AFRL-OSR-VA-TR-2014-0080

MULTI-PHASE, MULTI-FUNCTIONAL CERAMIC COATINGS

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03/14/2014
Final Report

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/ IOS
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
30-06-2013	final	30-06-2010-30-06-2013

4. TITLE AND SUBTITLE
Multiphase-Multifunctional Ceramic Coatings

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-10-1-0192

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NUMBER
CINVESTAV-CIMAV-RF-2013Final

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
* CONACYT. Av Insurgentes Sur 1582, Crédito Constructor, Benito Juárez, 03940 Ciudad de México, Distrito Federal
* CIMAV. Miguel de Cervantes 120, Industrial Chihuahua, 31109 Chihuahua
* Southern Office of Aerospace Research and Development (SOARD),

10. SPONSOR/MONITOR'S ACRONYM(S)
CONACYT - CIMAV - SOARD

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT
Distribution A- Approved for Public Release.

13. SUPPLEMENTARY NOTES
Prepared as a joint report in cooperation with the University of California, Santa Barbara

14. ABSTRACT
This project deals with ceramic coatings deposited by thermal spray and based on La2Zr2O7 (LZO) + toughening phase. The phase that showed promising results in dense ceramics to be scaled up and prepare coatings is the LaAlO3 (LAO). LZO and LAO mixtures in a 70:30 mol% ratio were deposited on SS304 and FeCrAlY substrates. Milling followed by a spray drying process enabled production of 70LZO:30LAO mixture in the form of spherical agglomerates with adequate size distribution and flow properties for feeding into a thermal-spray system. The as-sprayed coating comprises crystalline LZO and partially amorphous LAO. The amorphous phase resulted from the high cooling rate experienced by the molten particles. The coatings were annealed at 1100°C for promoting crystallization of the amorphous phase. The elastic modulus and hardness clearly increased after the annealing treatment. However, the fracture toughness tested on the annealed coating showed low values of 1.04 MPa√m. Further research is required to mitigate the formation of amorphous LAO by proper control of the quenching conditions. Although the fracture toughness improves moderately as the LaAlO3 fraction increases in dense ceramics, the values are still lower than those considered acceptable.

15. SUBJECT TERMS
Rare-earth zirconates, high temperature ceramic coatings, thermal spray deposition, mechanical properties

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
					Gerardo Trapaga Martinez
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	UU	6	**19b. TELEPHONE NUMBER** *(include area code)*
U	U	U			+52 442 2119925

FINAL PROGRESS SUMMARY

To:	***technicalreports@afosr.af.mil*** ***jamesfillerup@afosr.af.mil***
Subject:	***Final progress report***
Contract/Grant Title:	***Multiphase-multifunctional ceramic coatings***
Contract/Grant #:	***FA9550-10-0192***
Reporting Period:	***1 July 2012 to 30 June 2013***

Annual accomplishments (200 words max):

The broader goals of this project were to develop an infrastructure and expertise in Mexico to deposit ceramic coatings by thermal spray and to explore novel multi-phase systems that may offer superior temperature capability with emphasis on improving toughness and phase stability. The primary goal was clearly accomplished by developing an instrumented air plasma spray facility and training students in its use and the underlying processing science. While a material system with superior characteristics was not identified, several accomplishments resulted also from the second goal. The team developed expertise in the synthesis of complex oxides by chemical methods, as well as by high energy milling and solid state reaction. The team also generated understanding on the densification behavior of these systems, and produced specimens to measure thermal and mechanical properties. None of the systems investigated exhibited the desired improvement in toughness, a finding tentatively attributed to an inadequate grain structure. Coatings based on $La_2Zr_2O_7$ with $LaAlO_3$ dispersoids were synthesized for comparison with the dense oxides. For that purpose the team developed expertise in spray drying to generate particulate material suitable for spraying. The coatings exhibited interesting forms of metastability detrimental to the properties. Avenues to circumvent this problem were identified.

Archival publications (published) during reporting period:	***None*** ***There are 3 publications in preparation***
Changes in research objectives, (if any):	***None***
Changes in AFOSR program manager (if any):	***None***
Extensions granted of milestones slipped, if any:	***None***
Include any new discoveries, inventions, or patent disclosures during this reporting period (if none, report none):	***None***

Report Information – Final Report

1. General Information

Program:	CONACYT – CIMAV – Southern Office of Aerospace Research and Development (SOARD)
Grant Title:	Multiphase-Multifunctional Ceramic Coatings
Performing Organization names:	Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional – Unidad Queretaro / University of California, Santa Barbara
Principal Investigator / Organization:	Dr. Luis Gerardo Trápaga Martínez CINVESTAV-Querétaro
Principal Investigator US collaboration / Organization:	Dr. Carlos G. Levi University of California, Santa Barbara
Reporting Period	Final
Dates covered:	June 2010 – June 2013

2. Summary

This project dealt with ceramic coatings deposited by thermal spray and based on the candidate insulating oxide $La_2Zr_2O_7$ (LZO), as representative of the rare earth zirconates (REZ), with second phases intended to modify its toughness. Three types of second phases were investigated: (i) a tetragonal zirconia solid solution co-doped with La and Ce, (ii) a disordered fluorite phase of nominal composition $La_2Ce_2O_7$ (LCO), and (iii) a perovskite phase $LaAlO_3$, (LAO). The relative proportions of the two phases were varied by proper control of the chemical composition. Coating compositions were synthesized by atmospheric plasma spray (APS) at CINVESTAV facilities, and dense monolithic counterparts were fabricated by conventional powder processing methods. A critical step in the synthesis was to ensure that the prepared materials are homogeneous. For this reason, powders of the relevant compositions were synthesized from precursors and consolidated into compacts at UCSB. This approach is ideal for achieving superior homogeneity as needed for fundamental laboratory studies, but generally inadequate to produce the volumes required for APS. Powders suitable for spraying were prepared by high energy milling of individual oxide mixtures (mechanosynthesis) using facilities developed at CINVESTAV as part of this project. Compacts of powders prepared by mechanosynthesis and by precursor methods were used for property measurements.

