RHV (to allow a preliminary assessment of industrial capability)
- APS system
  - Sulzer Metco F4 Ar/H_2 system at SEI

At RTD performers UNOTT and SEI coatings were sprayed onto coupons for microstructural analysis and bond strength testing as well as onto specially designed non-magnetic rings (Al or ferritic stainless steel) for magnetic permeability measurements at AFT by the shorted co-axial line method (SCLM). At SME partner RHV a stainless steel rod (approx dimensions 350 mm x 18 mm diameter) and test coupons were sprayed for microstructural characterization and magnetic permeability measurement by the coaxial transmission line method. A number of different HVOF TopGun and DJ 2600 parameters were investigated and selected spray parameter conditions which gave promising results are detailed in Table 8**.**

Furthermore, to assist in parameter development SprayWatch particle diagnostic measurements were made at UNOTT (Top Gun HVOF) in month 8 of the project. Average particle temperature and velocity were measured at various stand–off distances for different gun settings. The values obtained were used to provide an indication of what effect parameter changes had on particle conditions and their relationship to coating microstructure.

Microstructural analysis of deposits

It was found that spraying with the HVOF DJ2600 gun and H_2 produced low deposition efficiency (DE) and only around 20 μm thick coatings after 20 passes. The coatings were found to be somewhat porous with poorly bonded particles and little evidence of melted spats. With a narrow size range e.g. 7 – 37 μm some deposition occurred that there was significant Zn loss. When a wider size range was used e.g. 7 – 75 μm there was insufficient powder heating to form a well bonded coating resulting in poor deposition efficiency and porous coatings.

Using the TopGun with H_2 it was possible to spray both MA+F and MA+SHS powders with quite wide size ranges e.g. 19 – 75 μm to obtain low porosity, well bonded coatings. The deposition efficiency (DE) was better with the H_2 fuelled Top Gun used at UNOTT than with the DJ gun at SEI and it was possible to build up coatings of 200 to 300 μm thickness with a sufficient number of passes as shown in Figure 9 (where lamellar splats are clearly visible). At best, the DE was around 30%. However, bond strength measurements showed that this was in excess of 40 MPa which is sufficiently high for the application envisaged by AFT.

Table 7: Summary of properties for powders used for HVOF spraying of ferrite coatings

element	Method of production	wt%O at%	wt%Fe at%	wt%Ni at%	wt%Zn at%	wt%Co at%	wt%Mn at%	Crystal Structure	Cystallite Size nm	Domain Size nm	Particle Size (1) µm +[0.1]-[0.9]	Aspect Ratio
Target AFT Tile	n/a	28.6±0.11 58.8±0.48	49.4±0.35 29.1±0.53	15.0±0.40 8.4±0.22	5.2±0.21 2.6±0.09	0.7±0.15 0.6±0.24	1.1± 0.09 0.7±0.05	NiZn Ferrite	236	-	-	
FP350-2	Commercial powder	26.2±2.3 56.0±2.9	53.1±2.2 32.8±2.5	7.3±0.3 4.3±0.3	11.5±0.4 6.0±0.4		1.4±0.2 0.9±0.1	NiZn Ferrite			+6.1 -45.8	0.760
PMI(5)-SHS2(2)	MA-SHS	28.7±0.60 59.1±0.71	49.6±2.05 29.2±1.35	11.2±1.46 6.3±0.79	8.9±0.48 4.5±0.27	0.7±0.15 0.4±0.08	1.1±0.08 0.6±0.09	NiZn Ferrite	72	28	+2 -140	0.721
PMI(5)-SHS2 small	MA-SHS sieved	28.7±0.60 59.1±0.71	49.6±2.05 29.2±1.35	11.2±1.46 6.3±0.79	8.9±0.48 4.5±0.27	0.7±0.15 0.4±0.08	1.1±0.08 0.6±0.09	NiZn Ferrite	72	28	+7.4 -37.5	0.721
PMI(5)-SHS2 large	MA-SHS sieved	28.7±0.60 59.1±0.71	49.6±2.05 29.2±1.35	11.2±1.46 6.3±0.79	8.9±0.48 4.5±0.27	0.7±0.15 0.4±0.08	1.1±0.08 0.6±0.09	NiZn Ferrite	72	28	+6.9 -75.4	0.721
PMI(5)-SHS3(3)	MA-SHS ground (4)	28.5±0.6 58.8±0.6	51.3±4.0 30.3±2.0	10.9±2.1 6.1±1.25	7.8±3.00 4.0±1.53	0.7±0.16 0.4±0.09	0.8±0.20 0.5±0.13	NiZn Ferrite	162	37	+10.3 -62.5	0.736
PMI(6)	MA+F	28.9±0.51 59.4±0.60	44.6±0.49 26.3±0.44	14.8±0.31 8.3±0.22	9.8±0.35 4.9±0.18	0.8±0.08 0.4±0.04	1.2±0.09 0.7±0.04	NiZn Ferrite	154	39.2	+19.3 -75.4	0.819
PMI(7)- SHS4	MA-SHS	28.9±0.41 59.3±0.47	48.9±2.11 28.8±1.19	11.2±0.94 6.3±0.55	9.4±1.09 4.7±0.56	0.7±0.23 0.4±0.13	0.9±0.16 0.67±0.21	NiZn Ferrite	145	38.1	+11.2 -54.5	0.776

1. This column contains the d_{10} lower limit diameter and d_{90} upper limit diameter.
2. 2nd phase present in PMI(5)-SHS2 5.3 wt%O, 10.2 wt%Fe, 80.7 wt%Ni, 1.4 wt%Zn, 2.0 wt%Co and 0.4 wt%Mn
3. Also contained 0.3 wt%Cl and 0.4 wt%Na remaining from the SHS reaction.
4. Gy-ro crushed for 10 min and afterwards sieved with a 75 µm sieve

Table 8: Spray parameters used for coating deposition.

Run number [1]	Spray System	Powder	Fuel	N_2 [SLPM]	Fuel [SLPM]	O_2 [SLPM]	O_2/fuel ratio / stoich ratio [2]	Powder carrier gas [SLPM]	feed rate [g/min]	Stand off distance / [mm]	Number of passes	Coating thickness / [µm]	Deposition efficiency / [%]
RHV rod	Top Gun RHV	FP350(2)	Ethene C_2H_4	-	80	250	1.04	30		250		300	
SEI19	DJ2600 SEI	PMI(5)-SHS2 large	H_2	300	588	212	0.72	35	10	250	20	20	10
SEI20	DJ2600 SEI	PMI(5)-SHS2 large	H_2	300	650	235	0.72	35	10	270	20	20	10
SEI21	DJ2600 SEI	PMI(5)-SHS2 small	H_2	300	588	212	0.72	35	10	250	20	20	10
SEI22	DJ2600 SEI	PMI(5)-SHS2 small	H_2	300	367	133	0.72	35	10	250	20	30	15
RHV ring & rod 1	Top Gun RHV	PMI(5)-SHS2	Ethene C_2H_4	-	80	250	1.04	30		250			
NU56	Top Gun Nottingham	PMI(5)-SHS3	H_2	-	788 1670 (scfh)	274 580 (scfh)	0.70	21 45 (scfh)	10	175	20	40	22
NU57	Top Gun Nottingham	PMI(6)	H_2	-	788 1670 (scfh)	274 580 (scfh)	0.70	21 45 (scfh)	27	175	10	48	31
RHV ring & rod 2	Top Gun RHV	PMI(7)	Ethene C_2H_4	-	70	250	1.19	27 (N_2)		250			
		Powder		current [A]	Ar [SLPM]	H_2 [SLPM]			Feed rate [g/min]	distance	passes	coating thickness [µm]	
SEI Ring 2	APS SEI	PMI(5)-SHS2	-	600	50	2	-	5 (Ar)	-	110	20	337	

1. except where noted coatings were sprayed on flat steel substrates.
2. Ratio of oxygen to fuel divided by the stoichiometric ratio - <1 fuel rich, >1 oxygen rich

Table 9: Composition, crystallite and domain sizes of ferrite coatings and powders

	Powder	Sprayed by	wt%O at%	wt%Fe at%	wt%Ni at%	wt%Zn at%	wt%Co at%	wt%Mn at%	Crystallite size nm	Microstrain
AFT tile			28.6±0.11 58.8±0.48	49.4±0.35 29.1±0.53	15.0±0.40 8.4±0.22	5.2±0.21 2.6±0.09	0.7±0.15 0.6±0.24	1.1± 0.09 0.7±0.05	236	0.084
PMI(5)-SHS2		*Powder*	*28.7±0.60* *59.1±0.71*	*49.6±2.05* *29.2±1.35*	*11.2±1.46* *6.3±0.79*	*8.9±0.48* *4.5±0.27*	*0.7±0.15* *0.4±0.08*	*1.1±0.08* *0.6±0.09*	*72*	*0.280*
'Ring 2'	PMI(5)-SHS2	APS SEI	26.0±0.18 55.5±0.26	48.9±0.42 29.9±0.25	15.6±0.57 9.1±0.34	6.7±0.50 3.5±0.26	0.9±0.16 0.5±0.10	1.1±0.08 0.7±0.05	35.3 22.3[1]	1.430 0.363[1]
PMI(5)-SHS 2	PMI(5)-SHS2	DJ2600 SEI	28.7±0.60 59.1±0.71	49.6 ±2.05 29.2±1.35	11.2±1.46 6.3±0.79	8.9±0.48 4.5±0.27	0.7±0.15 0.4±0.08	1.1±0.08 0.6±0.09	-	-
RHV Ring 1	PMI(5)-SHS2	Top Gun RHV	25.8±0.16 55.4±0.26	48.1±0.43 29.6±0.33	15.5±0.08 9.1±0.07	8.1±0.2 4.2±0.10	1.0±0.08 0.6±0.05	1.3±0.056 0.8±0.03	41.4 18.0[1]	0.671 1.260[1]
PMI(5)-SHS3		*Powder*	*28.5±0.68* *58.8±0.64*	*51.3±4.00* *30.3±2.00*	*10.9±2.11* *6.1±1.25*	*7.8±3.00* *4.0±1.53*	*0.7±0.16* *0.4±0.09*	*0.8±0.20* *0.5±0.13*	*162.4*	*0.172*
Run56	PMI(5)-SHS3	Top Gun NU	26.1±0.19 55.6±0.25	55.2±0.84 33.7±0.50	13.4±0.76 7.8±0.45	3.2±0.50 1.7±0.26	0.9±0.22 0.5±0.12	1.2±0.08 0.7±0.05	21.5 15.1[1]	1.195 1.588[1]
PMI(6)		*Powder*	*28.9±0.51* *59.4±0.60*	*44.6±0.49* *26.3±0.44*	*14.8±0.31* *8.3±0.22*	*9.8±0.35* *4.9±0.18*	*0.8±0.08* *0.4±0.04*	*1.2±0.09* *0.7±0.04*	*154*	*0.105*
Run 57	PMI 6	Top Gun NU	26.5±0.28 56.3±0.36	49.1±0.32 29.9±0.25	15.8±0.30 9.2±0.20	6.4±0.42 3.3±0.23	0.9±0.17 0.5±0.10	1.3±0.12 0.8±0.08	28.0 20.2[1]	0.936 1.102[1]
PMI(7)		*Powder*	*28.9±0.41* *59.3±0.47*	*48.9±2.11* *28.8±1.19*	*11.2±0.94* *6.3±0.55*	*9.4±1.09* *4.7±0.56*	*0.7±0.23* *0.4±0.13*	*0.9±0.16* *0.67±0.21*	*145*	*0.153*
RHV Ring/rod 2	PMI(7)	Top Gun RHV	26.7±0.27 56.2±0.44	47.0±1.49 28.4±0.78	15.4±1.06 8.9±0.62	8.2±0.58 4.2±0.31	0.9±0.21 0.5±0.12	1.2±0.09 0.8±0.04 (2)	N/A	N/A

1. $Fe_{0.9536}O$
2. also contains ~1 at% Na

XRD analysis showed that some FeO formed during spraying by TopGun HVOF and peak broadening allowed crystallite size and microstrain to be calculated as listed in Table 9**;** a crystallite size of under 50 nm was computed. However, EDXA showed that the wt% Zn decreased from typically 10% in the powder to around 5-6% in the coating. With a powder size fraction containing a reduced percentage of fines, the degree of particle melting and resultant lamellar-like microstructure was modified significantly.

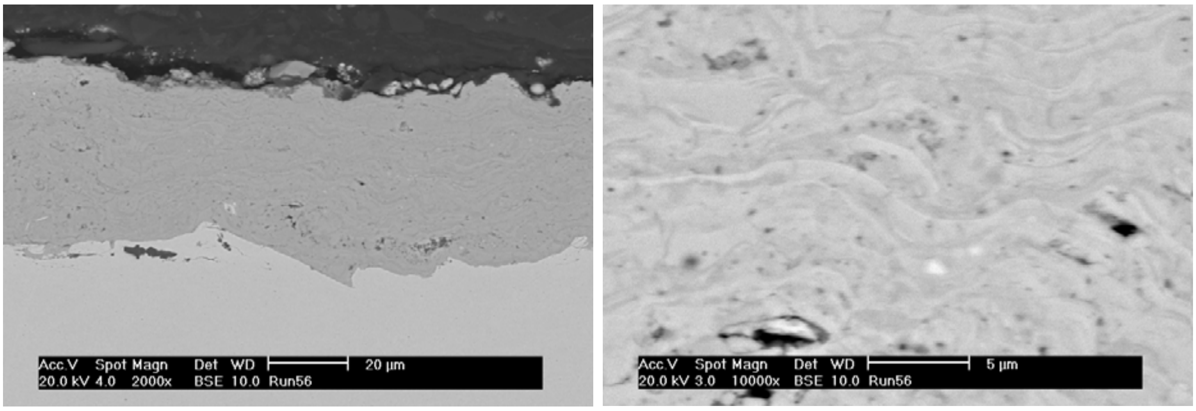


Figure 9 Back scattered electron images of coating Run 56 with PMI(5)-SHS2 powder

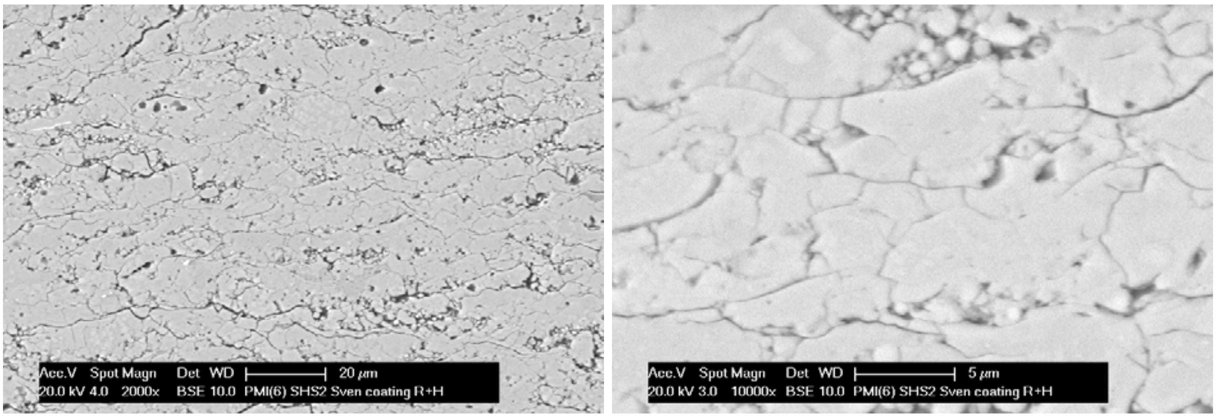


Figure 10 Back scattered electron images of RHV TopGun coating with PMI(5)-SHS2 powder at low and high magnification.

