SIXTH FRAMEWORK PROGRAMME
PRIORITY 3
Nano-technologies and nano-sciences, knowledge-based multifunctional materials, and new production processes and devices – 'NMP'

Project no.: STRP NMP3-CT-2004-001470

Project acronym: *NAMAMET*

Project full title: *Processing of NAnostructured MAterials through MEtastable Transformations*

Instrument: STREP

D44 – Non-confidential summary of Final Report

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Project co-funded by the European Commission within the Sixth Framework Programme (2002-2006)		
Dissemination Level		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	

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Summary and Aim of the Project

The purpose of the project was the development of nanostructured materials through an innovative approach based on **metastable transformations** in some selected systems.
The basic idea proposed by the project was the use of metastable processing through plasma spray and combustion processes for the synthesis of a broad class of nanostructured materials.
The synthesis of the investigated materials was successfully obtained by means of high temperature processes like Air Plasma Spray (APS) and Self–propagating High–temperature Synthesis (SHS), followed by rapid quenching in order to achieve metastability.

The systems under investigation were selected during the proposal set up for their strategic importance among the materials candidate for advanced technological applications.
Within the broad scope of the research and development, the following material systems were investigated each one representative for a specific application field:

- Al_2O_3–TiO_2 and ZrO_2–Al_2O_3 systems for the class of ceramic materials for *engineering applications;*
- TiC–TiB_2 as refractory and wear/abrasion resistant ceramic;
- Ti–Al_2O_3 for the class of metal–ceramic composites;
- $NbAl_3$ for the class of intermetallic materials;
- Ni–Ti SMAs for smart materials.

The project development was organised through the following activities:

1. Development of processes based on the metastability concept with the aim of achieving nanostructured and metastable powder agglomerates.

The following technologies were set up for the synthesis of nanostructured powders:

- SHS + quench approach (based on the Self–propagating High–temperature process);
- APS + quench approach (based on the Atmospheric Plasma Spray process).

The results achieved on the process development for the synthesis of nanostructured composites demonstrated the feasibility of the achievement of metastable powders by both the processing routes.

2. Set-up of processes for the densification of the nanostructured and metastable powders and the achievement of nanostructured and stable bulk composites.

The metastable nanopowders were consolidated into nanostructured bulk materials by means of both conventional processes and advanced densification techniques like spark plasma sintering, high velocity forging/extrusion and dynamic compaction for most of the materials under investigation.
Among all the densification processes investigated during the project, the materials consolidated through the following technologies were identified as most promising and therefore subjected to the assessment activity:

- Conventional Hot Pressing (HP);
- High–Pressure High–Temperature (HPHT) sintering;
- Spark Plasma Sintering (SPS).

3. Assessment of the developed nanostructured bulk composites and relative fabrication technologies.

The innovative approach allowed to successfully achieve nanostructured materials with outstanding properties, potentially suitable for a wide range of application fields, like e.g. tough ceramics for structural applications, metal–ceramic composites and intermetallics for thermo–mechanical applications, and shape memory alloys for biomedical applications.

The developed bulk materials were assessed following two approaches:

- Comparison against same or similar commercially available materials;
- Bench tests relevant to the identified potential applications for each system.

The criteria adopted for assessing a successful achievement for the investigated materials were the following:

1. Clear progress beyond the state of the art
2. Properties suitable for the identified application
3. Pass the bench test

The results of the assessment activity provided evidence that most of the materials successfully passed the evaluation, exhibiting a significant improvement of the properties with respect to the state–of–the–art counterparts. Specifically, a successful achievement was measured regarding the wear resistance and thermal shock resistance of the **ceramic and metal–ceramic composites** (Al_2O_3–TiO_2, ZrO_2–Al_2O_3, TiC–TiB_2 and Ti–Al_2O_3–TiC). On the other hand, the results obtained on the $NbAl_3$ intermetallic and the Ni–Ti alloy didn't prove a clear progress against the state of the art, mainly due to the problems of contamination connected with the processing of these materials through the selected technologies.

The detailed results of the overall activity carried out during the NAMAMET project are described in the Final Activity Report.
This deliverable contains the main publishable outcomes generated by the project.

Expected results and impact

The main project expected achievements and end results were the following:

- To introduce the metastability criterion as a method to obtain nanocrystalline materials.
- To define processes capable of giving nanostructured materials starting from metastable structures.
- To obtain nanocrystalline materials with a set of outstanding properties for the targeted applications.

In particular, the achievement of nanostructures and of functional properties responding to the ones required to each system for the specific technological application (high temperature structural components, biomaterials, protective coatings, nanostructured smart materials…) were expected for the bulk nanomaterials.

The results achieved during the entire project and particularly in the last reporting period were very encouraging for the successful achievement of the above described end results.