Synthesis and the ensuing microstructure evolution studies was a central part of the proposed work. The characterization (XRD, SEM, TEM) of the as-deposited microstructures was of particular interest because of the likelihood that they might exhibit one or more forms of metastability, as was the study of their subsequent phase transformations and morphological evolution upon thermal exposure. The results offered an opportunity to

understand the genesis and evolution of the second phases in the context of their potential for toughening of the primary LZO oxide.

The characterization of the mechanical behavior of complex oxides and its connection to chemistry and microstructure was a key element of the research. For this purpose the CINVESTAV team performed nanoidentation studies aimed at identifying second phases that might offer greater potential for toughening by tailoring the residual stress field around cracks, by ferroelastic switching or by phase transformations. Analysis of dense ceramics based on various RE perovskites led to the selection of the REZ-RAO system as a primary candidate for investigation. The composition that showed promising results in dense ceramics were scaled up for coating deposition. The produced coating compositions included LZO, LAO and LZO+LAO mixtures in a 70:30 mol% ratio, deposited on SS304 and FeCrAlY substrates. Toughness studies of nominally dense ceramic specimens were done by microindentation.

The outcomes of the project include several Masters' and PhD theses of students from Cinvestav's graduate programs. Additionally, the project had the participation of post docs and researchers spending sabbatical leaves at CINVESTAV. In general, the technical outcomes from the project are highly satisfactory although manuscripts are still in various stages of preparation for submission. However, a number of additional products were obtained (see lists in the next sections) that are expected to serve as a basis for the publication of at least three manuscripts.

3. Project objectives

3.1 General objectives:

- To understand the synthesis and evolution of two-phase systems involving the $La_2Zr_2O_7$ Pyrochlore with a second phase, and assess the fracture behavior of those systems to identify pathways and develop guidelines for optimum toughening behavior in both monolithic samples and APS coatings.
- To develop the process understanding and expertise needed to deposit promising materials as coatings by air-plasma spray (APS) and undertake a preliminary assessment of their behavior.

3.2 Specific objectives:

- To synthesize ceramic powders of ZrO_2-La_2O_3-CeO_2 system by two methods (mechanosynthesis and chemical precipitation methods, followed by thermal treatments) to get two-phase ceramic systems of LZO plus a potential toughening phase. The initial candidate second phases were:
    - a tetragonal, non-transformable, nominally ferroelastic zirconia-based solid solution t-$Zr(Ce,La)O_2$
    - cubic fluorite solid solutions approximately based on $La_{0.5}(Zr_xCe_{1-x})_{0.5}O_{1.75}$ or $Ce_{1-x}(La_{0.5}Zr_{0.5})_xO_{2-x/4}$, expected to induce different degrees of residual stress in the LZO matrix.
    - a $LaAlO_3$ perovskite which could be tailored to undergo an energy-absorbing phase transformation during fracture

- To determine the thermodynamic equilibrium regions of the proposed phases and the compositions that would yield a 50% volume of the second phase.
- To produce dense bulk samples adequate for characterization of their microstructure, the toughness and the thermal conductivity
- To understand toughening mechanisms of ceramic two-phase field REZ-systems by controlling composition, mixture of phases and microstructure. This includes studies of the local response of phases to nanoindentation as well as the behavior under microindentation.
- To develop an understanding of the APS process as needed to determine the appropriate conditions for producing high quality coatings of LZO with the candidate second phases.
- To deposit ceramic coatings of selected compositions by APS and characterize the relationship between chemistry, microstructure and process parameters.
- To understand the effect of chemistry and microstructure on the performance of coatings under thermal exposure, with emphasis on sintering resistance, phase stability, and the mechanical properties of interest, namely toughness and elastic modulus.

4. Activities

Activities were organized according to the materials systems of interest and processing methods:

	Pyrochlore-tetragonal	Pyrochlore-Fluorite	Pyrochlore-Perovskite	Al_2O_3 (model)	Commercial YSZ
High Energy Milling + Thermal Treatment		X	X		
Co-Precipitation + Calcination	X	X	X		
Co-Precipitation + Milling + Calcination	X				
Spray Drying			70LZO:30LAO	Process Development	
Air Plasma Spray			70LZO:30LAO		Process Development

Commercial powders of La_2O_3, Al_2O_3, ZrO_2 and CeO_2 were used for the synthesis of the different compositions by high-energy milling and subsequent thermal treatment to enable the reaction of the powders into the final products. Lanthanum oxide (99.9%, Alfa Aesar), zirconium oxide (99% + metals basis excluding Hf, HfO_2=2%, Alfa Aesar), aluminum oxide (99% Alfa Aesar), and ethyl alcohol (ethanol) were used as raw materials. Prior to using the precursor powders, the powders were placed in alumina crucibles and subjected to a heat treatment at 1000 ° C for 6 h in a Thermolyne M46100 box furnace in order to remove the hydroxides which might have formed during storage. The more significant hygroscopic behavior was observed for the La_2O_3 powders. After 6 h of heat treatment the precursor powders where characterized using X-ray diffraction. The zirconia powders were found to be predominantly monoclinic, the lanthana powders contained a hexagonal phase corresponding to La_2O_3 and also minor amounts of $La(OH)_3$, the ceria powders were predominantly fluorite and the alumina powders were corundum (alpha-alumina).