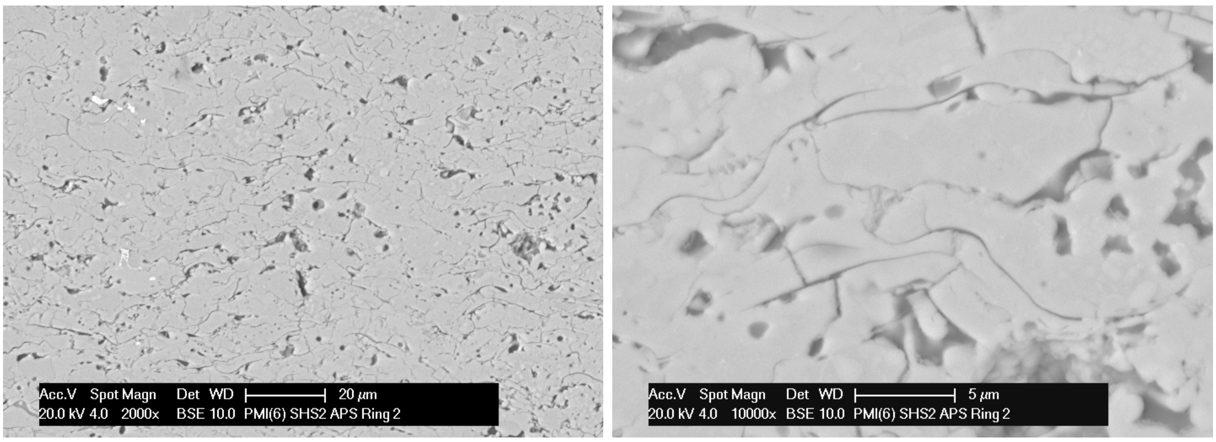


Figure 11 Back scattered electron images of APS coating with PMI(5)-SHS2 powder.

Using the ethene fuelled TopGun at RHV the rod for magnetic measurements and coupons for microstructural analysis were successfully prepared. The coating microstructure shown in Figure 10 reveals that little melting of the powder had taken place but the XRD pattern showed that little FeO had formed and little Zn loss was noted. However, the coating had a some porosity and the degree of particle melting was limited. This result demonstrates that use of TopGun with ethene is feasible for deposition of single phase ferrite but that power input from ethene is lower than from hydrogen and gives reduced lamellar formation and reduced Zn loss.

For the reasons set out previously, it was agreed to explore APS spraying. Initial APS spraying of the large size fraction of MA+SHS powder showed promising results particularly in terms of good bonding combined with relatively low Zn loss; the Zn content only fell from 10 to ~ 7 wt% which is a significantly reduced loss compared to HVOF. An SEM image of an APS coating cross section is shown in Figure 11. Clearly this reveals more porosity than with TopGun coatings but a less distinct lamellar structure is observed compared with Figure 9 indicating less severe powder melting probably due to the larger size of powder employed. From analysis of the XRD patterns some FeO also appeared to form following APS spraying but similar to TopGun spraying at UNOTT. Nevertheless, the crystallite size was also less than 50 nm and the DE was better than that for HVOF coatings at over 35%. Therefore, it was agreed to continue with this parallel approach using APS and HVOF to deposit trial coatings for magnetic measurements.

Magnetic measurements

Rings were sprayed for magnetic permeability measurements by APS (SEI/IOT) and TopGun HVOF (UNOTT), see Figure 12. The magnetic properties of rings produced by TopGun HVOF or APS were measured with the shorted coaxial line method (SCLM), where aluminium (or ferritic steel) rings coated with the ferrite were measured.

UNOTT	IOT
D_o = 28.8 ± 0.2 mm	D_o = 28.8 ± 0.1 mm
D_i = 16.0 ± 0.2 mm	D_i = 19.5 ± 0.1 mm
$h_{Ferrite}$ = 0.4 ± 0.05 mm	$h_{Ferrite}$ = 0.8 ± 0.05 mm
h_{Al} = 3 mm ± 0.05 mm	h_{Al} = 1 mm ± 0.05 mm

Figure 12 Rings used for magnetic measurements by SCLM

The SCLM method is described in the deliverable report **D6**. For the purposes of the present work, the main interest is in the measurement of the complex magnetic permeability at microwave frequencies i.e. 10 MHz up to 3 GHz. Measurements were performed at room temperature (~22°C). The real part μ´ (relative permeability) and imaginary part μ" (losses) of the complex magnetic permeability were measured over a range of frequencies. For the applications envisaged by AFT, the important property is the value of μ'' in the range 2-3 GHz.

Data collected from a range of baseline materials and coatings over the range 10 to $3x10^3$ MHz are presented in Figs 14 -18 of deliverable report **D6**. An example of one of the plots of real and imaginary permeability as a function of frequency is shown in Figure 13 below for HVOF sprayed and APS sprayed rings respectively using the same powder type. (Open symbols correspond to the right hand μ'' axis)

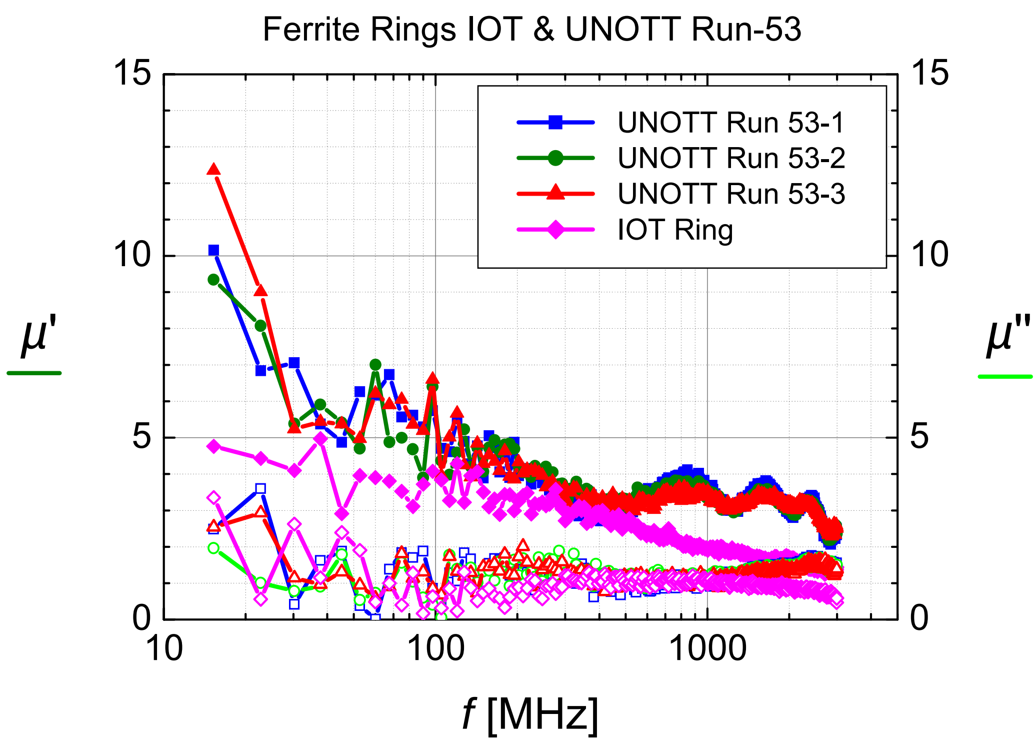


Figure 13 Results of magnetic permeability measurements of ferrite coated rings sprayed by HVOF (UNOTT) and APS (IOT)

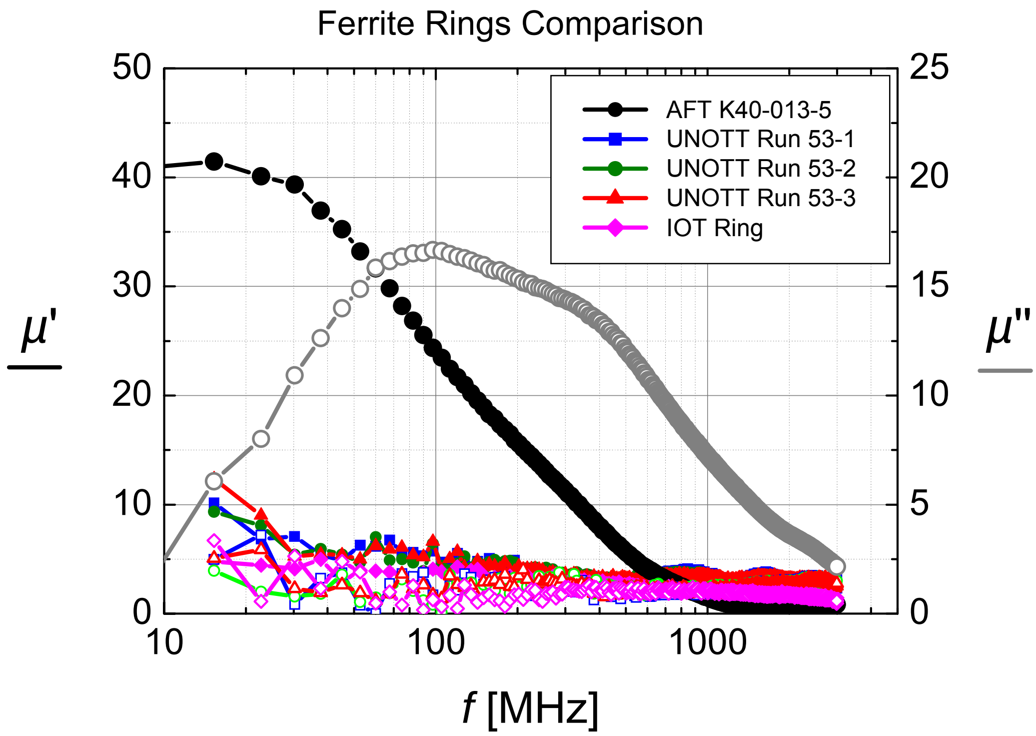


Figure 14 Measured complex permeability μ´-jμ” vs. frequency of a HVOF sprayed and APS rings sprayed compared to a pressed and sintered K40 ring.

A further comparison is shown in Figure 14 between sprayed samples and pressed and sintered K40 which is the baseline material currently used for manufacturing sintered tiles by AFT. The pressed K40 possessed better magnetic loss behaviour (μ′′) over most of the measured frequency range than the coatings. However, around the frequency of 3 GHz, which is the important frequency for the absorber applications, the coatings had nearly the same magnetic loss (μ′′ = 1.8) as the sintered material (μ′′ = 2.0). There is also very little difference in the behaviour of the two coatings. This shows that around the frequency range of interest (2-3 GHz) satisfactory types of absorption can be achieved for the AFT application.

<u>*Conclusions*</u>

- Ni-Zn-ferrite powders can be sprayed using Top Gun HVOF spraying systems and coatings have been successfully deposited onto steel and aluminium substrates. However, it is difficult to control Zn loss and achieve good bonding simultaneously. This is due to the fact that loss of Zn scales with the inverse of powder particle diameter.
- Provided the correct choice of powder size range is made, APS systems can produce relatively low porosity coatings (but higher than with HVOF) which are satisfactorily bonded. Surprisingly, Zn loss is relatively low in APS spraying when a larger particle size fraction is employed. This is because Zn loss is dominated by particle size effects rather than by temperature or residence time over the range of parameters studied
- With both APS and HVOF spraying a range of coating structures has been produced, all with nanostructures (crystallite sizes in the range 20 – 50 nm).

- Comparison of the magnetic loss factor, μ'', between pressed and sintered ferrite samples and sprayed samples showed that in the frequency range of interest (2-3 GHz) the sprayed coating has a value of 45% of the pressed and sintered sample at 2 GHz and nearly 90% at 3 GHz. These are acceptable for the microwave absorbing application envisaged by AFT
- It is clear from the work conducted that there are complex structure-magnetic property relationships that have not been fully understood from a scientific point of view in this work. Among the many factors, those listed below could be important as their effect was not fully resolved from the work undertaken:
    - Zn content of the spinel crystal structure
    - Fraction of FeO in the microstructure
    - Micro and macrostrain in a thermally sprayed coating
- The magnetic properties of the sprayed Ni-Zn-ferrite are sufficiently promising to warrant industrial thermal spraying trials being conducted by Top Gun HVOF and APS spraying leading to the definition of process parameters for the manufacture of a demonstration component. It is also recommended to trial using the DJ2600 in industry using propane as results with hydrogen showed only borderline capability.

Workpackage 2.1 Start date: Month 13 **End date:** Month 24

Title: Industrial Thermal Spraying Trials

Contractors Involved: AFT, RHV, Rasceur, Oseir, PSI, Pyro, Met, UNOTT, SEI and PMI

Objective

To optimise conditions for the HVOF deposition of ferrite coatings on an industrial scale.

Deliverable

An industrial HVOF process capable of demonstrating the deposition of high quality ferrite. Deliverable report **D8**, month 24.