In particular:

- The first milestone of the project, i.e. the **feasibility of achievement of metastable nanocomposite powders and coatings**, was successfully demonstrated for a wide range of materials (i.e. Al_2O_3–TiO_2 and ZrO_2–Al_2O_3, TiC–TiB_2, Ti–Al_2O_3, $NbAl_3$ and NiTi) through the designed approach based on metastability.
- The densification of the powders led in many cases to the evolution of the metastable structures into **nanostructured crystalline materials** by means of several technologies, both conventional, like hot pressing, and advanced, like Spark Plasma Sintering (SPS), High Pressure High Temperature (HPHT) sintering, hot pressing, dynamic compaction and High–velocity forging/extrusion;
- The most promising densification techniques turned out to be the High Pressure High Temperature (HPHT) and Spark Plasma (SPS) sintering, for most of the investigated systems;
- The densification activity demonstrated in many cases the achievement of **bulk nanostructured materials** characterised by very interesting properties in terms of nanostructure, homogeneity and enhanced mechanical properties (in particular hardness);
- The microstructure and the mechanical properties of the densified materials were in many cases **superior** to the values that are reported in the literature;
- The understanding of the correlations between nanostructure and properties of the developed composites was successfully gained and further knowledge was acquainted through the mechanical characterisation;
- The results of the assessment activity provided the evidence that most of the developed materials exhibited a significant improvement of the properties with respect to the state–of–the–art counterparts. Specifically, a successful achievement was measured regarding the wear resistance and thermal shock resistance of the **ceramic and metal–ceramic composites** (Al_2O_3–TiO_2, ZrO_2–Al_2O_3, TiC–TiB_2 and Ti–Al_2O_3–TiC);
- An innovative process named Mechanically Activated Reactive Extrusion Synthesis (MARES) was successfully set up for the Ni–Ti alloy representing a suitable and promising PM route for producing dense intermetallics compounds potentially extendable to many other metallic systems.
- The innovative approach allowed to **successfully achieve nanostructured materials with outstanding properties**, potentially suitable for a wide range of application fields, like e.g. tough ceramics for structural applications, metal–ceramic composites and intermetallics for thermo–mechanical applications, and shape memory alloys for biomedical applications.

- Remarkable **interest** was encountered in the exploitation of the results of the materials/processes developed in the project, in particular for the production of metastable nanopowders for the fabrication of cutting tools and wear parts.

To sum up, the **planned key objectives were successfully achieved** at the end of the project.

The highly advanced knowledge gained will be crucial for the long–term exploitation of the new class of materials developed. The understanding of the role played by the interfaces and by the grain boundary diffusion in the determination of the behaviour of nanostructured materials is a key factor for the full exploitation of these materials, and was studied in the last project period.

The exploitable results achieved during the project are mainly constituted by the developed nanostructured bulk composites and materials. These results were successfully obtained for most of the investigated materials, and particularly will be immediately exploitable for the TiO_2–Al_2O_3 and ZrO_2–Al_2O_3, TiC–TiB_2 and Ti–Al_2O_3–TiC systems.
The **successful evolution of the metastable condition exhibited by the powders into nanostructures** during the densification activities of NAMAMET was a very encouraging result. The *exploitation of this evolution to obtain nanocomposites* has been definitively confirmed after the characterisation and assessment activity carried out during the last period.

The procedures for exploitation of the research results were preliminarily explored during the second part of the project. The significant **interest** encountered in the **exploitation of the results** of the materials/processes developed in the project led to search cooperation with actors outside the Consortium. The knowledge generated by each partner and the nature of the developed products allowed a group of partners of the Consortium to define the strategy for manufacturing metastable powders and coatings for the production of **metastable nanopowders for the fabrication of cutting tools and wear parts** at a pre–competitive industrial level, through the involvement of companies belonging to NAMAMET or outside the Consortium interested in the field.

The following results have been identified as the most promising ones in terms of exploitation potential:

- **TiC–TiB_2 material for cutting tools** or **PVD coatings**
- **ZrO_2–Al_2O_3** and **TiO_2–Al_2O_3** bulks and coatings by **APS + quench**
- **Ti–Al_2O_3–TiC** bulk material **for wear parts**

The metastability–based approach followed for the production of such materials is highly innovative, knowledge–intensive and with a high technological content, thus providing a strategic role from the exploitation view point.

The Consortium intends to evaluate the possible products that can be commercialized. At present, commercial contacts have been taken with industries interested in the commercialization. This action will be further investigated after the end of the NAMAMET project. Commercial partners have been recognized, and the transfer of non–exclusive licences will be evaluated, as well as the creation of possible joint–ventures to be set up after the end of the project.