Two approaches were used for the mechanosynthesis of the compound powders. One type of synthesis was performed using a vibratory mill Retsch MM400. The oxide powders were mixed in the desired proportions and placed in Nylamide vials with a capacity of 5 g (two vials per run). YSZ balls with a 10 mm diameter was using as a milling media with a powder:media mass ratio of 1:10. The milling time was 5 h at 25 Hz. After milling the powders were separated from the media, placed in alumina crucibles and heat treated in a box furnace. The powder mixtures were calcined for 5h at different temperatures depending on the compound of interest (1250°C for LZO and LCO, 1450°C for LAO). The calcined powders were milled again for 5 minutes in order to break up an agglomerates formed during the calcination process. The powders were uni-axially pressed using a stainless steel die (10 mm in diameter) and a 750 MPa pressure in order to produce 1 g pellets. The final size of the sample after compaction was about 1 cm diameter and about 0.4 to 0.5 cm thick. The green pellets were sintered for 6 h at 1500°C for the LZO and/or LCO, and 1550°C for LAO samples.

The second method used for the mechanosynthesis of LZO and LAO powders was based on a planetary mill (Retsch PM 400) operating at 250 rpm and using YSZ balls. The requisite amounts of oxides in each compound were weighed and mixed homogeneously with ethanol, and milled for 3 h. Each suspension was dried after milling and then heat treated for 5 h in a high-temperature furnace (Thermolyne M46100), at 1250 °C for LZO, and at 1450°C for LAO, to promote the solid state reaction to effect the formation of the desired phases. The powders were then mixed in 20, 30, 40 and 50 mol% contents of LAO in LZO and sintered to measure their mechanical properties.

Powders of the desired compositions were also synthesized by co-precipitation from mixed precursor solutions followed by pyrolysis. The initial materials were reagent grade salts of $ZrO(NO_3)_2$, $La(NO_3)_3$, $Ce(NO_3)_3$ and $Al(NO_3)_3$ (Alfa Aesar, Ward Hill, MA). Each of the salts was individually dissolved in deionized water and the resulting solution was calibrated by one aliquot poured into a pre-weighed alumina crucible. The solutions were dried using an oven at 60°C for 24 h and then placed in a furnace for calcination at 850°C for 4 h. Thereafter the crucible was weighed and the difference in weight was recorded as yield in terms of grams of oxide per gram of solution. Once the solutions were calibrated they were mixed in the requisite proportions to yield the desired compositions. The precipitation was effected by pouring the mixed precursor solution into a large volume of NH_4OH solution while stirring continuously. Additional NH_4OH was periodically added to the precipitation bath to ensure that the pH was maintained at ~11. The resulting suspension was initially filtered, re-dispersed in ethanol to remove residual NH_4OH that might have been adsorbed in the precipitated, and filtered again. The wet precipitate was dried in while gently grinding in an alumina mortar heated using a laboratory hot plate, and subsequently calcined in an alumina crucible at 650-850°C, depending on the intended use of the powders. After calcination a 10 mm powders were formed into pellets using a 300 MPa pressure for subsequent sintering. Sintering treatments were conducted at 1200-1600° C from 10-24 h.

Densification of powders in the pyrochlore-fuorite system was also performed by Spark Plasma Sintering. It was found, however, that the phases present in the as-densified material did not correspond to those expected at equilibrium. X-ray diffraction reveals peaks suggestive of La_2O_3. While other phases could not be clearly identified, it is likely that the high temperature exposure in vacuum would have induced the reduction of Ce^{4+} to Ce^{3+}. The expected phases develop after heat treatment but their lattice parameters were somewhat different than those observed in conventionally sintered materials, suggesting that complete equilibrium had not reached.

Neither of the methods used to produce powders yields particle sizes and/or morphologies suitable for efficient injection into a plasma spray torch, requiring an additional step for agglomeration into spherical aggregates. For this purpose, stoichiometric amounts of $LaAlO_3$ (LAO) and La_2ZrO_7 (LZO) powders produced by mechanosynthesis and solid-state reaction using the procedure described above were weighted and mixed in ethanol in the proportions needed to form the desired composition. (The technique was first developed using commercial alumina powders to optimize the utilization of the relatively limited amounts of LZO-LAO powders produced in house). The resulting suspensions were milled for one hour in a planetary mill to break agglomerates and homogenize the distribution of phases. After drying this mixture the mixed powders were suspended in distilled water to a concentration of 70 % of solids and subsequently converted into spherical agglomerates suitable for APS using a spray dryer (Triowin SD-1500). The spray parameters determined to be adequate for yielding powders of the right characteristics were a spray pressure of 25 kPa, feed rate of 0.5 1/h, and inlet temperature of 230°C. The resulting powders were calcined at 1000 °C to rigidize them to the consistency needed for APS. Size classification was performed using a sieve shaker to yield a desired size powder distribution. These parameters were chosen based on the experience derived from the process development using Al_2O_3 powder. The optimal parameters were practically the same for both systems.