Progress

Introduction

On the basis of the findings of Deliverables **D4** and **D6** the Steering Committee agreed to conduct industrial trials with both HVOF and APS systems for the deposition of ferrite coatings using MA+SHS powder optimised for composition and size distribution under workpackage 1.2.

The industrial scale-up trials for HVOF were undertaken jointly by the appropriate SMEs and RTD providers. This involved specific collaborations between the following: UNOTT and RHV for scale up of TopGun HVOF coatings; SEI and Pyro for scale up of DJ2600 coatings; and SEI and Met for scale up of APS deposition.

Oseir and Met conducted particle diagnostic measurements using SprayWatch in support of the scale up trials and to facilitate transfer of spray conditions from RTD providers to the industrial environment. The in-flight particle diagnostic measurements with SprayWatch were also designed to establish the repeatability, reliability and limits of the processes. In the case of the APS trials, taking account of the fact that this was brought into the programme at the end of year 1, it was agreed that scale-up trials on this should mainly be based at SEI since they have an industrial size robot for part handling and an industrial Sulzer Metco F4 APS gun. Once the APS procedures had been established at SEI, then SME partner Met would become involved in the spraying of a demonstrator part under workpackage 3.1

The main emphasis of the spraying trials were to optimise coating characteristics in relation to deposition efficiency (DE), coating porosity, bond strength, composition, phases present and magnetic permeability (μ''). The outcome of the workpackage was a **Deliverable Report D8** which was submitted on 13th October 2008.

Selection of case study component

In determining how the scale up trials in this workpackage were to be conducted, it was necessary to establish the nature of the case study component as this affects, for example, the quantity of powder required and the procedures which had to be put in place for holding and handling the component and manipulating the torch/component during spray deposition.

The demonstration part was designed by AFT, Figure 15 as a means of measuring the effectiveness of various sprayed NiZn-ferrite coatings. An inner conductor was to be coated by spraying on both sides and then sealed into an outer casing and the water cooling installed (see Deliverable report **D8**). The aim of the unit is to absorb high frequency (2 - 3GHz) high power microwaves and, when connected into a system, prevent microwaves being reflected back into the microwave generator. The principle of operation is that microwaves enter and are reflected off the walls of the unit onto the central inner conductor which is the part being manufactured as an absorber. The NiZn-ferrite coating absorbs the microwaves reducing reflection but generating heat in the coating. This heat is conducted into the cooling water passing through the cooling channels in the part and hence the energy is removed from the system. The effectiveness of the unit is measured by the microwave attenuation and the target figure to be achieved was set by AFT at -26dB. A low power attenuation test would be conducted at AFT and, if successful, a high power test conducted at a customer site in the USA.

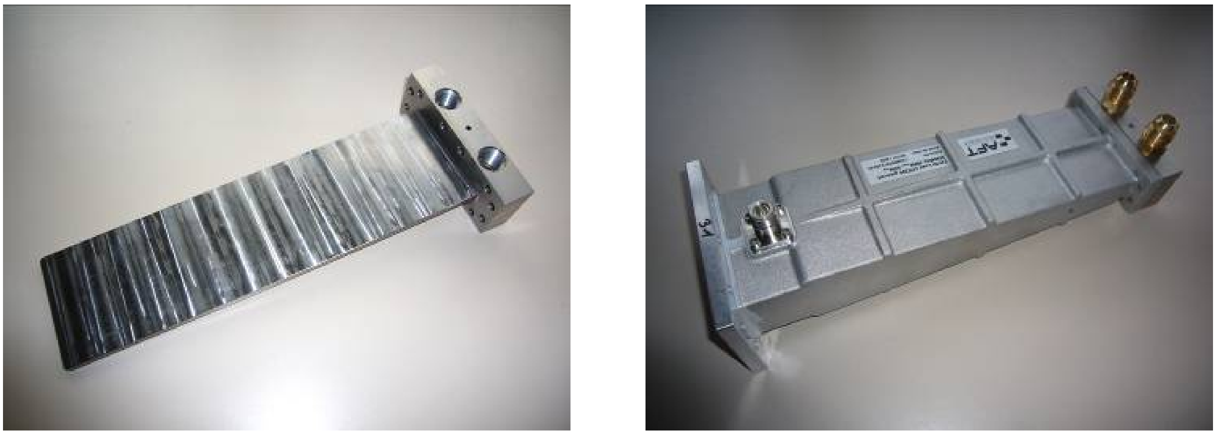


Figure 15 Inner conductor of (left) waveguide absorber device for 3GHz to be sprayed with 500µm of Ni-Zn-ferrite and outer casing of waveguide (right).

Powder manufacture

On the basis of the initial spray work MA+SHS batches of powder were produced and classified into sizes of +5 -53 µm for HVOF trials and into coarser fractions for APS trials. Quantities of around 2 kg were supplied for the first phase of the work in this workpackage. Once this had been completed and deposition efficiencies had been established along with spray patterns for the case study component larger batches were manufactured for HVOF (6 kg of +5-53 µm) and APS (6 kg of +53 -90 µm). These were produced to the previous specifications in terms of morphology, composition, grain size and crystal structure.

HVOF Top Gun spraying

This involved collaboration between UNOTT and RHV as both organisations possess the TopGun system and successful deposition of ferrite coatings had already been demonstrated on test coupons (UNOTT) and stainless steel rod for co-axial transmission line method (CTLM) by RHV. Because of the extent of work performed in previous work packages, it was deemed unnecessary to conduct a lengthy set trials based around a fractional factorial design approach. There was already sufficient knowledge and understanding to move more rapidly towards optimised parameters. This was also facilitated by a second set of SprayWatch measurements in May 2008 at UNOTT to supplement those already performed in June 2007 at UNOTT and at RHV in February 2008. An additional benefit of the SprayWatch measurements at UNOTT was that parallel data collection was performed by both Oseir and Met (with their respective SprayWatch set ups). This enabled the reproducibility of the method to be investigated.

At UNOTT a number of runs were performed with +5-53 µm powder, concentrating on varying oxygen to fuel (O/F) ratio and stand-off distance (SOD) as these had been identified as key variables in optimising deposits. Under best conditions DE was measured to be ~ 35% with bond strength around 40 MPa and porosity less than 5%. Also identified was the crucial importance of controlling cooling rate of the component after spray deposition to reduce the risk of coating spallation; particularly as coating thickness was built up over 250 µm.

Examples of SprayWatch data on average particle temperature and velocity are illustrated below, Figure 16.

Average temperature and velocity are plotted against total gas flow rate (oxygen / fuel (O/F) ratio = 0.8) and against oxygen to fuel ratio (total gas input rate = 1876 scfh) for different stand off distances ranging from 150 → 300 mm. Clearly total gas flow affects both particle temperature and velocity. However, O/F ratio affects the particle temperature but with a negligible effect on velocity.

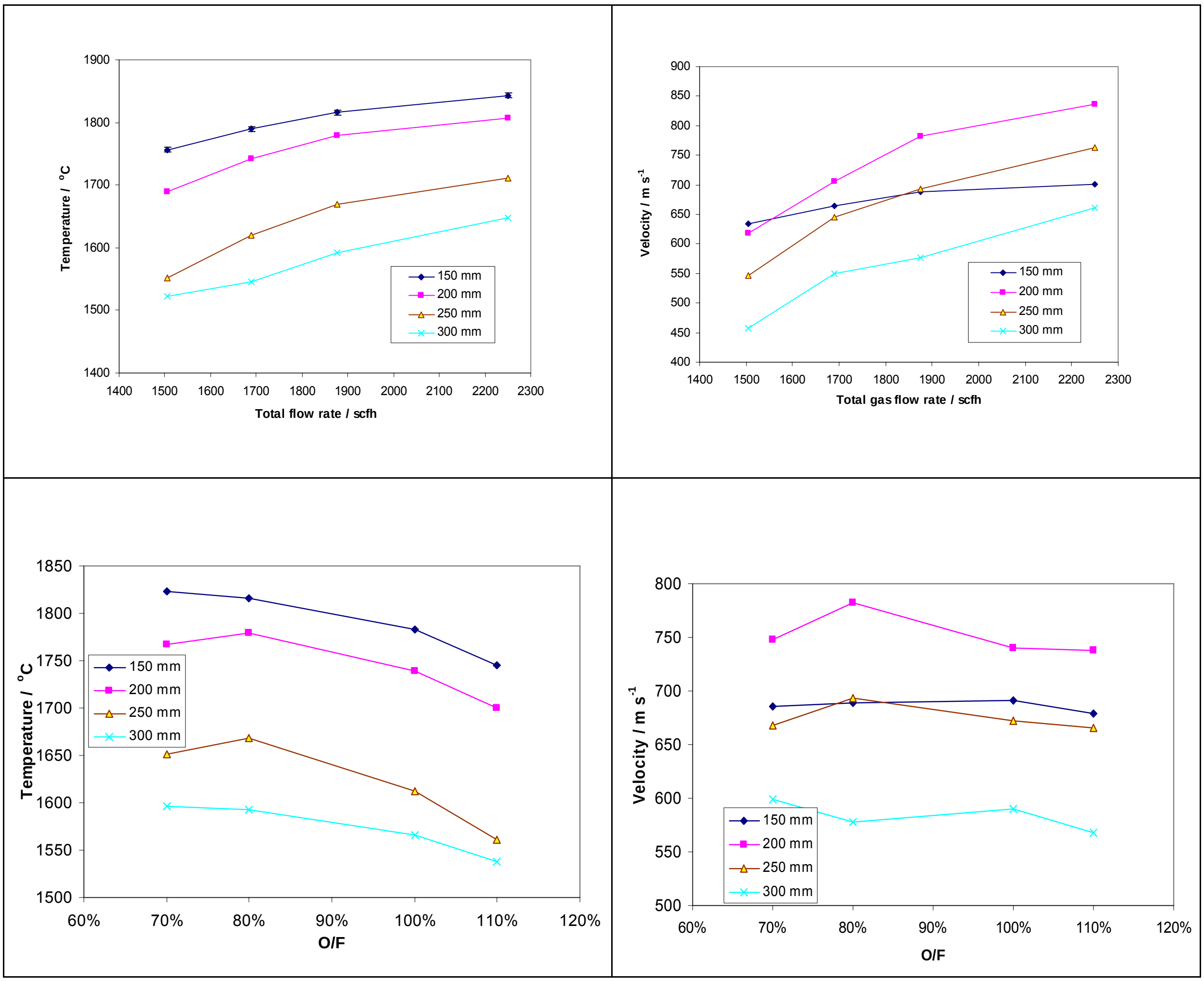


Figure 16 SprayWatch data for UNOTT spray trials.

At SME partner RHV, initial scale up trials involved the spraying of a stainless steel rod (approx dimensions 350 mm x 18 mm diameter). This is of significantly larger size than the test coupons sprayed by UNOTT (55 mm x 25 mm) and was the first stage in moving towards the conditions needed for the demonstrator component. A successfully sprayed rod is shown in Figure 17.

Analysis of the microstructure showed relatively little porosity and a Zn loss of only around 1.5wt%. Some decomposition of the ferrite phase to produce FeO occurred as expected from the UNOTT trials. The success of this approach indicated that it would be appropriate to use the parameters developed in terms of fuel, oxygen, stand-off distance, cooling procedures etc for the demonstrator part described above

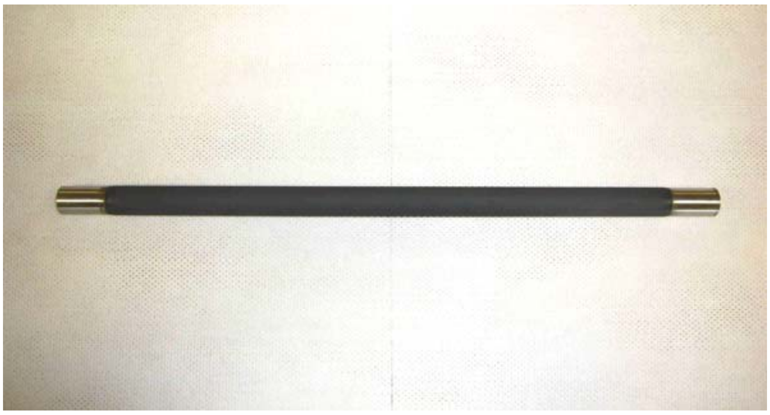


Figure 17 Rod sprayed with NiZn Ferrite by RHV

HVOF DJ2600 spraying

Following on from the DJ2600 trials at RTD performer SEI, powder was supplied to SME partner PyroGenesis for industrial scale up trials. This involved assessment of the effect of industrial spray parameters on particle temperature and velocity performed by Oseir in May 2008. The results showed that particle temperatures varied from 1360°C to 1570°C while particle velocities varied from 470 ms^{-1} to 790 ms^{-1}. When compared with Nottingham's results on the hydrogen fuelled TopGun, it can be seen that while the DJ2600 had a maximum particle velocities of the same order, but the maximum particle temperature was 250°C lower.

Once these trials had been analyzed scale up deposition was undertaken on a full size demonstrator component with the parameter settings given below in Table 10. The demonstrator part is show in Figure 18 before and after spraying at Pyro.

Table 10 DJ2700 HVOF spray parameters used by PyroGenesis

Spray Parameters			
Fuel	propane	Powder	-53+5 µm
Fuel flow rate [SLPM]	70	Powder feed rate [g min-1]	30
O_2flow rate [SLPM]	280	Traverse speed [mm s-1]	600
Air flow rate [SLPM]	380	Step [mm]	5
O_2 / fuel ratio	5.5	Stand off distance [mm]	230
Average Particle Temperature [ºC]	1560	Average Particle Velocity [ms-1]	660

It was found that deposition rate was low at around 2 µm per pass with a target thickness of at least 250 µm. A coating of this approximate thickness was built up as shown below. However, the residual stresses built up in this coating caused it to spall off during handling prior to testing. Consequently the Steering Group agreed that further evaluation of the HVOF DJ2600 deposition process should be discontinued in order to concentrate project resources on more promising processes.