I. IDENTIFICATION OF POTENTIAL TARGET APPLICATIONS

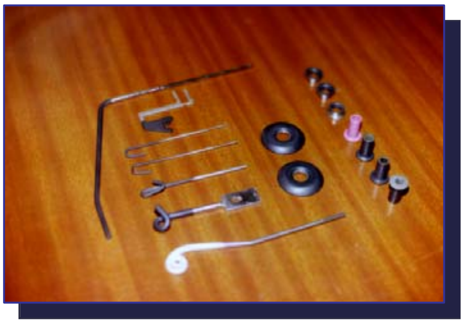
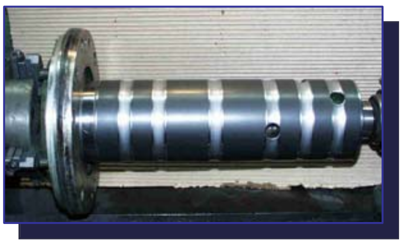
1). $ZrO_2 – Al_2O_3$ system

System Leader: UNIBA

SYSTEM: $ZrO_2 – Al_2O_3$	
Main identified and/or required Properties	• Abrasive and erosive wear resistance • Medium hardness • Corrosion resistance • Thermal fatigue resistance • High Toughness • Low porosity
Main Identified Applications	• Wiring machine components • Pharmaceutical components • Ceramic clay extrusion moulds • Cement and coal powdered piping • Thermal barriers
Examples	   

2). Al_2O_3–TiO_2 system

System Leader: UNIBA

SYSTEM: Al_2O_3 – TiO_2	
Main identified and/or required Properties	• Abrasive and friction wear resistance • Low friction coefficient • High hardness • Corrosion resistance • Thermal fatigue resistance • High Toughness • Electric Conductive properties • Low porosity
Main Identified Applications	• Textile machine components • Food / Beverage machine components • Sealing zones moving parts • Thermal barriers
Examples	   

3). <u>$TiC–TiB_2$ system</u>

System Leader: <u>POLITO</u>

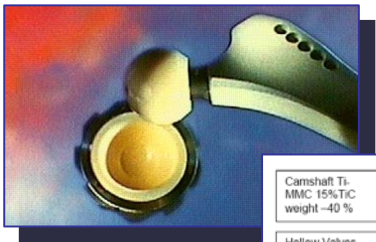
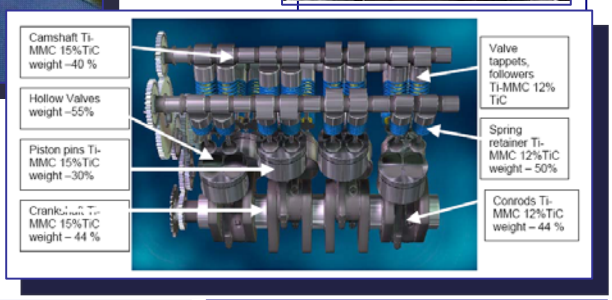
SYSTEM: $TiC – 33mol\% TiB_2$	
Main identified and/or required Properties	• High wear resistance • High hardness, at room and high T • Medium / high toughness • High oxidation temperature • High corrosion resistance • Chemical stability • Good electrical and thermal conductivity • Anti sticking properties
Main Identified Applications	• Cutting tools • Moulds for plastic and die–casting • Automotive – Recirculation engine exhaust gas systems • Pharmaceutical – punches and dies • Heat exchangers • Propulsion and space thermal protection in aircrafts • Wall tiles in nuclear fusion reactors • Cathodes in Hall – Heroult cells • Vapourising elements in vacuum–metal deposition installations
Examples	

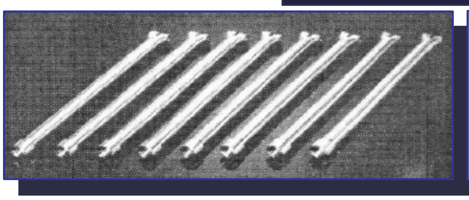
4). <u>Ti–Al_2O_3–TiC system</u>

System Leader: <u>ICV–CSIC</u>

<table>
<tr><th colspan="2">SYSTEM: Ti–Al_2O_3–TiC</th></tr>
<tr><td>Main identified and/or required Properties</td><td>• Good specific mechanical properties (strength/weight ratio)
• Good corrosion resistance
• Good hardness and wear resistance
• Good toughness</td></tr>
<tr><td>Main Identified Applications</td><td>• Automotive: valves, camshafts,…
• Aeronautics: turbine blades, drums, blisks, blings, exhaust nozzles, compression links,…
• Structural, electrical and optical applications
• Armor parts
• Biomedical structural applications: prosthesis
• Daily use: tennis rackets, golf club head,…</td></tr>
<tr><td>Examples</td><td>