Deposition of the 70/30 powder into coatings was performed using a 9MB plasma spray gun from Sulzer Metco.[1] The feedstock powders produced by spray drying (or acquired commercially for practice runs) were directly sprayed on grit-blasted SS304 or FeCrAlY commercial substrates (22% Cr, 5.0% Al, 0.1% Y and 0.1% Zr) with no bond coat. The substrate temperature was maintained approximately at 300°C for all experiments as measured by a thermometer allocated behind the sample. The torch scanning velocity was kept constant at 1 $m \cdot s^{-1}$. The spray parameters used for the preparation of the coatings on SS 304 substrates are shown in Table I. These

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[1] As in the case of the spray drying, the initial experiences were developed with commercial 7-8YSZ powder of the type normally used for the production of thermal barrier coatings (HOSP ZrO_2-8%Y_2O_3 Sultzer Metco 204NS). The motivation was to develop this expertise in parallel with the synthesis and spray drying of powders described earlier. Because of the complexity of the process and the need to educate students along the way, this activity consumed a considerable fraction of the total project time.

parameters were tuned based on measuring and a monitoring system of the plasma spray deposition process: Accura Spray- G3C (Tecnar) for the temperature and particle velocity of the in-flight particles of the plasma spray. Othe monitoring system used is the In-situ Coating Property (ICP) sensor for monitoring evolution of residual stresses build-up during thermal spraying (ReliaCoat Technologies, LLC).

Table I. Parameters used for the preparation of coatings

Fixed spray parameters		
Primary gas flow, Ar, SLPM		80
Secondary gas flow, H_2, SLPM		15
Voltage, V		67
Carrier gas flow, SLPM		25
Variable spray parameters		
Coating	Spray distance (mm)	Current (A)
1	90	515
2	90	568
3	90	620
4	120	515
5	120	568
6	120	620

The powders and coatings were characterized by X-ray diffraction using a Rigaku D/max-2100 with Cu radiation and operated at 30 kV. Transverse cross-sections of powder and coatings were ground using standard metallographic techniques, grinding from 120 to 2400 grade SiC and subsequently polishing with a colloidal silica suspension (Buehler Mastermet II). SEM micrographs (JEOL JSM 5800-LV) were used to estimate the morphology and particle size distribution of the powders as well as the thickness and morphology of the coatings.

A Hysitron Ubi1 nanoindentation system with a Berkovich diamond tip and variable load (1000 to 9000 µN) was used to measure the apparent hardness and elastic modulus on the transverse cross-section of the coatings. Indentation imprints were performed in a "load control" mode of force versus time. The fracture toughness of the coatings was estimated by micro-indentation using a Vickers instrument (HMV2000 Shimadzu). Determination of crack lengths was done in SEM micrographs of the indentation imprints.

The thermal diffusivity of the samples was measured by the laser-flash method [2] (LFA LINSEIS 1000) using a Nd-glass laser with a wavelength of 1064 nm. Thermal diffusivity values were obtained at room temperature, 300, 500, and 1000 °C under vacuum.

[2] Moskal, et al, Arch. Of Mat Sci. and Eng. 36[2]:76-81 (2009)

5. Conclusions

5.1 Pyrochlore-$La_2Zr_2O_7$ - t' Zr(Ce,La)O_2 System

The initial approach suggested by the earlier phase diagram calculated by Du et al. [3], suggesting a small region of equilibrium between $La_2Zr_2O_7$ and a non-transformable t' solid solution was proven incorrect. An early activity aimed to produce a dispersion of tetragonal phase in pyrochlore and explore potential toughening of the latter. However, all approaches yielded a mixture of monoclinic zirconia with the pyrochlore phase. This was clarified by a phase diagram published by Andrievskaya et al[4] after the start of this project. The more recent experimental diagram reveals a much smaller tetragonal field than proposed by Du, with no composition in potential equilibrium with the pyrochlore immune to the monoclinic transformation. This negates access to the ferroelastic toughening mechanism typical of 7YSZ. A possible option is to produce a transformation toughened pyrochlore by dispersing metastable tetragonal phases within the LZO matrix, but the dopant mechanism was deemed unlikely to promote the desired degree of metastability in the tetragonal phase and further efforts were focused on other design concepts.

5.2 Pyrochlore- fluorite solid solution $La_x(Zr,Ce)_{1-x}O_{2-x/2}$ System

This system was of significant interest because the combinations along the tie-line $La_{0.5}(Zr_xCe_{1-x})_{0.5}O_{1.75}$ (substitution of Ce for Zr at constant La content) offered different degrees of lattice mismatch with the pyrochlore than those along $Ce_{1-x}(La_{0.5}Zr_{0.5})_xO_{2-x/4}$ (substitution of Ce into LZO while keeping the La:Zr ratio constant). The implication is that one could control the residual stresses around second phase particles in the microstructure, with potential effects on the toughness. There were, however, significant barriers to the experimental confirmation of this hypothesis, arising primarily from the substantial resistance to sintering of the powder mixtures.

Conventional sintering methods were not successful in producing samples dense enough for toughness testing from precursor-derived powders (co-precipitation + pyrolysis), even after major efforts to change the particle size distribution by milling. Pyrochlore-fluorite microstructures were produced where the second phase was finely dispersed, but they did not show a significant effect on fracture toughness. Notably, the samples along the $Ce_{1-x}(La_{0.5}Zr_{0.5})_xO_{2-x/4}$ tie-line exhibited toughness values as low as the single phase LZO.

Materials produced by high energy milling showed better sintering performance. However, the toughness values measured by microindentation were not significantly different from the samples densified by SPS from coprecipitated-pyrolized powders. It is not clear why the initially encouraging results of mixtures of LZO and LCO that motivated this part of the research were not reproducible after multiple efforts using different parameters, but it was decided to focus the remainder of the effort on the LZO-LAO system.

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3 Du, et al, Calphad 20[1]: 95-108 (1996)

4 Andrievskaya et al, J. Am. Ceram. Soc., 94 [6]:1911 (2011)

5.3 Pyrochlore-perovskite System

The LZO-Pyrochlore/LAO-Perovskite system was of interest because the perovskite alone has been shown to exhibit ferroelastic behavior and also has a displacive phase transformation, both of which could potentially translate in energy dissipation mechanisms when it is embedded in a more brittle matrix. The combinations explored did show some improvements in fracture toughness over the LZO, to a higher degree than the Pyrochlore-Fluorite system, but the toughness measured on dense compacts were nowhere near those competitive with 7YSZ.