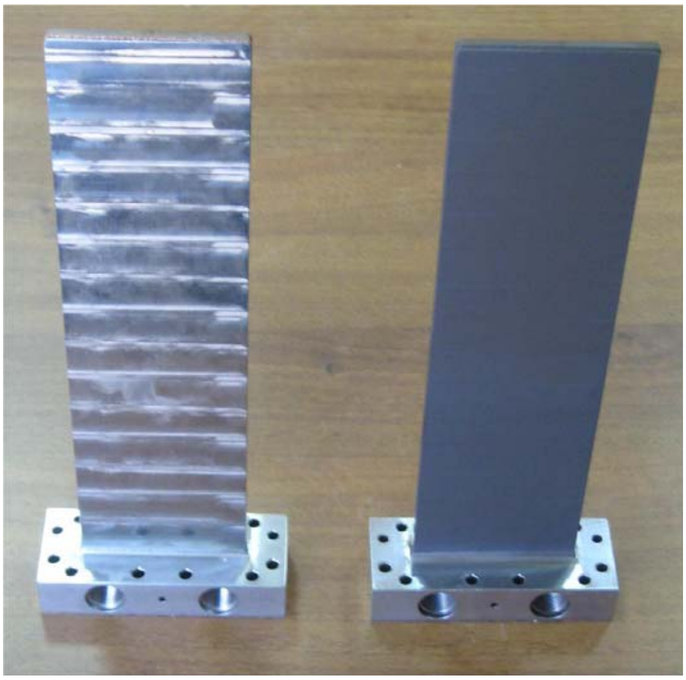


Figure 18 Demonstrator part sprayed at Pyro

APS Metco F4 Spraying

Initial scale up trials to look at process variability and sensitivity were conducted with +45 – 90 µm and +65 – 125 µm powder fractions. A fractional factorial (sometimes termed DOE) matrix of spray runs was set up involving the normal parameters of current, H_2 flow rate, powder feed rate and stand-off distance (SOD). Deposition efficiencies (DE) were found to vary from 5 – 26% with 5-10% porosity and 23 – 32 MPa values. Figure 19 shows an APS coating cross-section with DE of 45% and porosity of ~ 10%. Clearly there is greater porosity than with HVOF but there is less Zn loss and reduced decomposition to FeO compared with TopGun HVOF at UNOTT.

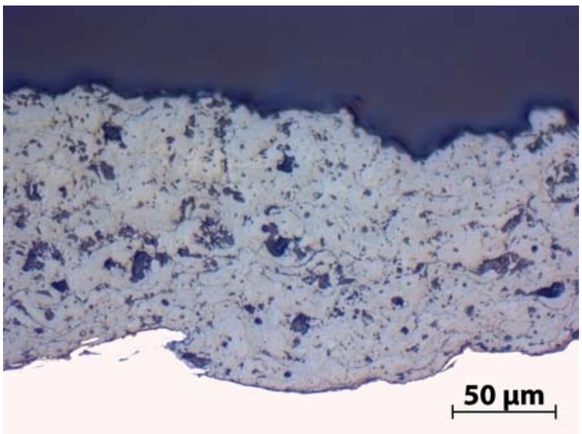


Figure 19 Optical micrographs of cross-section of APS coating deposited by SEI

SprayWatch measurements were performed as part of these trials to monitor repeatability of runs and to investigate particle characteristics i.e. average velocity and temperature. Table 11 gives a comparison of SprayWatch data from APS and TopGun HVOF. The APS velocity is lower and temperature higher than with TopGun HVOF and so it is surprising that Zn loss is lower but this is rationalized in terms of the smaller surface-to-volume ratio of the particles used for APS.

Table 11 SprayWatch measurements made during HVOF and APS

Coating type	Average particle temperature °C	Average particle Velocity ms^{-1}
HVOF	1780	780
APS2	2875	123±5

As a result of microstructural analysis and the above process characteristics a further matrix of conditions was explored using only the + 53 -90 µm powder size range (i.e. that which was too large for HVOF but below a critical upper cut off limit). Six further conditions were explored and from this it was found that DE values in the range 28 – 49% were obtained with porosity varying from 9-19%.

On the basis of this work an optimised set of parameters was arrived at for APS deposition as given in section 5 of the deliverable report **D8.** The suitability of the scale up parameter derivation was confirmed by a successful initial trial on coating a demonstrator part as shown in this report section.

These parameters were subsequently transferred to SME partner Met prior to them spraying a demonstrator part (see workpackage 3.1 for details).

Magnetic measurements

In this workpackage magnetic measurements were made to allow comparison between coatings produced on small scale rings with coatings on scale up components such as long cylinders produced by SME partner RHV. The long cylinders were measured by the CTLM approach as compared with the SCLM method used for rings as described in detail in deliverable report **D6**.

The results shown in Figure 20 below demonstrate that TopGun HVOF coatings at UNOTT on rings and RHV on larger scale cylinder/rod components give similar µ'' values within the limits of accuracy and reproducibility of the measuring techniques. The data plotted in Figure 21 shows magnetic permeability data for pressed and sintered K40 material (the baseline material used in the manufacture of the current absorber tiles by AFT) It is clear that in the frequency range of interest (2-3 GHz) the Top Gun HVOF sprayed coating gives comparable µ'' values to the sintered K40 material.

Figure 22: Measured complex permeability µ´-jµ´´ vs. frequency of a HVOF sprayed rod compared to baseline sintered material showing the comparison between TopGun HVOF sprayed material on a rod with APS sprayed coating on a ring and here it is evident that the APS sprayed material gives similar behaviour to the HVOF material over a range of frequencies.

The coating magnetic properties characteristics of each of the developed process are included in summary form in deliverable report D8.

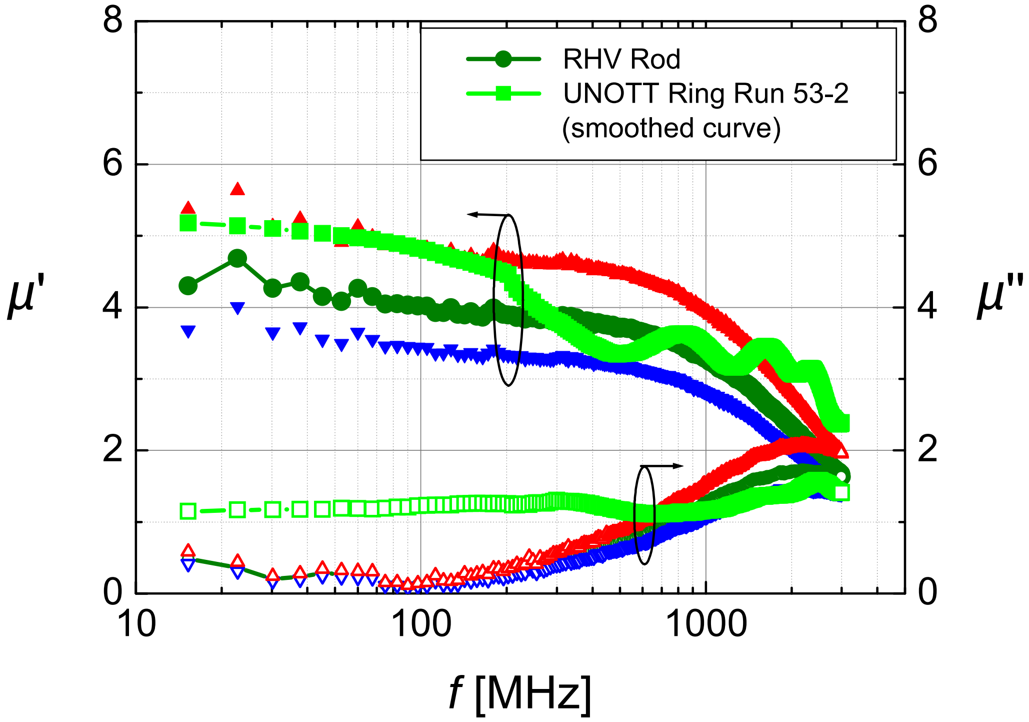


Figure 20 A comparison of magnetic measurements for coatings on rod and ring samples HVOF sprayed with FP350(2) Ni-Zn ferrite powder

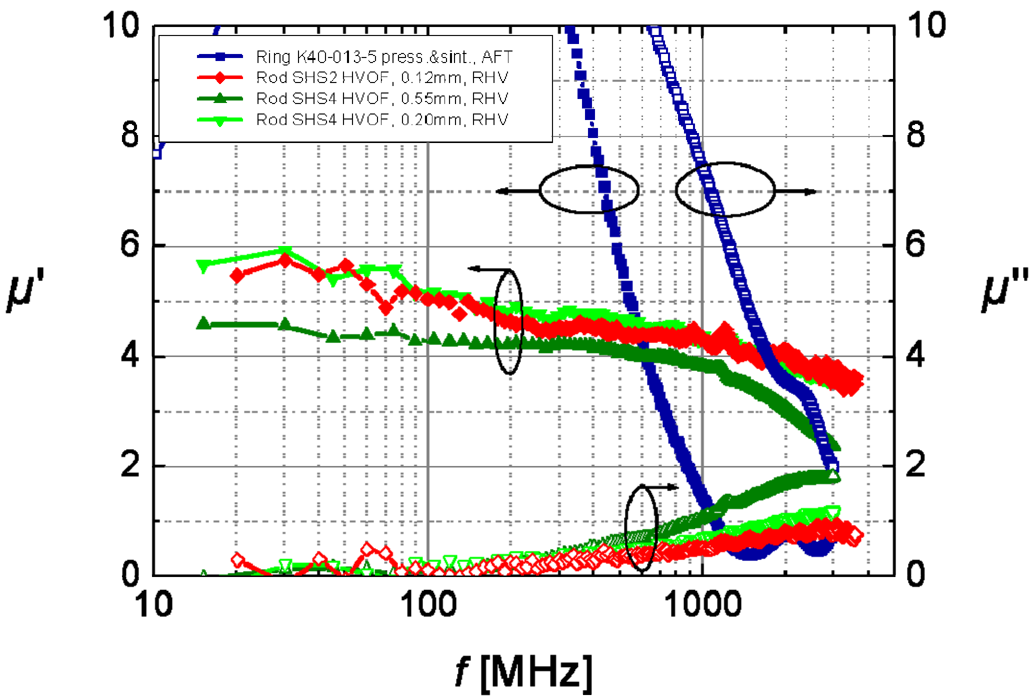


Figure 21 A comparison of magnetic measurements between pressed and sintered K40 ring (tile material) and rod samples sprayed with SHS N-Zn ferrite powder

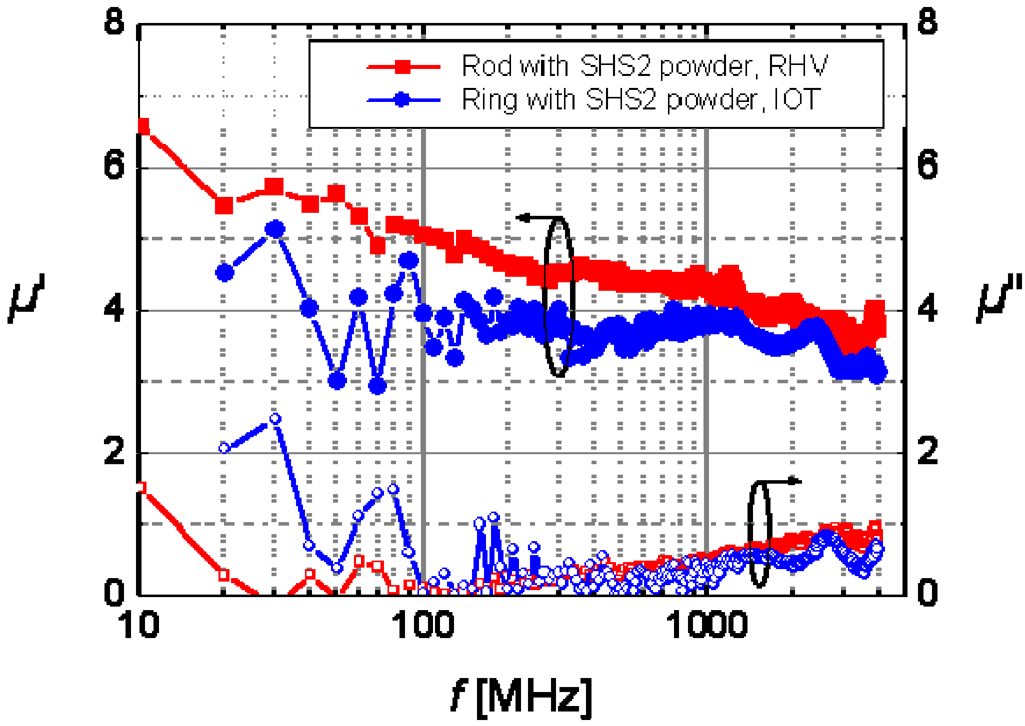


Figure 22 Magnetic measurements made on rod and ring samples sprayed with SHS2 Ni-Zn ferrite powder

Conclusions

The industrial development phase of TopGun HVOF and APS spray deposition of NiZn ferrite coatings has been successfully completed and procedures for manufacture of case study demonstrator components have been determined as described in Deliverable Report D8.

Magnetic properties of deposited coatings (in particular μ'' in the 2-3 GHz range) have been determined and found to be comparable to existing performance data for baseline material used by AFT to manufacture their current microwave absorbing tiles.

Workpackage 2.2 **Start date:** Month 17 **End date:** Month 24

Title: Definition of Process Parameters

Contractors Involved: AFT, RHV, Rasceur, Oseir, PSI, Pyro, Met, UNOTT, SEI and PMI

Objective

To document powder production and spraying procedures, and the characteristic structures and properties of the coatings deposited.

Deliverable

User guide detailing equipment specifications, ferrite powder production and thermal spraying process parameters. Deliverable report **D9**, month 24

Progress

The main aim of this workpackage was to support project exploitation activities by producing a document that details the industrialised processes of powder manufacture and thermal spraying, the equipment required and the nature and performance of ferrite coatings that can be produced.

The result of this workpackage is the Deliverable report **D9** which was submitted on 14th October 2008.

The **table of contents** of this document are reproduced below, for information:

Three industrial spray processes (TopGun HVOF, Diamond Jet DJ2600 HVOF and APS) had been assessed as a means of applying coatings on components, as described in the deliverable report **D8**. However, at the time of submitting the **D9** deliverable report the Diamond Jet coatings were still under evaluation and so this process was not included. Following evaluation of the Diamond Jet coatings (which took place after the submission of the **D9** report), it was concluded that the Diamond Jet method is less well suited to industrial application than either TopGun HVOF or APS. Therefore, it is these latter TWO processes that have the most promising capability to successfully deposit ferrite coatings and which have been taken forward into workpackage 3.1 for the manufacture of a case study demonstrator component which will be evaluated and tested.