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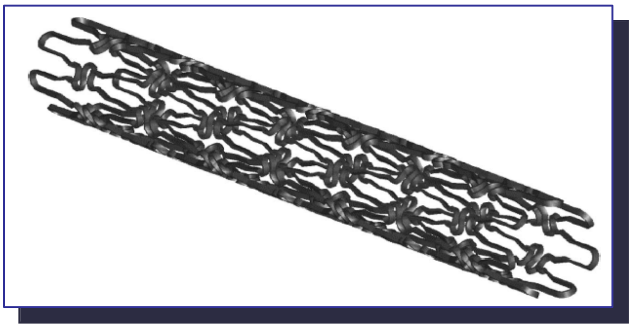
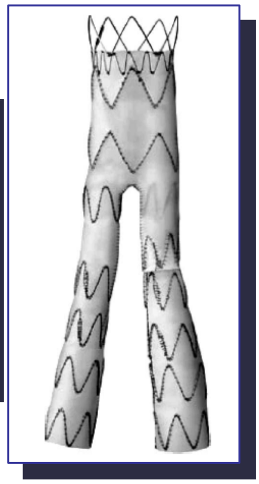
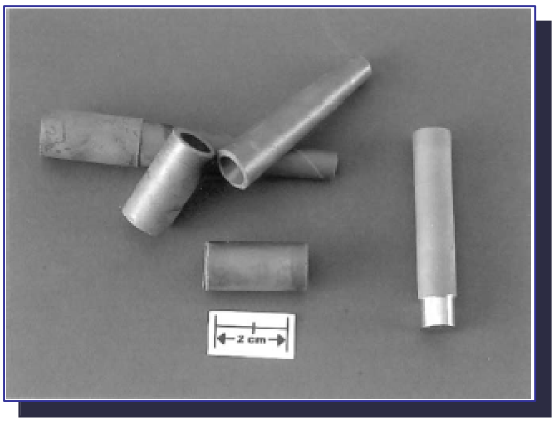
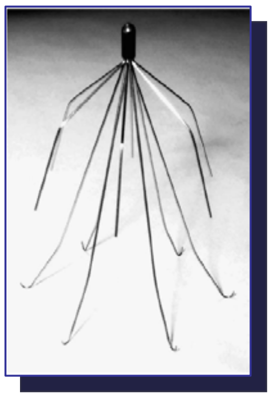
5). NbAl$_3$ system

System Leader: UNICA

SYSTEM: NbAl$_3$	
Main identified and/or required Properties	• High temperature physical / mechanical properties • High temperature corrosion / oxidation resistance
Main Identified Applications	• Air, land and sea turbines (hot zone) components
Examples	  

6). <u>Ni – Ti system</u>

System Leader: <u>**INETI**</u>

SYSTEM: Ni – Ti	
Main identified and/or required Properties	• Shape memory behaviour • Good bio–compatibility • High erosion resistance
Main Identified Applications	• Surgical implants: replacement of bone and soft tissues in traumatology, dental surgery, otolaryngology and urology • Biomedical devices: guidewires, stents, graft stents, inferior vena cava filters • Orthopaedics • Clinical instruments: biopsy forceps, tissue ablators, hingeless graspers and retrieval baskets for laparoscopy
Examples	   

II. END RESULTS

The main achievements obtained during the entire project are_reported below on a system–by–system basis.

Metastability in ceramic systems: Al_2O_3–TiO_2 and ZrO_2–Al_2O_3. Powders; Densified materials and Properties.

System Leader: **UNIBA**

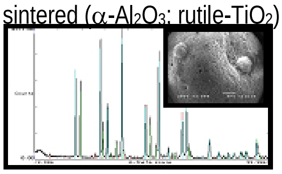
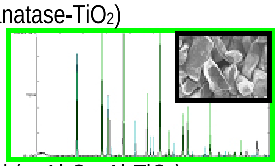
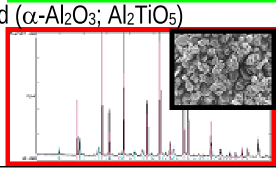
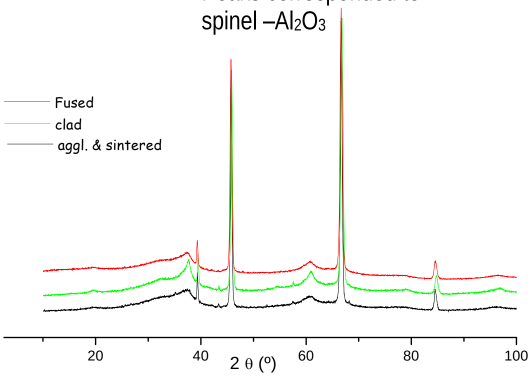
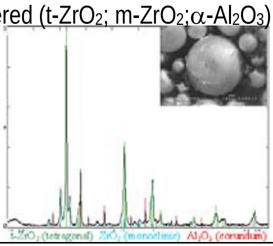
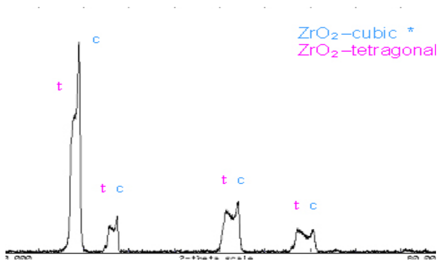
Staff: I.G. Cano, S. Dosta, J.R. Miguel, J.M. Guilemany