The ferroelastic behavior was confirmed in samples with relatively large grain sizes, but grain growth is naturally inhibited when LAO is dispersed within a majority LZO matrix. There are some indications that the crack path becomes more tortuous in the samples containing perovskite particles, as the crack tends to avoid the second phase. In spite of these relatively positive findings, proof of concept was not accomplished in the compacts produced by co-precipitation or milling. Because of the potential for achieving significantly different microstructures in the coatings, this was the system selected for further study by APS.

5.4 Pyrochlore- perovskite coatings

Valuable experience on APS deposition of ceramics was gained with 8YSZ coatings. The fact that preheating substrates at 300°C leads to a fully crystalline material was confirmed. Preheating also reduced splashing, leading to disk-shaped splats. A spray distance of 90 mm, feed rate of 40 g/min and current of 600A resulted in the best combination of footprint symmetry, splat quality, spray efficiency and coating characteristics.

70LZO+30LAO coatings were successfully produced by air plasma spray without significant deviation of the target composition from powders produced by mechanosynthesis, solid state reaction and spray drying. The high cooling rate that the molten powder particles undergo when impacting the substrate during the deposition process resulted in a mixture of crystalline and amorphous phases, which is detrimental to the coating toughness. The amorphous phase was determined to be primarily based on $LaAlO_3$, but it was also determined that this condition could be modified by heat treatment (and presumably by higher substrate temperature during deposition). Further work will be aimed to mitigate the deposition of amorphous $LaAlO_3$ by minimizing the quenching effects during deposition. Although the fracture toughness is improved as the $LaAlO_3$ fraction increases, the values are still low.

5.5 Effectiveness of the collaboration

A primary goal of this project was to enable the development of local expertise in Mexico on the processing of multifunctional ceramic materials as high temperature coatings for gas turbines. In spite of the technical difficulties with the materials selected this goal was clearly accomplished as an APS facility and associated expertise in the deposition of thermal barrier coatings exists now at CINVESTAV. Not only was there an active collaboration between the US and CINVESTAV PIs, but the project facilitated the connection of CINVESTAV to the Center for Thermal Spray Research at State University of New York in Stony Brook, which is the premier center for thermal spray processing science in the US and a top center worldwide. It is expected that this three-way collaboration UCSB-CINVESTAV-USB will continue in other projects in the future, to the continued benefit of the state of technology in Mexico.

In spite of the effective participation of the US investigator this was limited primarily to periodic visits to discuss the progress of research at CINVESTAV and help advice the students on the planning and execution of their research. The funding available to the US collaborator was insufficient to have personnel at UCSB working on the project, since by agreement with AFOSR it was dedicated primarily to support the research and living expenses of the Mexican researchers when visiting UCSB (with the exception of a small amount of summer salary support for the PI and travel expenses for the UCSB PI visits to CINVESTAV). The funding agencies may want to consider an approach that allows more effective participation of students and/or post-docs at the US institution.

6. Open questions for future work

- Rare-earth zirconates remain strong candidates for next-generation TBCs owing primarily to their low thermal conductivity and resistance to penetration by molten silicate deposits, which are a major hindrance to higher temperature operation in aircraft engines, especially those of interest to AFOSR. Their major disadvantage is a much lower fracture toughness than existing materials, which makes them susceptible to a variety of mechanisms involving crack propagation through the TBC, notably erosion and foreign object impact but also intrinsic mechanisms associated with the bond coat oxidation. An overarching question is whether dispersion of second phases is indeed a viable mechanism to increase their toughness and, if not, what are the feasible alternatives. There is no evidence in the literature that a solution to this problem exists at this time, so efforts in this direction are still needed.
- It is not clear if the lack of significant success in toughening LZO is partly associated with the types of phases compatible with LZO that may be used for improved material designs, so efforts are underway to identify similar two phase concepts in other zirconate systems. Possible quaternary systems where a second rare earth may be used to modify, for example, the stability of the tetragonal phase or the switching charcteristics of the perovskite, are also of interest.
- Understanding of microstructural effects on these two phase systems is still very limited. There is evidence that switching occurs in LAO at large grain sizes upon indentation, but is likely suppressed at the small grain sizes. A path to control grain size to optimize second phase effects and the processing approaches required for implementation are a worthwhile research goal.
- All fracture toughness studies to date have been performed at ambient temperature, largely because of a lack of a suitable test to evaluate this behavior in coatings at higher temperatures. This is still relevant to

mechanisms that involve crack propagation within the coating on cooling as the engine is turned off, but it provides only limited insight into the potential behavior at higher temperatures. It is possible that some of the mechanisms postulated in this project may operate at the higher temperatures even if they are not effective at ambient, but this clearly requires additional research.

7. Work group

7.1 Investigators

- Dr. Gerardo Trápaga Martínez. Principal Investigator, CINVESTAV-Qro.
- Dr. Carlos G. Levi. Principal Investigator, University of California, Santa Barbara.
- Dr. Juan Muñoz Saldaña (CINVESTAV-Qro). Synthesis, processing and characterization of mechanical properties
- Dr. Carlos Poblano Salas (CIATEQ). APS coatings deposition
- Dr. Juan Zarate Medina (UMSNH) Sabbatical leave at Cinvestav-Queretaro, from Universidad Michoacana de San Nicolás de Hidalgo. 2011-2012. Synthesis and processing of ZrO2- LaO1.5-AlO1.5 ceramics by chemical routes.