The key points of Workpackage 2.2 can thus be summarised as follows:

The preferred powder feedstock is produced by the (MA+SHS) route. This has the necessary external morphology, composition and crystal structure for the application. For HVOF the -53 + 5µm fraction is recommended to be employed whilst for APS the -90+53 µm size is found to be appropriate.

HVOF TopGun spraying using either H_2 or C_2H_4 as fuel gases leads to coatings which are well bonded to the substrate with low porosity. The process conditions have been optimised and calibrated using SprayWatch. The phases present and the coating composition have been identified, and the resultant µ'' values (imaginary part of the magnetic permeability) at 2 and 3 GHz have been determined. The values obtained in low power tests meet benchmark requirements.

APS spraying was also optimised to give well bonded coatings with higher porosity than HVOF but with lower Zn loss and reduced decomposition of the NiZn ferrite phase. The process conditions have been optimised and calibrated using the SprayWatch system. Although having somewhat different microstructural features to HVOF coatings, the magnetic permeability measurements (µ'') at 2 and 3 GHz (low power tests) also meet benchmark requirements.

Overall, the documented procedures showed sufficient promise for the consortium to take the next step involving the spray deposition of demonstrator components by HVOF and APS.

Conclusions

The documentation that has been developed and which is summarised in the **D9** deliverable report provides a sound reference point for future spraying of this material. Specifically, it supports the work of workpackage 3.1 involving the manufacture of demonstrator components and ultimately the commercialisation of the process in relation to microwave absorber applications.

Workpackage 3.1 **Start date:** Month 17 **End date:** Month 27

Title: Manufacture and Evaluation of Case Study Components

Contractors Involved: AFT, RHV, Rasceur, Oseir, PSI, Pyro, Met, UNOTT, SEI and PMI

Objective

To apply ferrite coatings, using the developed technology, for use as microwave absorber shields on at least one case study waveguide component. Deliverable report **D10**, month 27

A waveguide component was selected as the demonstration part, Figure 1. This was designed by AFT as a means of measuring the effectiveness of various sprayed Ni-Zn ferrite coatings. An inner conductor was selected to be coated by thermal spraying on both sides. This inner conductor is then to be installed into the outer casing and water cooling connected. The aim of the unit is to absorb high frequency (3 GHz), high power microwaves when connected into a system, thus preventing microwaves being reflected back into the microwave generator. The principle of operation of the demonstration part has been described previously in the report for Deliverable 8.

Figure 23: Inner conductor of waveguide after spraying with the APS system at IOT.

The aim of this workpackage was to spray the demonstration part using different spraying techniques. In this case the coatings were applied by the high velocity oxy-fuel (HVOF) process using a TopGun system at RHV and by atmospheric plasma spraying (APS) in using a Sulzer-Metco gun at IOT and a similar system at Met. The process parameters had been developed by the RTD performers then transferred to and optimised by the consortium SMEs in the workpackages 2.1 and 2.2.

Reported are details of the performance of the different sprayed demonstration parts during both low power laboratory tests and high power tests. The latter are the most important test for these applications as they give the chance to estimate the performance of the coating during industrial operation. The performance of the sprayed coatings was also compared to the state-of-the-art of the waveguide components which involves the use of sintered tiles.

A comparison between the cost of the component manufactured with sintered tiles and that of the thermally sprayed component has also been made. The main focus of this comparison is based on the production costs of the coating process of the demonstration versus that of tile manufacture and application to the part. The fabrication of the part is disregarded in the calculation of the cost as this is not a variable under consideration.

2.1 Production of the case study components

The case study components were sprayed by the HVOF and the APS processes. Various powder compositions were used; one was produced by PMI based on the sintered material already used by AFT and one a commercial NiZn ferrite powder, FP350, with a different material composition. The PMI NiZn ferrite powder was sprayed with the HVOF gun by RHV and also with the APS system by IOT. The process parameters used, which are displayed in Table 1, were derived from the spraying trials in workpackage 1.3 and 2.1. These parameters are also mentioned in the report D9, which can be used as a "user guide" for spraying NiZn ferrite powder.

During spraying the **waveguide** components these parts were cooled by several air jets. RHV also passed CO_2 through the cooling channel of the component to assist cooling of the part.

To achieve the desired **microwave** absorption rate and to reach a nearly uniform distribution of the microwave power loss, the ferrite coating thickness was varied along the inner conductor part. As indicated in Figure 24, a three-section step profile 0.4 mm – 0.6 mm - 0.8 mm was deposited, starting with the lowest ferrite thickness at the front of the inner conductor and with the highest thickness near the short-circuit flange (water manifold).

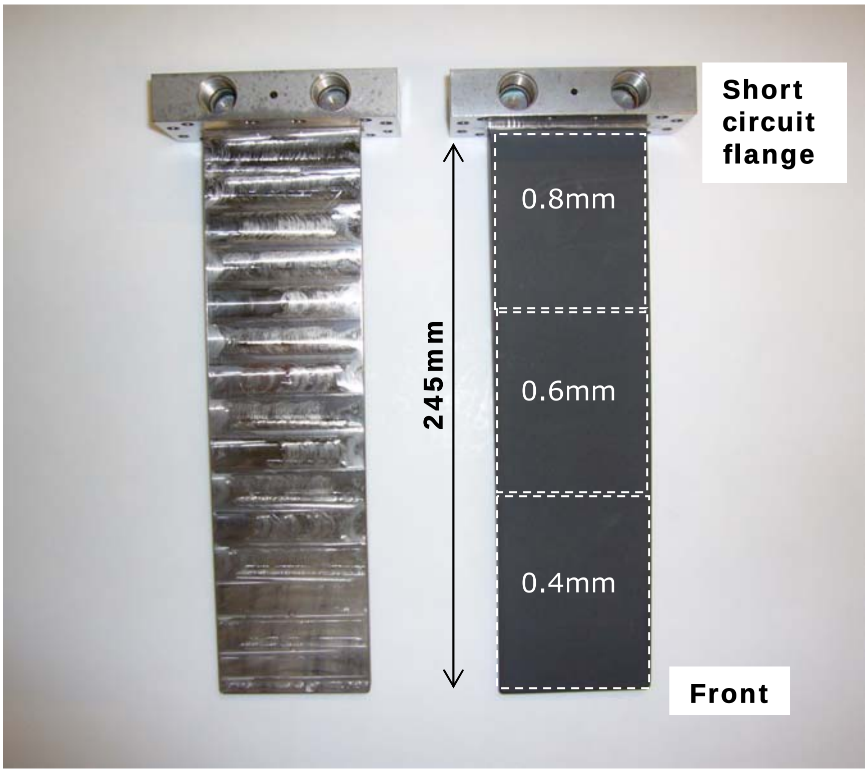


Figure 24 Inner conductor of waveguide uncoated (left) and ferrite-coated with a three-section step profile (right).

Table 12: Process parameter for spraying the case study component

Case Study Component	IOT1	IOT2	RHV1	RHV2	Met1
Partner	IOT	IOT	RHV TopGun	RHV TopGun	Metallisation
Spray System	APS Sulzer Metco F4	APS Sulzer Metco F4	HVOF TopGun	HVOF TopGun	APS
Powder	PMI10 PMI12	PMI11	PMI8	PMI11	FP350
Powder Size Range [µm]	-140+50	-130+30	-53+5	-35+5	-90+50
Combustion chamber length [mm]	-	-	22	22	-
Fuel	-	-	Ethene	Ethene	-
Fuel flow rate [SLPM]	-	-	90	90	-
O_2 flow rate [SLPM]	-	-	230	230	-
O_2 / fuel ratio (Stoichiometric ratio)	-	-	2,55	2,55	-
Primary plasma gas Ar [SLPM]	50	50	-	-	20
Secondary plasma gas [SLPM]	4 [H_2]	4 [H_2]	-	-	4 [N_2]
Current [A]	600	600	-	-	800
Voltage [V]	n/a	n/a	-	-	45
Carrier gas flow rate [SLPM]	4	4	27	27	4,5 [air]
Powder feed rate [g min^{-1}]	18	18	17	17	20
Stand off distance [mm]	90	90	250	250	85
Traverse speed [mm s^{-1}]	600	600	500	500	-
Coating thickness (step profile)	400µm 600µm 800µm	400µm 600µm 800µm	400µm 600µm 700µm	400µm 600µm 800µm	400µm 600µm 800µm

The case study component is a WR284 waveguide absorber device with high-power capability for the frequency range 2.6-3.9 GHz. A similar device is already in use using pressed and sintered ferrite tiles as absorbing elements. An absorber, in combination with a circulator, forms a key component of a microwave isolator unit. Isolators are used to protect microwave tubes from reflective power induced by applicators. Typical applicators in the S-band frequency range are cavities of linear particle accelerators in medical X-ray machines, with narrowband operation at 2.856 GHz or 2.998 GHz and with peak power levels up to 6MW and average power levels up to 6kW.

As shown in Figure 25 & Figure 26Figures 3 and 4, the investigated waveguide component consists of a ferrite coated inner conductor, incorporating a water cooling structure and a tapered waveguide housing (cast aluminium). The inner conductor is assembled into the housing via the backside flange, which serves as a short circuit for the microwave and as a water manifold with water connectors. The overall length of the compact device is about 320 mm. The WR284 waveguide aperture is 72 mm in width and 34 mm in height.

A total of five different case study components were assembled by using the ferrite coated inner conductors summarised in Table 1.

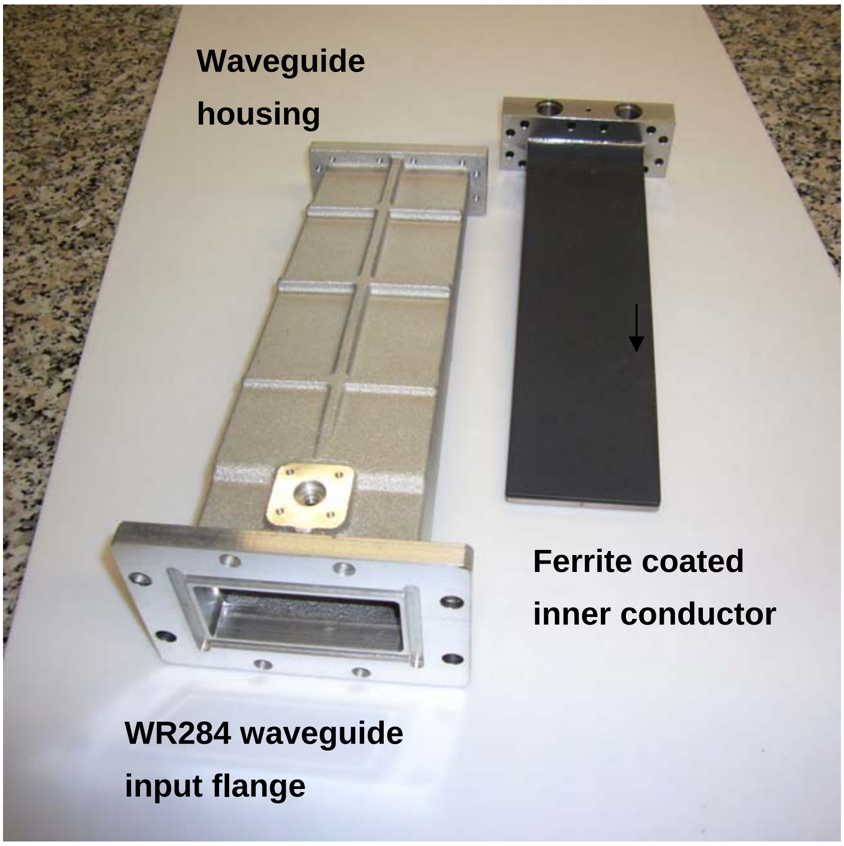


Figure 25: Two part assembly of the WR284 waveguide absorber, consisting of a tapered waveguide housing (Al) and the ferrite-coated inner conductor.

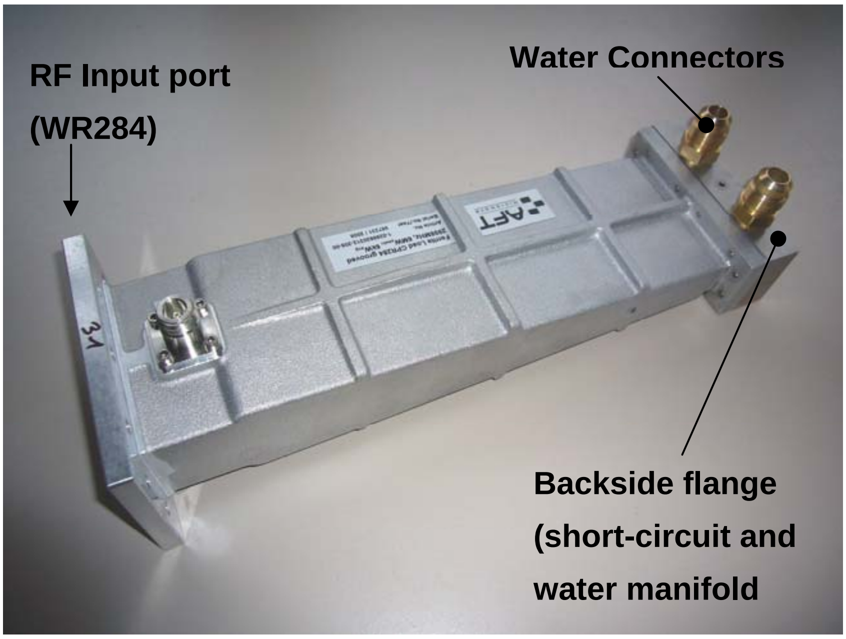


Figure 26: Completely assembled compact WR284 waveguide absorber as case study component.

2.2 Performance of the case study components

Before proceeding to evaluate the case study components in a high power test, an initial low power screening experiment was performed using laboratory equipment at AFT. This test was performed over a range of frequencies which included that at which the high power test would be conducted. However, low power tests involved average power inputs around a million times lower than in the high power experiments. Only those components (coatings) which were likely to perform well in the high power test were passed to this stage for further evaluation.