This summary involves a brief explanation about the metastable powders production and the consequent densification processes carried out to obtain bulk materials. These dense materials were mechanical and wear characterised. The aim of this project was achieve because the final materials present improved properties showing potential applications in fields as the aerospace, naval and automotive sectors. Due to the excellent abrasive and friction wear resistance at high temperatures, added to high Corrosion resistance Thermal fatigue resistance, and High Toughness, others attractive sectors are the Civil engineering, electrical / electronic and food. Some examples of applications where the conventional Al_2O_3-TiO_2 and ZrO_2- Al_2O_3 materials are used are shown in Figure 1.

Figure 1. Some examples of applications ofA Al_2O_3-13wt% TiO_2 and (B) ZrO_2-20wt% Al_2O_3 systems

Powder Production: The Alumina-Titania and Zirconia-Alumina *powders* in *metastable* state were produced for different compositions and from different feedstock powders in order to evaluate the metastability degree obtained in the final product. For the Al_2O_3-13wt%TiO_2 and the ZrO_2-20 wt% Al_2O_3 compositions a fully metastable powder was obtained using a process that combines thermal spray technology and a quenching system. Different cooling rates were tested and evaluated being a liquid nitrogen based system the more suitable one. Metastable phases were produced from micron-sized feedstock powders as is shown in table I.

Table 1. Characteristics of metastable powder.

System	Initial powder used	Final metastable powder
Al_2O_3-13wt%TiO_2	Agglomerated & sintered (α-Al_2O_3; rutile-TiO_2)  Clad (α-Al_2O_3; anatase-TiO_2)  Fused & crushed (α-Al_2O_3; Al_2TiO_5) 	Peaks corresponded to spinel –Al_2O_3 
ZrO_2-20wt%Al_2O_3	Agglom. & sintered (t-ZrO_2; m-ZrO_2;α-Al_2O_3) 	

In order to evaluate the behaviour of these metastable powders during the consequent consolidation process, heat treatments were carried out in laboratory scale. As a consequence of heat treatments, a phase evolution from metastable to equilibrium states was observed. During the heat treatments of the material, the metastable structure evolves into a binary structure where the grain growth stops when the crystallites reach their respective equilibrium grain size. The mutual suppression of the grain growth is a direct consequence of the immiscibility of the two phases in the solid state. The final structure for both systems, was composed by nanometric grains (<100nm). Hence, it can be said that the main advantage of using metastable structures was confirmed by these studies. In Figure 2, an example of these materials after heat treatment is shown.

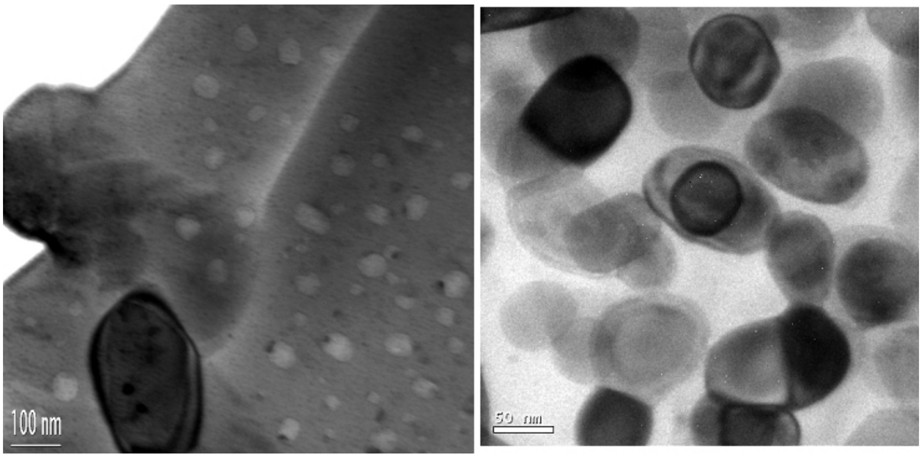


Figure 2. TEM images of metastable powders treated at 1200ºC:
A Al_2O_3-13wt% TiO_2 and (B) ZrO_2-20wt% Al_2O_3

Afterwards, dense materials were obtained from metastable powders. Some of the tested ***densification processes*** were the following: High Pressure-High Temperature (HPHT); High Velocity Forging (HVF); Pressureless Sintering (PS); Dynamic Compaction (DC) and Spark Plasma Sintering (SPS).