7.2 Students

- Bertha María Esparza Esparza: PhD. Student; Cinvestav Querétaro 2009-2014. She worked in the synthesis of powders and dense ceramics of $La_2Zr_2O_7$ and $La_2Ce_2O_7$. Her main objective was to study the extent of toughening in mixtures of phases in this system.
- David Lozano Mandujano: PhD. student; Cinvestav Querétaro 2009-2014. His work focused specifically in the production of powders in various stable phases having convenient granulometry for coating applications, as well as the production of coatings by thermal spray.
- Luis Fernando Tovar Landín: Master's student; Cinvestav Querétaro 2010-2011. He worked in the synthesis of powders and bulk materials of the system ZrO_2-$LaO_{1.5}$-$AlO_{1.5}$. Monophasic and biphasic dense (LZO-LAO) bulk samples are used to study the structural, microstructural and mechanical properties by X-ray diffraction, Scanning Electron Microscopy and nanoindentation.
- Ississ Sarahai Feria Cortés: Master's student; Cinvestav. Thesis: "Strengthening of dense $La_2Zr_2O_7$ ceramics with non-transformable tetragonal phase". Advisors: Dr. Gerardo Trápaga Martínez, Dr. Juan Muñoz Saldaña. Graduation date: December 15, (2010).
- Eduardo Zúñiga Márquez: M.Sc. with specialty in Materials, Cinvestav. Thesis: "Characterization of mechanical properties by nanoindentation of Zirconia coatings for thermal barrier applications". Advisors: Dr. Juan Muñoz Saldaña y Dr. David Torres Torres. Graduation date: September 8, 2011.

- Adriana del Carmen Gallegos Melgar: M.Sc. with specialty in materials, Cinvestav. Thesis: "Ferroelasticity studies in multiphase ceramic systems for high temperatura applications". Her work mainly focused in the study of ferroelasticity of thermal spray coatings by mean nanoindentation. Thesis in progress up to 2016.
- Cortes Durán Mario Jorge. Instituto Politécnico Nacional, 2011-2012. Mechatronics engineer. He carried out a research stay at Cinvestav and performed the instrumentation of various experiments in the multifunctional laboratory. 2012
- Rangel Camacho José Carlos. Instituto Politécnico Nacional, 2011-2012. Mechatronics Eng. He carried out a research stay at Cinvestav working in the instrumentation of various experiments.
- Islas García Joel Bernabé. Instituto Tecnológico de Sonora, 2012. Mechatronics engineer. He carried out research stay at Cinvestav working in the processing of materials in the systems under study.

7.3 Post-docs.

- Dr. Luis A. Gutiérrez Ladrón de Guevara (CINVESTAV-Qro.). He worked in the synthesis, processing and characterization of multiple two phase systems, including ZrO_2-$LaO_{1.5}$-CeO_2, and was involved in several extended research visits at UCSB.
- Dr. Andres Garay (Cinvestav-Qro). Temporary participation in the project, he worked focused in the understanding of the thermodynamic properties of the system ZrO2-LaO1.5-CeO2. Currently Professor-Researcher at CIMAV-Monterrey.
- Dr. David Torres Torres (Cinvestav-Qro). Temporary participation in the project, he performed characterization of the mechanical properties of the system ZrO2-LaO1.5-CeO2 by nanoindentation. Former Ph.D. student at Cinvestav. Currently Professor-Researcher at CIMAV-Monterrey.

8. Mobility

8.1 Research Stays of Mexican researchers abroad

Name	**Date and place**	**Activities/Comments**
Bertha Esparza Esparza	August-November, 2010, Texas A&M Univ., College St, TX.	Characterization and evaluation of samples by mean of Raman Spectroscopy
Luis A. Gutierrez L. de G.	April-September, 2011 January-December, 2013 UCSB-Santa Bárbara, Ca	Stay at UCSB during 14 months. He learned the methodology for the synthesis of ceramic materials by mean of inverse co-precipitation. The optimal compositions for systematic structural and thermodynamic studies related to the performance were identified.

Name	Date and place	Activities/Comments
Gerardo Trápaga Martínez Juan Muñoz Saldaña Luis A. Gutiérrez L. de G.	January 10-11, 2012 UCSB-Santa Bárbara, Ca	Winter Workshop on High Temperature Coating. Assistance to the UCSB Winter Workshop on High Temperature Coating. Poster presentation
Carlos Poblano Salas David Lozano Mandujano	March 12-17, 202 Center for thermal Spray Research, Stony Brook New York.	Training in the development of process maps for thermal spray applications. Tests of spraying coatings using $LaAlO_3$ powders processed at CINVESTAV.

8.2 Research Stays of foreign researchers at Cinvestav.

Name	Date and place	Activities/Comments
Prof. Carlos Levi Materials Department, College of Engineering, University of California at Santa Barbara	CINVESTAV-Querétaro CIATEQ July, 2011	Presentation and discussion of results by the students. Presentation of the thermal spray facilities at CINVESTAV.
Prof. Carlos Levi Materials Department, College of Engineering, University of California at Santa Barbara	CINVESTAV-Querétaro November 29-December 2, 2011	Participation at the Seminary *"CMAS: A Critical Barrier to Progress in Gas Turbine Technology"*. Revision and discussion of the results presented by the students. Discussion of the results proposed for the meeting at Dayton, OH.
Prof. Sanjay Sampath Center for thermal Spray Research. Materials Dept. State University of New York at Stony Brook	CINVESTAV-Querétaro CIATEQ January, 2012	Presentation of the research projects related to thermal spray at CINVESTAV. Seminary talk by the professor Sampath about the application of process maps for optimal selection of spraying parameters in thermal spray.
Prof. Carlos Levi Materials Department, College of Engineering, University of California at Santa Barbara	CINVESTAV-Querétaro November 13-15 October, 2013	Discussion of joint results for the preparation of final report.