2.2.1 Low-Power Measurements

Microwaves enter the device and then reflect off the backside short-circuit (Figure 27). Attenuated by the ferrite absorber occurs both on the ingoing and outgoing wave. The absorber is characterised by a complex reflection coefficient S_{11}. The absolute value of S_{11} describes the relation between the forward (P_{in}) and the reflected power (P_{out}) at the waveguide port, and hence is a measure for the microwave absorption. It is typically expressed in log-scale:

$$|S_{11}| = 10 \cdot \log \frac{P_{out}}{P_{in}} \quad [\text{dB}]$$

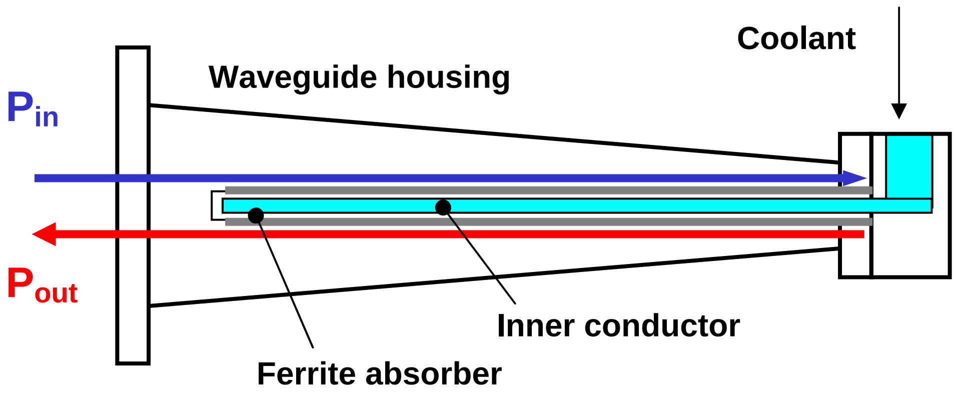


Figure 27: Principle of ferrite waveguide absorber.

The goal of this research is to obtain a reflection coefficient, of less than −23dB over a broad frequency range.

S_{11} can be measured very precisely by a vector network analyser at low-power levels, i.e. a few milliwatt (mW) of input power. The applied measurement set-up is shown in Figure 28. The absorber device under test (DUT) is connected to the network analyser via a waveguide-to-coaxial-line adapter and a coaxial cable. The measurement system is well calibrated to the waveguide port and allows measurements over the entire WR284-waveguide band from 2.6GHz to 3.9GHz. By passing water of various temperatures through the cooling channels of the unit, the device/ferrite temperature could be controlled in the range of 20°C and 60°C.

Table 13 and Figure 29summarise the low-power measurement results for all investigated demonstrator components, including an absorber coated with solid-state ferrite tiles (AFT-tiles). The reflection coefficient $|S_{11}|$ depends on the ferrite coating thickness, the absorption coefficient (μ”) of the coating material and the quality of the sprayed coating (porosity, degree of decomposition etc). The ripple of $|S_{11}|$ vs. frequency, obvious for all devices, is due to a standing wave pattern along the shorted waveguide. At 2.856GHz and 2.998GHz, two characteristic operating frequencies of microwave-driven linear particle accelerators, the reflection coefficient of component IOT2, RHV2 and MET1 shows values below −23dB, without matching or optimisation of the structure. This is regarded as a threshold value for satisfactory operation in the high power test and so these components were the ones selected for such trials.

Obviously, there is potential to optimise the devise for use with sprayed coatings. The device performance could be significantly improved by redesigning the microwave waveguide, e.g. tailoring the inner dimensions of the waveguide to match it to the sprayed ferrite coating; presently it is matched to the materials properties of absorber tiles.

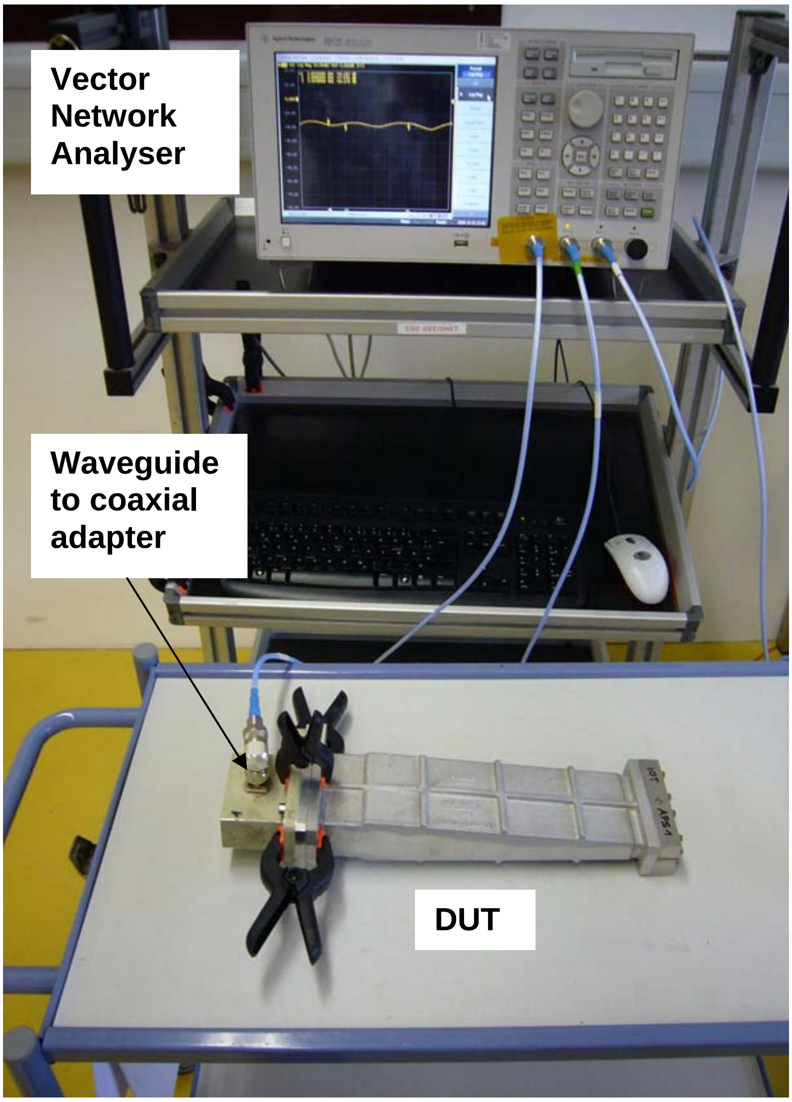


Figure 28: Low-power test set-up with a microwave vector network analyser for measuring the reflection coefficient of the absorber device in the frequency range 2.6-3.9 GHz.

As indicated in Figure 30 & Figure 31 the temperature drift of $|S_{11}|$ due to heating of the sprayed ferrite coating is quite low. It can be controlled by accounting for a proper margin of absorption during the design phase. The design should be optimised to the performance at 60°C, as this is the approximate ferrite temperature range under high-power operation for a water input temperature of 30°C to 40°C.

Table 13: Low power RF absorption properties of case study components and related ferrite coatings at room temperature (22 ± 2°C)

Case Study Component		IOT1	IOT2	RHV1	RHV2	Met1	AFT-tiles
Ferrite absorption coefficient μ″ *	2 GHz	2.0	2.0	1.0	1.0	n.a.	3.7
	3 GHz	1.95	1.95	1.5	1.5	n.a.	2.2
Absorber reflection coefficient $\|S_{11}\|$	2.6-3.9 GHz	<-19dB	<-23dB	<-17dB	<-22dB	<-20dB	<-26dB
	2.856 GHz	-23.2 dB	-26.2 dB	-19.4 dB	-29.0 dB	-27.9 dB	-30.8dB
	2.998 GHz	-21.8 dB	-26.8 dB	-18.2 dB	-23.7 dB	-24.2 dB	-42.9 dB

* μ″ was measured with the SCLM technique on an Al- or SS-ring sample, coated under the same spray conditions as for the related case-study inner conductor.

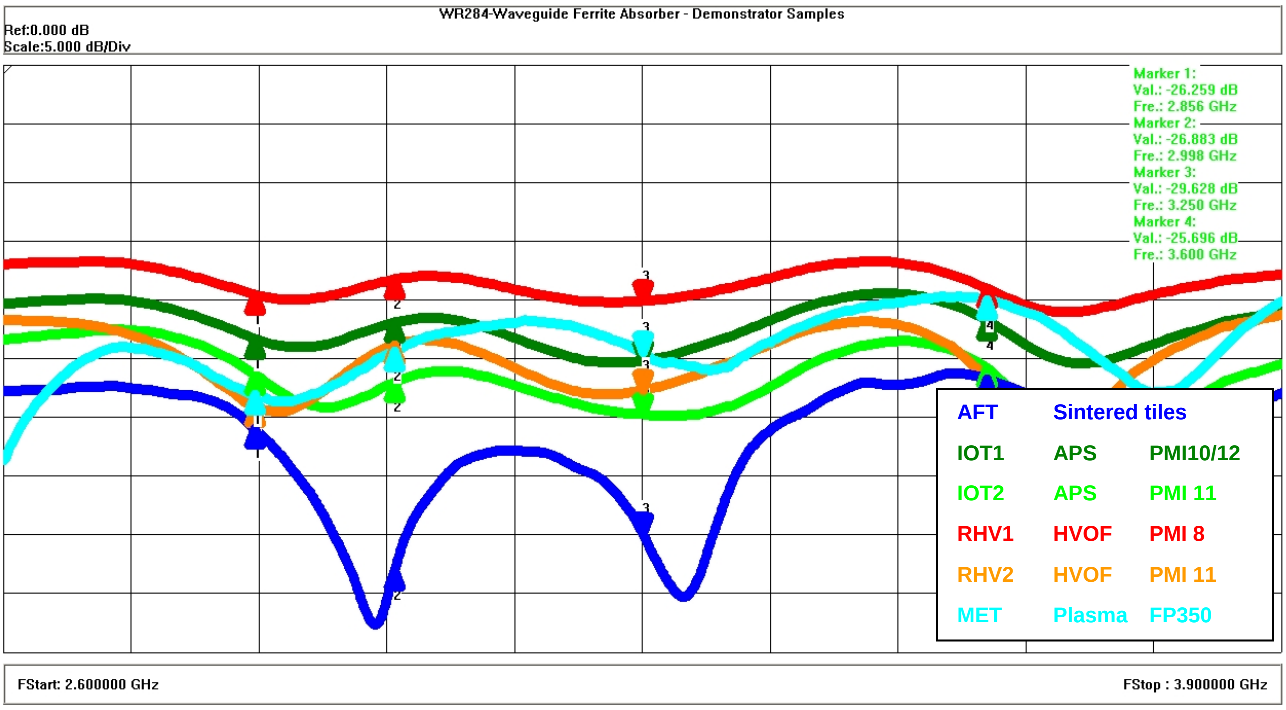


Figure 29: Measured reflection coefficient $|S_{11}|$ vs. frequency (2.6-3.9GHz) at room temperature (22 ± 2°C) of all investigated WR284 absorber components. The legend refers to the light green curve and 0 dB lies along the top horizontal axis

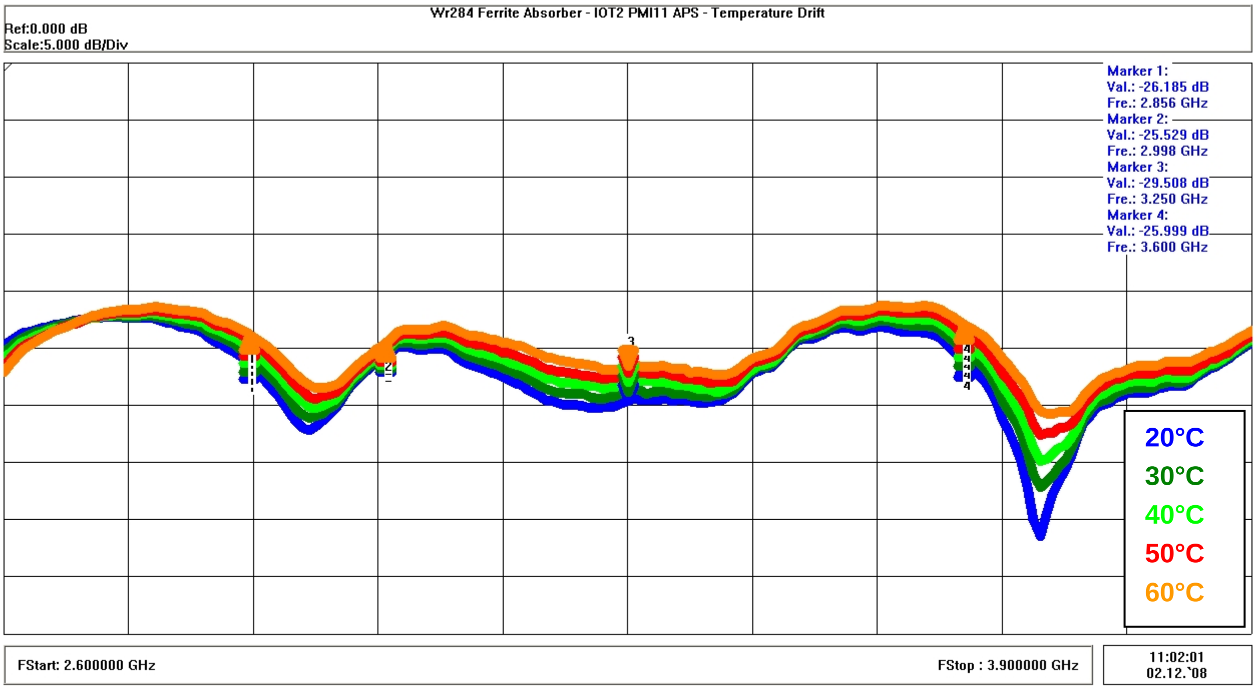


Figure 30: Measured reflection coefficient $|S_{11}|$ vs. frequency with water temperature as a parameter. WR284 absorber component IOT2. The legend refers to the blue curve and 0 dB lies along the top horizontal axis