The best results were obtained with HPHT and SPS whereas HVF and PS do not provide a satisfactory densification. In order to obtain a good dense material by PS a later milling process was necessary. Dense materials were obtained by DC although the dimensions were not enough to test the mechanical and wear behaviour.

For the HPHT and SPS processes, the dense materials showed densities close to theoretical one and grain size less than 50 nm except of AT densified by SPS.

The final materials were characterized both physically and mechanically following the analysis of these ***properties***:

- Physical and mechanical properties: Density and Elastic constants determination; Knoop's hardness; Vickers hardness and fracture toughness (K_{IC})

- Friction and wear behaviour (Ball-on-disc method)

- Thermal shock behaviour (Bath immersion)

Concluding remarks:

The <u>end results</u> can be summarized with the following conclusions:

- Powders composed of metastable phases were obtained through ***APS + quench*** process for the Al_2O_3–TiO_2 and ZrO_2–Al_2O_3 systems.
- After heat treatments, an evolution from metastable to stable phase was shown obtaining **nanostructured** materials.
- APS + quench process turned out to be an optimal **metastability route**
- Densified bulks **without cracks** were obtained from metastable powders
- A high **densification** degree was obtained in HPHT densified materials, whereas SPS compacts showed higher porosity.
- During the densification, single phases in the microstructure evolved into micron–sized grains

that consist of **nanograins (<40nm)**.For HPHT bulks, the hardness of nanostructure material was higher than the values found in the literature (130%)Both HPHT and SPS bulks showed higher thermal shock resistance (~150–200%). The bulk materials showed high resistance to crack initiation and propagation as confirmed by the thermal shock parameters.For the investigated materials, the friction coefficient values were lower than their conventional counterparts.

Metastability in TiC–TiB_2 ceramic system. Powders; Densified materials and Properties.

System Leader: **POLITO**

Staff: D. Vallauri, I. Atias Adrian, Y. Lopez, I. Amato, B. DeBenedetti

Powder Production: Nanostructured TiC_{1-x}–TiB_2 powder agglomerates were produced by POLITO by SHS + quench through the addition of different amounts of additives acting as gasifying and/or particle–size controlling agents into the reactant mixture. The purpose was to produce the maximum possible disaggregation of the reacting sample during the SHS reaction, in order to enhance the effect of the quench and to obtain a rapid cooling throughout the sample.
The considered SHS reaction was used for the production of the powders with a stoichiometry optimised in order to obtain a sub–stoichiometric TiC_{1-x} phase and a composition approximately corresponding to the eutectic composition of the TiC–TiB_2 system.
In this way the theoretical constraint for operating by the metastability approach, i.e. the achievement of two–phase composites with complete solubility in the liquid phase, was satisfied.

The formation of agglomerates characterised by fine structures was observed in the SHS–quenched powders with non–stoichiometric compositions, as can be observed for the products shown in Figure 3. The morphology of the powder agglomerates was observed to consist of regular spherical particles with a very small average size (30–100 nm) and of elongated platelet–like phases, as shown in Figure 4.

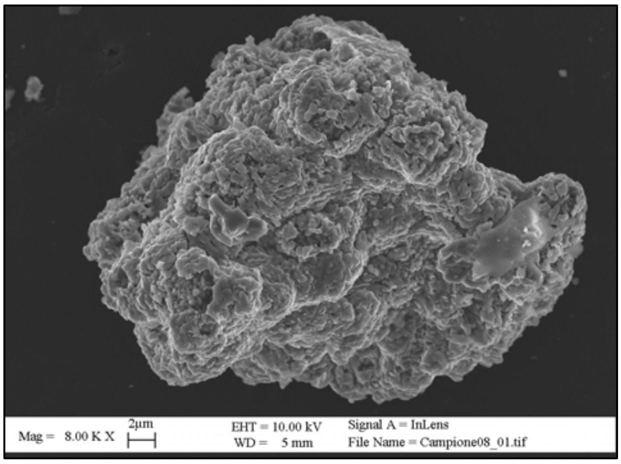


Figure 3. Hypostoichiometric TiC_{1-x} –TiB_2 products obtained by SHS + quench of *6Ti + B_4C + 1.8C* with addition of 1%wt borax.