9. Human resources formation

Student	Thesis project	Status
Ississ Feria Cortez (M.Sc.)	"Strengthening of dense $La_2Zr_2O_7$ ceramics with non-transformable tetragonal phase obtained in the system SS-ZrO_2-CeO_2" "Reforzamiento de cerámicos densos de $La_2Zr_2O_7$ con fase tetragonal no transformable (t') obtenida en el sistema SS-ZrO_2-CeO_2"	Graduation date: December 15, 2010.

Eduardo Zúñiga Márquez (M.Sc.)	"Characterization of mechanical properties by nanoindentation of Zirconia coatings for thermal barrier applications" "Caracterización de propiedades mecánicas por nanoindentación de recubrimientos de zirconia para su aplicación en barreras térmicas"	Graduation date: September 8, 2011.
L. Fernando Tovar Landin (M.Sc.)	"Study of ceramic compound of the system $La_2Zr_2O_7$ - $LaAlO_3$" "Estudio de compuestos cerámicos del sistema $La_2Zr_2O_7$ - $LaAlO_3$"	In progress
David Lozano Mandujano (Ph.D.)	"Fabrication of $La_2Zr_2O_7$ thermal barrier coatings deposited by Air Plasma Spray and characterization of their mechanical and structural properties". "Fabricación de recubrimientos para barreras térmicas de materiales base $La_2Zr_2O_7$ depositados mediante aps, y caracterización de sus propiedades mecánicas y estructurales"	In progress (start: September, 2009)
Bertha M. Esparza Esparza (Ph.D.)	"Strengthening mechanisms in multiphase base zirconia ceramics". "Mecanismos de reforzamiento en cerámicos multifásicos base zirconia".	In progress (start september, 2009)
Adriana del Carmen Gallegos Melgar (Ph.D.)	"Ferroelasticity studies in multiphase ceramic systems for high temperatura applications" "Estudios de Ferroelasticidad en Sistemas Cerámicos Multifásicos para Aplicaciones en Alta Temperatura"	In progress (start September, 2011)

10. Publications and participation in congress

10.1 Presentations in national and international congresses:

- *"Studies on the enhanced toughness of $La_2Zr_2O_7$ - $La_2Ce_2O_7$ composite materials made by high energy ball milling"*. B.M. Esparza Esparza, J. Muñoz Saldaña, L.G. Trápaga Martínez, L. A. Gutiérrez Ladrón de Guevara. M. M. Gentleman. besparza@qro.cinvestav.mx. Oral presentation in 4th symposium, ADVANCED STRUCTURAL MATERIALS of the XIX International Materials Research Congress. (2010).
- *"Co-precipitation synthesis and processing of tetragonal prime zirconia stabilized with cerium oxide"* I. Feria Cortez, J. Muñoz Saldaña, J. Zárate Medina, B. M Esparza Esparza, L. A. Gutiérrez Ladrón de Guevara, G. Trápaga Martínez. iferia@qro.cinvestav.mx. Poster presentation in 4th symposium, ADVANCED STRUCTURAL MATERIALS of the XIX International Materials Research Congress. (2010).

- *"$LaAlO_3$ - $La_2Zr_2O_7$ composites: processing and mechanical characterization"*. L.F. Tovar-Landín, D. Torres-Torres, J. Muñoz-Saldaña and L.G. Trápaga Martínez. Oral presentation in XIX International Materials Research Congress. (2011).

- *"Comportamiento Físico-Mecánico de Granos de Zirconia Dentro de una Matriz de Alúmina" ("Physico-mechanical behavior of Zirconia grains within an alumina matrix")* D. Trejo Arroyo, M.E. Contreras García, J. Muñoz-Saldaña, J. Zárate Medina. 8° Foro de Ingeniería e Investigación en Materiales. (2011).

- *"Influencia de la temperatura de sinterización en la microestructura y propiedades mecánicas de aglomerados esféricos de alúmina reforzados con zirconia tetragonal no transformable t´" ("Influence of sintering temperature on the microstructure and mechanical properties of spherical agglomerates of alumina reinforce with tetragonal zirconia nontransformable t")*. D. Trejo Arroyo, J. Zárate Medina, M.E. Contereras García, J. Muñoz-Saldaña. XXXII Encuentro Nacional y 1er. Congreso Internacional de la AMIDIQ. (2011).

- *"Pyrochlore-Fluorite two-phase materials of the CeO_2-ZrO_2-$LaO_{1.5}$ system for applications as thermal barrier coatings"* L. Gutierrez, J. Muñoz, G. Trápaga, UCSB Winter Workshop on High Temperature Coatings. (2012).

- *"Fracture toughness of the $LaO_{1.5}$ - ZrO_2 system in the pyrochlore composition"* B.M. Esparza Esparza and J. Muñoz Saldaña. Poster presentación in 4th symposium, ADVANCED STRUCTURAL MATERIALS of the XIX International Materials Research Congress. (2012).

- *"Effect of spray distance on in-flight particle characteristics and quality of coatings"* D. Lozano-Mandujano, C.A. Poblano-Salas, L.G. Trápaga-Martínez, J. Muñoz-Saldaña. Oral presentation in XXI International Materials Research Congress (2012).

- "*Processing and microstructural characterization of lanthanum aluminate obtained by two different routes*", J. Zárate Medina, Gerardo Trapaga Martinez, Juan Muñoz Saldaña, Bertha Esparza Esparza, Juan P. Tapia Olarra, MS&T'13: Materials Science & Technology 2013, October 27-31, 2013, Montreal, Quebec, Canada.