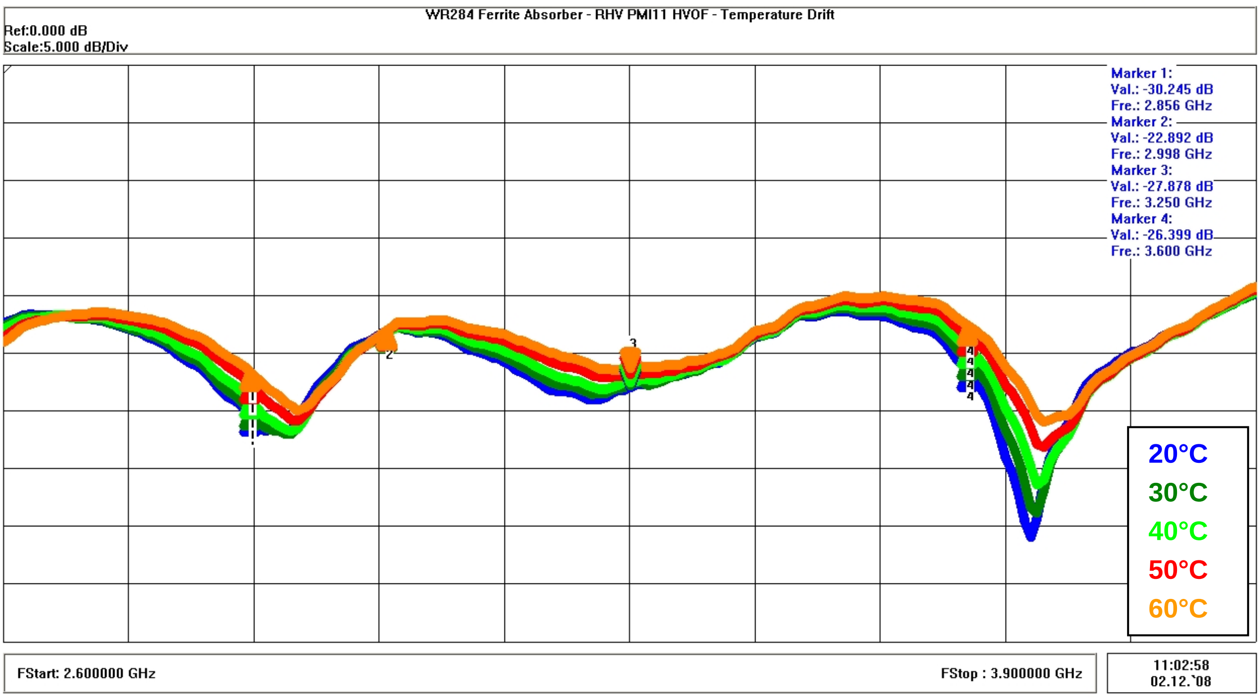


Figure 31: Measured reflection coefficient $|S_{11}|$ vs. frequency with water temperature as a parameter. WR284 Absorber component RHV2. The legend refers to the blue curve and 0 dB lies along the top horizontal axis

2.2.2 High-Power Measurements

These industrial trails were carried out at Varian Medical Systems, Palo Alto, USA, one of the customers of AFT USA.

Three case study components (IOT2, RHV2, MET1) were selected for high-power testing, due to their superior performance in terms of $|S_{11}|$, particularly at 2.856GHz along with an absorber device with sintered and bonded ferrites (AFT tiles) as a base line reference.

High-power microwave tubes in the megawatt region inherently offer a pulsed single-frequency operation, e.g. at 2.856GHz ±5MHz. Figure 32 illustrates, schematically, the applied high-power measurement setup in waveguide technology. The RF power at 2.856GHz is generated by a klystron microwave tube and fed through an isolator device and a waveguide network to the device under test, i.e. the WR284 ferrite absorber. The forward and reflected powers are picked up by RF directional couplers and RF detectors, in order to measure the magnitude of the reflection coefficient S_{11} of the absorber. The waveguide is pressurized with SF6 dielectric gas to handle the applied peak power levels. The cooling water temperature for the removal of the dissipation loss is set to 40°C. The applied water flow amounts to 14 l/min.

The test conditions were as follows:

Frequency:	2.856GHz ± 5MHz
RF-Power:	4.5MW_{peak} max.
Pulse width:	4.7µs
Pulse repetition rate:	180 Hz
Water temperature:	40°C (for water cooling of ferrite absorber)
Water flow:	14 l/min
Waveguide pressurization:	SF6 dielectric gas, 2-3 bar gauge

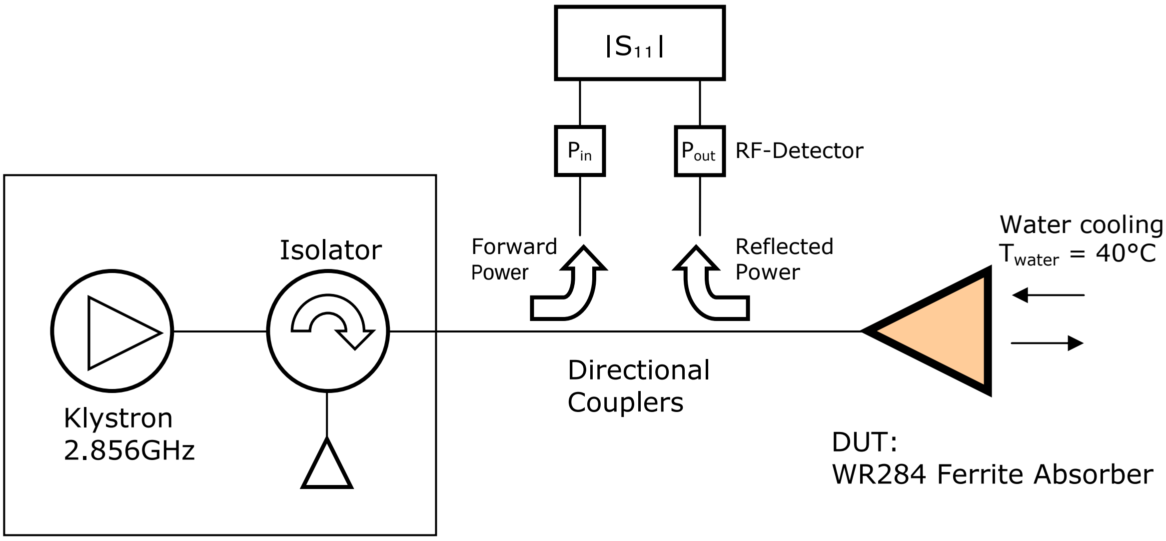


Figure 32: High-power waveguide test set-up at 2.856GHz where DUT represents the device under test.

The peak power was increased stepwise from 2.5MW up to 4.5MW. The corresponding average power levels lie between 2.1kW to 3.8kW. The reflection coefficient $|S_{11}|$ was monitored as a function of the increasing power level. All case study components were successfully tested non-destructively up to the maximum applied power level of 4.5MW peak (3.8kW average) power level. The ferrite layers remained in tact without cracking. No electrical breakdown, overheating or thermo-mechanical problems occurred. This indicates that there was a good thermal heat transfer from the absorbing ferrite coating to the water cooling. Table 14 summarises the measurements results for $|S_{11}|$ vs. the applied power levels.

Table 14: High-power test results of case study components: Reflection coefficient at 2.856GHz for different power levels at a cooling water temperature of 40°C.

Frequency = 2.856 GHz, T_{Water} = 40°C					
Power		**Absorber reflection coefficient $\|S_{11}\|$**			
peak [MW]	average [kW]	**IOT2**	**RHV2**	**MET1**	**AFT-tiles**
$<10^{-6}$ *	$<10^{-6}$ *	-24.8dB	-28.8dB	-26.5dB	-30.8dB
<1 #	«1 #	-25.3dB	-27.1dB	-23.2dB	-27.8dB
2.5	2.12	-23.3dB	-23.8dB	-20.5dB	-25.2dB
3.0	2.54	-22.8dB	-23.0dB	-19.9dB	-24.8dB
3.5	2.96	-22.3dB	-22.4dB	-19.5dB	-24.6dB
4.5	3.81	-21.5dB	-20.8dB	-18.6dB	-24.2dB

Note:
* calibrated low-power measurement with network analyser at AFT
# quasi-low power measurement with high-power test equipment

The results given in Table 3 show that the reflection coefficients measured during the high-power test campaign at a low power level (#) were very similar to the precisely calibrated low-power data (*) reported in section 3.1. Therefore a comparison of the variation of $|S_{11}|$ with the applied power level for the different coatings can be considered to be valid.

Table 3 shows that a certain degradation of $|S_{11}|$ with increasing power is observed for all absorber components in the high power tests, mainly due to the heating of the ferrite during the test. Up to a power level of 3.5MW peak power (2.96kW average power) the drift of $|S_{11}|$ was comparable to the thermal drift observed at low power by varying the cooling water temperature from 40°C to 60°C. This drift at 3.5MW/2.96kW leads to the conclusion that the effective temperature of the ferrite coating had reached 60° The observed power-induced drift of the APS-sprayed component IOT2 was comparable to the AFT-tile absorber, while the APS-sprayed absorber MET1 and particularly the HVOF-sprayed RHV2 varied slightly more as the power level was increased. The greater drift could be explained by a greater build-up of heat in the ferrite due to a lower heat transfer from the sprayed coating. However, the thermal drift values of $|S_{11}|$ are seen to be quite low and could be allowed for by designing an absorber margin of at least 3dB.

2.3 Economic analysis of the case study components

The economic advantage of thermal spraying the waveguide component is a very important issue of this project. Because of this, a comparison between the cost of a sintered AFT component and a thermal sprayed component has been made and the results summarised in Table 15. The cost calculation was made on a limited lot production of 50 pieces. The material cost for the AFT made waveguide component is calculated at 132 € and the other production costs (e.g. salary) are 50 €. So the overall costs for the AFT waveguide component is 182 €. After spraying the demonstration component the costs for thermal spraying were calculated. Spraying the demonstration part required 700 g of ferrite powder and the costs for this amount of powder is estimated with 45.50 €. The other production costs for spraying the waveguide component are 57 €, so the overall costs for the production of the component by thermal spraying is 102.50 €. The comparison of the two overall costs for the production of the waveguide component shows that the costs could be reduced by over 40 % by thermal spraying. This economic benefit will even increase for higher production lot quantities. Therefore, thermal spraying exhibits a high economic potential for industrial production of the waveguide components. The results within this project also show that the thermal spraying process could be used for other components, which leads to further cost reduction within the waveguide production.

Table 15: Production costs and material costs for the demonstration part with regard to a limited lot production of 50 pieces.

Process	Material costs	Cost of production	Overall costs
Sintered tile component	2 € x 66 tiles = 132 €	50 €	182 €
Thermal sprayed component	Approx. 700 g spraying powder = 45.5 €	57 €	102.50 €

2.4 Conclusion and Outlook

Four case study components, waveguide based ferrite microwave absorbers, have been successfully designed, fabricated and tested at low and high microwave power levels. The innovative WR284 waveguide device is based on a water cooled inner conductor thermally sprayed with a nano-scale NiZn ferrite powder, using HVOF and APS.

The three thermally sprayed devices tested exhibited good RF absorption properties between 2.856 and 2.998 GHz. The performance is only slightly lower than that of an absorber with conventionally sintered and bonded ferrites, although the waveguide design had not been optimized for thermally sprayed ferrite coatings.

A high power capability up to 4.5 MW_{peak} and 3.8$kW_{average}$ has been demonstrated successfully at 2.856GHz, underlining the robustness and good thermal properties of sprayed ferrite absorbers. The absolute power limits are still to be investigated. The average power limit will depend on the thermal conductivity and any thermal stresses created in the ferrite coating.

An improvement of the RF absorbing properties of the sprayed ferrites would lead to the ability to use thinner coatings that would offer the benefits of superior heat dissipation, lower thermal stress in the ferrite, and even lower thermal drift of the RF absorption. Beyond this, it could reduce the costs of thermal spraying by reducing the demand on material and fabrication time.

The cost estimation made in this report suggests that a cost reduction of about 40% could be obtained compared to the conventional fabrication technology with sintered and bonded ferrites. Even higher economical benefits could be expected for larger production lot quantities.

As an outlook, the investigation of other ferrite powder compositions for thermal spraying could lead to more broadband devices or RF absorbers suited for other frequency bands. Particularly, the frequency range below 1 GHz is interesting, where application potential is seen in large-sized high-power waveguide or coaxial absorbers for broadcast and scientific applications. Furthermore, as thermal spraying allows conformal coatings, nearly any kind of shape and surface could be coated, e.g. EMC-shieldings in housings or walls of RF anechoic chambers.

Workpackage 3.2 **Start date:** Month 25 **End date:** Month 27

Title: Technology Transfer and Dissemination

Contractors Involved: AFT, RHV, Rasceur, Oseir, PSI, Pyro, Met, UNOTT, SEI and PMI

Objective

1) To document and transfer the developed technology from research providers to SMEs
2) To prepare information to assist in the future exploitation of the technology.
3) To set up facilities to demonstrate the process to the wider industrial audience

Progress

To document and transfer the developed technology from research providers to SMEs

A full process manual has been produced for WP 3.1 and presented under Deliverable 9. This covers the technical set-up and spray parameters used to coat the demonstration parts using HVOF at UNOTT, RHV and PyroGenesis and APS at SEI (IOT) and Metallisation.

To prepare information to assist in the future exploitation of the technology.

Publications in papers or journals planned by the consortium partners in the coming 12 months as of 1st of January 2009 are:

- A paper prepared by the University of Nottingham has been accepted for publication entitled "Quantitatively evaluating the effect of oxygen / fuel ratio on Fe^{+2} content in HVOF sprayed Ni-Zn ferrite coatings" Deen Zhang, D. G. McCartney accepted by Journal Thermal Spray Technology
- A paper has been prepared and will be presented by UNOTT/SEI/PMI at the next ITSC 09. This paper will deal with the properties and production of the ferrite coatings. The title of the manuscript is:- "Novel NiZn-Ferrite Powders and Coatings for Electromagnetic Applications"; Prof. D.G. McCartney, D Zhang, M. Brühl, K Bobzin, T. Talaka, A Ilyuschencko and J Y Yellup, to be presented at International Thermal Spray Conference May 4-7, 2009, Las Vegas, Nevada, USA.
- Another paper is planned by RWTH Aachen together with other consortium partners on powder production. This paper could be published in the Journal of Materials Science.
- AFT will organise a workshop or conference and write a technical publication concerning the demonstration part and the microwave material characterization of ferrite coatings
- Oseir will prepare an article for the Spraytime Magazine (Magazine of Thermal Spray Society of American Society for Metals) in Spring 2009 after completion of the project

In support of the commercialisation of the research deliverables an AFT data sheet has been prepared for the WR284 High-Power Waveguide Absorber Device. A copy is provided in Figure 33.