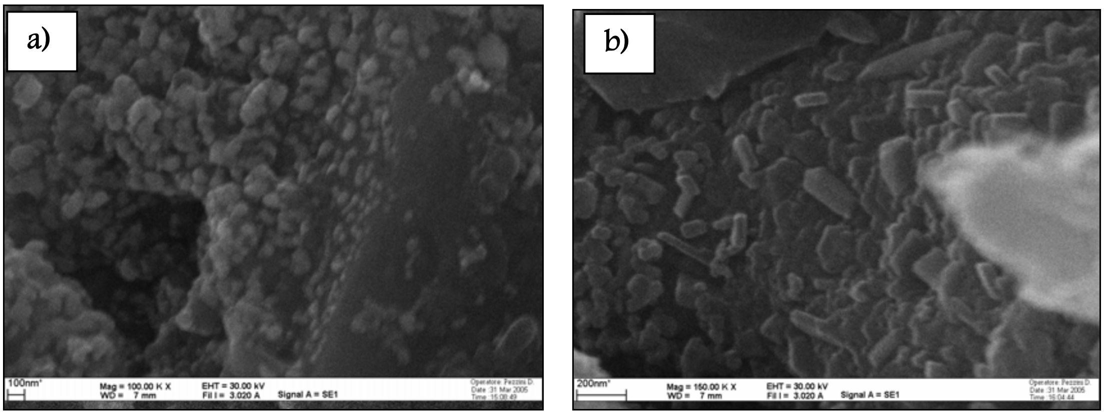


Figure 4. Microstructure of the nanostructured TiC_{1-x}–TiB_2 products of the SHS–quench process obtained by SHS + quench with 1%wt borax addition: nano–spherical (a) and platelet–like (b) structures.

The thermal stability of the $TiC_{0.7}$–TiB_2 products evaluated by annealing of the SHS–quenched powders showed an interesting evolution of the microstructure with a progressive recrystallisation and a limited grain growth of the constituent phases to form structures with a grain size that was maintained in the sub–micrometer range after annealing.

Therefore nanostructured TiC_{1-x}–TiB_2 powders with eutectic composition by a certain degree of metastability and suitable to be densified at moderate temperatures were obtained by SHS–quench.

Regarding the ***densification processes***, the best results were obtained by High Pressure–High Temperature (HPHT) and Spark Plasma (SPS) Sintering. Fully dense samples were achieved by SPS when operating at 1400°C and a pressure of 20 MPa.
The TiC–TiB_2 materials densified by SPS exhibited in general better properties than those obtained by HPHT. However, the HPHT composite showed better resistance to thermal shock with a critical quenching temperature difference ΔTc of 300°C against 250°C measured for the SPS materials.

Concerning the microstructural aspects, a comparison between the NAMAMET material and the literature works allowed to highlight that a **clear progress beyond the state of the art** has been experimentally obtained in terms of **achievement of nanostructured bulk TiC–TiB_2 composites**.
The materials obtained in NAMAMET represent one of the first experimental evidences of **nanostructured** (particularly for the case of the SPS material, with grain size in the range **200–300 nm**) and **ultra–fine sub–micron** and **micron–sized** (for the HPHT material, with grain size in the order ~1 μm) TiC–TiB_2 sintered composites, thus providing a very significant achievement for the project.

Since one of the most promising potential applications of TiC–TiB_2 materials is for the fabrication of **cutting tool inserts** and considering the encouraging measured properties, a set of cutting inserts were fabricated and some cutting tests were carried out to check the applicability of the developed material to this application.
The photographs of the cutting inserts after the cutting tests with their cutting areas evident are shown in **Figure 5**.

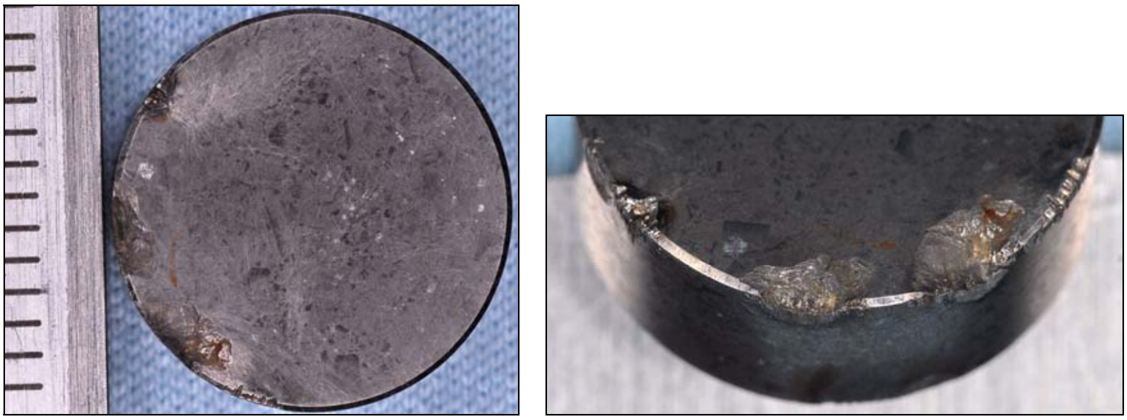


Figure 5. View of $TiC-TiB_2$ insert wear after cutting tests.