- "*Procesamiento y Evaluación Mecánica de Aluminato de Lantano Obtenido a partir de Pseudoboehmita y $La(NO_3)_3$*", J. Zárate Medina, Gerardo Trapaga Martinez, Juan Muñoz Saldaña, Bertha Esparza Esparza, Juan P. Tapia Olarra, Memorias del XXXIV Encuentro Nacional y III Congreso Internacional de la AMIDIQ, May 7-10 2013, Mazatlán, Sin. Mexico P. 3234-3239. AMIDIQ). ISBN: 978-607-95593-1-1]

10.2 Publications in Conference Proceedings:

- D. Trejo Arroyo, Zárate-Medina J., Contrereas García M.E., Muñoz Saldaña J. Influencia de la Temperatura de Sinterización en la Microestructura y Propiedades Mecánicas de Aglomerados Esféricos de Alúmina Reforzados con Zirconia Tetragonal no transformable ´t (Influence of sintering temperature on microstructure and mechanical properties of spherical agglomerates of alumina reinforce with tetragonal zirconia nontransformable t´). AMIDIQ Journal, (2011) 5605-5610.

- D. Trejo Arroyo, Contreras García M.E., Muñoz Saldaña J., Zárate Medina J. Comportamiento Físico-Mecánico de Granos de Zirconia Dentro de una Matriz de Alúmina (Physico-mechanical behavior of Zirconia grains within an alumina matrix). Foro de Ingeniería e Investigación en Materiales. Vol.8 (**2011**) 68-74.
- J. Zárate Medina, Gerardo Trapaga Martinez, Juan Muñoz Saldaña, Bertha Esparza Esparza, Juan P. Tapia Olarra, "Processing and microstructural characterization of lanthanum aluminate obtained by two different routes", MS&T'13: Materials Science & Technology 2013, October 27-31, 2013, Montreal, Quebec, Canada.
- J. Zárate Medina, Gerardo Trapaga Martínez y Juan Muñoz Saldaña, "Procesamiento y Evaluación Mecánica de Aluminato de Lantano Obtenido a partir de Pseudoboehmita y $La(NO_3)_3$", memorias del XXXIV Encuentro Nacional y III Congreso Internacional de la AMIDIQ, May 7-10 2013, Mazatlán, Sin. Mexico P. 3234-3239. AMIDIQ). ISBN: 978-607-95593-1-1]

10.3 Publications in preparation

- *Thermal spray deposition, phase stability and mechanical properties of $La_2Zr_2O_7$ / $LaAlO_3$ coatings. In preparation 2014.*
- *Nanoindentation study of zirconia with non-transformable tetragonal phase: experiments and simulation of nanoindentation with a conical indenter in the elastic and plastic regime. In Preparation 2014.*
- *Effect of Spray Parameters on In-Flight Particle Characteristics and Quality of 8YSZ Coatings. In preparation 2014.*
- *Processing and Microstructural Characterization of Lanthanum Aluminate Obtained by Two Different Routes, in Preparation for MS&T Congress 2014.*

11. Other Deliverables

Product title	Product	Date
Reforzamiento de cerámicos densos de $La_2Zr_2O_7$ con fase tetragonal no transformable (t') obtenida en el sistema SS-ZrO_2-CeO_2 – (Reinforcement of dense ceramics of $La_2Zr_2O_7$ with nontransformable tetragonal phase (t') obtained in the system SS-ZrO_2-CeO_2)	Master Thesis at Cinvestav-Querétaro. Ississ Sarahi Feria Cortés	December 15, 2010
Caracterización de propiedades mecánicas por nanoindentación de recubrimientos de zirconia para su aplicación en barreras térmicas –	Master Thesis at Cinvestav-Querétaro. Eduardo Zúñiga Márquez	September 8, 2011

(Characterization of mechanical properties of zirconia coatings by nanoindentation for use in thermal barriers)		
Estudio de compuestos cerámicos del sistema $La_2Zr_2O_7$ *–* $LaAlO_3$ *– (Study of ceramic composites of La2Zr2O7–LaAlO3 system)*	Master Thesis at Cinvestav-Querétaro. Fernando Tovar Landín	Thesis in progress. Possible date defense: in 2014.
Mecanismos de reforzamiento en materiales cerámicos multifásicos base zirconia – (Reinforcement mechanisms in multiphase ceramic materials based zirconia)	PhD thesis at Cinvestav-Querétaro. Bertha Esparza Esparza	Thesis in progress. Possible date defense: 2014.
Fabricación de recubrimientos para barreras térmicas de materiales base $La_2Zr_2O_7$ *depositados mediante aps, y caracterización de sus propiedades mecánicas y estructurales – (Fabrication of thermal barrier coatings of* $La_2Zr_2O_7$ *based material deposited by APS and characterization of its mechanical and structural properties)*	PhD thesis at Cinvestav-Querétaro. David Lozano Mandujano	Thesis in progress. Possible date defense: 2014.

12. Observations and Additional comments

The majority of the deliverables are still in preparation due to the complex characteristics of the project. However, the most important component of the project is a big number the human resources formation in the areas of research and a strong collaboration among different research groups (i.e., UCSB, Cinvestav, SUNY-Stony Brook).

Acknowledgements

Funding from CONACYT – CIMAV – Southern Office of Aerospace Research and Development (SOARD) for the project "Multiphase-Multifunctional Ceramic Coatings" is acknowledged. Research made use of the MRL Shared Experimental Facilities, supported by the MRSEC Program of the NSF under Award No. DMR 1121053; a member of the NSF-funded Materials Research Facilities Network.

Principal Investigators	Date
Carlos G Levi	January 28, 2014
Luis Gerardo Trapaga Martinez	