A public information section has been created on the project website at www.nottingham.ac.uk/~emzjyel/NaMaCo.

To set up facilities to demonstrate the process to the wider industrial audience

High-power microwave tests of the demonstrator part were made at one of AFT's customers in Jan. 2009. This was the first customer demonstration of the case study component and its features. The industrial trials were carried out at Varian Medical Systems, Palo Alto, USA.

Demonstrations of the developed device will be made by AFT to prospective customers during both visits to AFT by customers and by visiting customer's premises. Demonstration devices have been manufactured for this purpose, low- and high-power tested during WP 3.1 of the project.

Other Information

The specific intended actions for each partner have been listed in the "Plan for Using and Disseminating the Knowledge" which covers the exploitable knowledge and its use, the dissemination of knowledge and the publishable results.

Novel Ferrite Absorbers

A new range of broadband microwave absorbers have been designed based on a novel NaMaCo ferrite coating technology. These attenuators are intended for use in high-power microwave isolators within the GHz range for continuous power levels of several kW and peak power levels of several MW. High-power evaluation of WR284 waveguide absorbers as demonstration models has shown that a reliable attenuation performance can be obtained at 2.856GHz and at a pulsed power level of 3.8kW average and 4.5MW peak power.

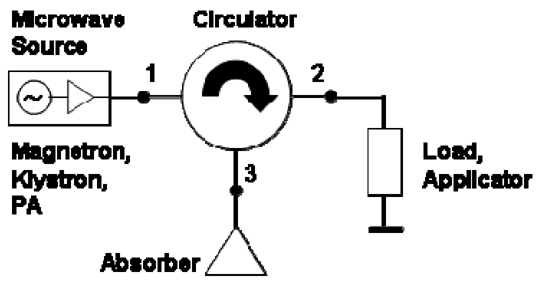
The NaMaCo technology is a sprayed Ni-Zn ferrite layer which offers advantages over conventional power absorber technologies, such SiC or water absorbers:

- high peak and average power capability
- broadband absorption
- thermal stability
- high reliability
- no special water conditioning

The sprayed Ni-Zn ferrite material shows similar magnetic absorption in the GHz frequency range as sintered ferrite ceramics. As the ferrite coating is sprayed directly on a cooled metal surface, the thermal performance is not limited to an adhesive layer conventionally used to bond ceramic tiles.
The NaMaCo ferrite layer may also be applied to curved and irregular surfaces increasing the versatility of unit design.
The spray process by which the ferrite is applied has been developed under an EC funded collaborative research project involving:

The University of Nottingham, UK
RWTH SEI/IOT, Aachen, Germany
PMI, National Academy of Sciences of Belarus
Rybak & Höschele GmbH & Co. KG, Germany
Rasceur Industrial Innovations BV, The Netherlands
Oseir Ltd, Finland
PSI Ltd, UK
PyroGenesis S.A., Greece
Metallisation Ltd, UK

Absorbers are key components of isolators used to protect power amplifiers and microwave tubes against reflections



Ferrite coated conductor

WR284 waveguide ferrite absorber device

For further details contact:
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1) Table 2: Deliverables List

Del. no.	Deliverable name	WP no.	Date due	Actual/Forecast delivery date	Estimated indicative person-months *)	Used indicative person-months *)	Lead contractor
D1	Specification of performance requirements of coatings for microwave applications; definition of target structural and compositional ranges of coatings; equipment availability; initial identification of other application areas	1.1	1/12/06	8/12/06	5.25	5	AFT
D2	Interim progress report on technical progress of tasks 1.1, 1.2 and 1.3	4	1/4/07	2/4/07	1	1.5	UNOTT
D3	Interim report on the manufacture of ferrite powder materials, suitable for HVOF spraying, having required properties as defined in specification of performance requirements WP1.1	1.2	1/10/07	30/9/07	13.5	13.9	PMI
D4	Report on the process-structure-performance characteristics of ferrite coatings deposited from conventional, large-grained feedstock powder by separate HVOF techniques	1.3	1/10/07	30/9/07	23	23.9	UNOTT
D5	Mid-term Assessment Report and Plan for using and disseminating knowledge (V1 – draft)	4	15/11/07	12/11/07	2	2.5	UNOTT
D6	Report on physical, compositional and electromagnetic properties of nanostructured ferrite coatings produced in the laboratory	1.4	1/2/08	3/3/08	24	7	SEI
D7	Final report on the manufacture of ferrite powder materials, suitable for HVOF spraying.	1.2	1/4/08	31/3/08	8	5	PMI
D8	An industrial HVOF facility capable of demonstrating the deposition of high quality ferrite coatings.	2.1	1/8/08	13/10/08	27	27	Met
D9	User guide detailing equipment specifications and thermal spraying processing parameters.	2.2	1/8/08	14/10/08	9.5	8.4	RHV
D10	Data on the manufacturing processes used, performance and economic analysis relating to the industrial case study waveguide application	3.1	1/10/08	14/3/09	11.5	11.5	AFT
D11	Promotional material, process manuals, data sheets, exhibition posters, technical papers and articles to support commercialisation of the research deliverables	3.2	1/10/08	14/3/09	8.5	7.7	Rasceur
D12	Final Technical Report and Plan for using and disseminating knowledge (V2 - Final)	4	15/11/08	14/3/09	3	8.5	UNOTT

Table 3: Milestones List

Milestone no.	Milestone name	WP no.	Date due	Actual/ Forecast delivery date	Lead contract or
1	The feasibility of thermally spraying ferrite powders to form coatings with retained feedstock powder structure has been demonstrated.	1	1/10/07	1/10/07	SEI
2	A laboratory-based process will have been established with optimised parameters for depositing nanograined ferrite coatings with electromagnetic properties exceeding those of baseline materials	2	1/2/08	3/3/08	MET
3	A fully documented, industrial thermal spraying process for the deposition of nanostructured ferrite coatings has been produced.	3.1	1/8/08	14/10/08	AFT
4	Case study components produced, evaluated and documented as aids for future exploitation/dissemination activities.	3.2	1/10/08	14/3/09	Rasceur

3 Section 3 – Consortium management

Consortium management has been undertaken by the University of Nottingham, who have been responsible for all communication between partners and with the EC, organisation of meetings with associated minuting, co-ordination and correlation of information for deliverables and reports and the submission of these reports to the EC via the CIRCA database and their distribution to the partners.

Most communication has been via email in addition to the establishment of a confidential project website where minutes, reports and all other documents are stored and available to partners.

The project met its targets to complete Deliverables and Milestones by specified dates within the extended timeframe for task completion. Partners have contributed to the tasks as prescribed in the workprogramme. Person months contributions to each Deliverable were close to that anticipated and contributions to the work packages were close to predicted.

Costs per partner for the whole project are such that the total contribution has been very close to budget (+€1019). Rasceur, PSI, Pyro and PMI reached their budgeted figure, AFT and Osier exceeded their contribution while UNott, SEI and Metallisation did not reach their budgeted contribution. UNott and Metallisation contributions were deflated by about 40% over year 2 due to the variation in £/€ exchange rate. SEI reached 98% of its contributions. Oseir significantly exceeded its budgeted contribution due to the travelling costs of visiting the spray partners to run trials with the SprayWatch particle monitoring system.

Project Meetings have been held at 6 month intervals with Technical Meetings at the interceding 3 months intervals. Project Meetings were held as follows:-

- Kick-off Meeting, Nottingham, Oct 2006
- 3 month Technical Meeting, Aachen, Jan 2007
- 6 month Management Meeting, Backnang (AFT), Mar 2007
- 9 month Technical Meeting, Nottingham, Jun 2007
- 12 month Mid-term Management Meeting M3, Aachen (SEI), Sept 2007
- 15 month Technical Meeting T3, Aachen (SEI), Germany, Jan 2008
- 18 month Project Meeting M4, PMI, Minsk, Belarus, April 2008
- 21 Month Technical meeting T4, Nottingham, UK, July 2008
- 24 Month Project Meeting M5, PyroGenesis, Athens, Oct 2008
- 27 Month Final Meeting M6, Aachen. Germany, Dec 2008

The Management Meetings were well attended (>90%) while the Technical Meetings in Nottingham and Aachen were mainly for the RTD performers to discuss scientific aspects of the work but these have also been attended by industrial partners interested in that particular aspect of the project. The meeting at PMI was most informative as it provided an opportunity for all partners to see the facilities for powder production.

Table 16: Workpackages - Plan and Status Barchart

Tasks		Partners Involved	Period (months)														
			2	4	6	8	10	12	14	16	18	20	22	24	26	27	
WP 1	**LABORATORY DEVELOPMENT OF POWDER & HVOF PROCESS**																
1.1	Definition of Industrial Requirements	ALL		D1													
1.2	Ferrite Powder Synthesis and Characterisation	1,6,9,10							D3			D7					
1.3	Preliminary HVOF Spraying Trials	1,2,3,5,6, 7,8,9,10							D4 M								
1.4	Thermal Spraying Trials Using Nanostructured Ferrite Powders	ALL									D6 M						
WP 2	**INDUSTRIAL VALIDATION OF PROCESS**																
2.1	Industrial Thermal Spraying Trials	1,2,3,5,6, 7,8,9,10													D8		
2.2	Definition of Process Parameters	1,2,3,6, 7,8,9,10													D9 M		
WP 3	**INDUSTRIAL EVALUATION & TECHNOLOGY TRANSFER**																
3.1	Manufacture and Evaluation of Case Study Components	1,2,3,4,5, 7,9,10															D10 M
3.2	Technology Transfer and Dissemination	ALL															D11
WP 4	**PROJECT MANAGEMENT & REPORT PREPARATION**	ALL				D2 R		D5 MTA									D12 FR

Key:- M- Milestone R – Delivery of Technical Report MTA – Mid-term Assessment FR – Delivery of Final Report

Shaded bars – estimated duration. Hatched bars – actual duration

Section 4 – Other issues

The University of Nottingham (UNOTT), as a RTD performer and the project co-ordinator, provided both the technical guidance and administrative lead to the project. Their expertise in HVOF Top Gun spraying was used to conduct the initial laboratory scale trials on both commercial and experimental ferrite powder and establish the feasibility of the process. Their facilities enabled the full microstructural characterisation of the coatings produced. Technology transfer to other partners included the specification of powder composition and particle size requirements and spray parameters. During the industrial trials Nottingham provided benefit to all the industrial spray partners by providing rapid feedback on the structural characterisation of the samples produced.

RWTH SEI/IOT, Aachen, as an RTD performer, conducted HVOF trials using a DJ2600 system and undertook characterisation of these samples. When it was realised that this system was less suited to spraying ferrite than the Top Gun system at Nottingham, IOT carried out preliminary trials using an APS system, which produced good results: this work resulted in the incorporation of APS into the work programme. IOT had the spray facilities to conduct an industrial scale trial and spray several demonstration components. They also worked closely with RHV assisting them with setting up industrial HVOF spray trials. IOT conducted all the powder size distribution measurements using their state-of-the-art unit. This enabled consistent quality control of the size distribution of all powders used.

PMI's main responsibility was to develop a method of ferrite powder production. Three techniques were evaluated and 2 were selected as feasible methods for production of large scale quantities. Initially, small lots were produced for evaluation by UNOTT and SEI/IOT. Composition adjustments were made to compensate for Zn loss during spraying based on feed back from UNOTT. Larger kilogram quantities of powder were produced for the industrial trials and the manufacture of demonstration components with the particle size distribution being controlled to give acceptable deposition efficiency and powder flowability. PMI responded well to the requests form the partners for powder and in general the supply and quality of powder for the trials was good. PMI also conducted grain size determination of both the nanostructured powder and the sprayed coatings using their X-Ray system and software analysis of peak broadening. The microstrain in the coating was also measured by the X-Ray broadening technique.

AFT was the lead SME as they were the designer and end user of the product. They designed and set-up the systems for measuring the low power magnetic properties of the sprayed coating and provided a comparison by manufacturing pressed and sintered rings of both their baseline ferrite and the experimental ferrites produced by PMI. AFT interacted well with the other partners relaying what was required and providing feed back on the results that were obtained. They designed and manufactured the demonstration part and distributed the part for coating by thermal spraying to the relevant partners. On return of the sprayed parts they assembled the waveguide absorber and tested it at low power. The high power tests were conducted by a customer of AFT in the USA. AFT organised and reported on all the magnetic measurement trials.

RHV, PyroGenesis and Metallisation are all thermal spray companies. Industrial trials were conducted by each using different systems. Test coupons and rings for magnetic measurement were produced and evaluated by UNOTT and SEI/IOT who provided feed back and advice on further trials. Demonstration parts were produced and the conditions under which they were produced documented. All partners provided their valuable industrial knowledge on thermal spraying to the project both at meetings and via other discussions.

PSI provided their expertise in particle size management and undertook some classification of specific batches of powder. Rasceur used their technology transfer and dissemination experience in surface engineering to assist AFT and UNott by co-ordinating the plan for using and disseminating. This was achieved by interaction with all the partners in order to establish their requirements.

Oseir expertise lies in the area of the temperature and velocity measurement of particles in flight in a thermal spray flame. The camera-based system that they have developed was used to establish these fundamental parameters for each of the systems used by the thermal spray partners (both SMEs and RTD performers). Oseir visited each of these establishments with their equipment and made measurements on the HVOF or APS systems at UNOTT, SEI/IOT, PyroGenesis, RHV and Metallisation (who purchased and now operate a SprayWatch unit). Oseir provided a wealth of knowledge based on experiences with thermal spray systems.

In general the partners worked well together providing a complete chain of requirements from the powder supply, through the deposition technique with monitoring facilities to product evaluation and end-user dissemination. The industrial partners gained from the research experience of the RTD performers in both thermal spraying and coating characterisation while the RTD performers gained an industrial perspective on the processes. All partners learnt about the requirements for microwave absorbing materials from AFT and most became reacquainted with imaginary numbers after many years.

There was no change to the consortium throughout the project.