As results of the cutting tests, the $TiC–TiB_2$ inserts resulted to be a <u>**very promising candidate for cutting difficult–to–cut materials**</u> like titanium alloys in both with the use of a coolant and in dry conditions.

To corroborate the use of this class of materials as cutting tools, a comparison between $TiC–TiB_2$ composites and commercial materials based on the <u>Abrasive Wear Factor</u> (AWF) provided by Evans and Marshall [1] was performed. The wear factor provides an evaluation of the wear resistance of ceramic materials and be computed from the fracture toughness (K_{Ic}), Young's modulus (E) and hardness (H). The higher the AWF, the higher the expected resistance of a ceramic material to abrasive wear.
The comparison was extended to the NAMAMET materials, that showed a value of <u>AWF</u> **significantly higher (20%) than all the other competing (commercial or state-of-the-art) materials.**

<u>This represents a very significant achievement for the positive assessment of the NAMAMET $TiC–TiB_2$ composites for potential cutting tools/wear resistant applications.</u>

Also the thermal shock resistance of the NAMAMET materials resulted is superior than that exhibited by some commercial cutting tool material (like e.g. Al_2O_3 – 30 wt.% TiC – ΔTc of ~150°C ÷ 200°C [2]), for both the SPS and HPHT composites.

Therefore, the developed $TiC–TiB_2$ composites **are wear resistant and show thermal shock resistance comparable or superior to other competing commercial (Al_2O_3 – 30wt.% TiC) cutting tool materials,** and **the high hardness and fracture toughness render the NAMAMET $TiC–TiB_2$ an excellent candidate for cutting tools applications.**

The results provide evidence that the combination of good wear resistance and relatively high thermal shock and oxidation resistance coupled with the encouraging results of the cutting tests render the $TiC–TiB_2$ composites developed in the NAMAMET project an <u>**excellent candidate for cutting tools**</u>.

Concluding remarks:

- Metastable and nanostructured powder agglomerates were obtained by means of both ***SHS + quench*** and ***APS + quench*** processes.
- After heat treatments, the evolution from metastable to stable phase was observed yielding **nanostructured** materials.

1 Evans, A.G., Marshall, D.B., Wear Mechanisms in Ceramics. In *ASM Fundamentals of Friction and Wear of Materials*, ed. D.A. Rigney. ASM International, Metals Park, OH, 1981, pp. 439–452.
2 Wayne, S. F. & Buljan, S. T., The Role of Thermal Shock on Tool Life of Selected Ceramic Cutting–Tool Materials. *J. Am. Ceram. Soc.*, 1989, **72(5)**, 754–60.

- **Nano– or submicron–sized grains (<100nm)** were retained in the bulk materials densified by SPS and HPHT sintering respectively.The material developed by HPHT is promising as **cutting material** for turning of **difficult–to–cut materials** like Ti–based alloys, showing very low wear rate when turning with a coolant and moderate wear rate under hard dry turning conditions.

- The material developed by SPS exhibited very low wear rate and average thermal shock resistance. Therefore it is suitable for application in **wear–resistant parts** (moulds for plastic and die casting, punches and dies in the pharmaceutical industry, etc.).
- The TiC–TiB_2 materials developed by both HPHT and SPS were **wear resistant** and show **thermal shock resistance comparable or superior to other competing commercial (Al_2O_3 – 30wt.% TiC) cutting tool materials.**
- The **high hardness** and **fracture toughness** render the NAMAMET TiC–TiB_2 an **excellent candidate for cutting tools applications.**

Concerning the possible exploitation of the developed TiC–TiB_2 composites as cutting material, the following conclusions can be drawn:

- The TiC–TiB_2 inserts resulted to be a valid candidate for cutting difficult–to–cut materials like titanium alloys.
- It can be anticipated that the application can be extended to other difficult–to–machine materials, such as nickel–based alloys, and may lead to much improved performances and test the potentiality of the developed nanostructured TiC–TiB_2 composites for cutting a wide range of materials.
- In the view of limiting the coolant use in cutting operations (ideal conditions of dry cutting), the addition of a metal binder (like e.g. Ni) to the TiC–TiB_2 hard material can be anticipated.

In the view of possible exploitations, the fact that no actual application of TiC–TiB_2 materials is commercially available is due to the lack of a cost–effective and reliable processing route allowing an accurate control of the microstructure for this class of materials. Regarding this, the SHS process seems to offer a promising way provided an accurate control of the process parameters is achieved.
According to the properties reported in the literature and those measured on the NAMAMET TiC–TiB_2 materials (good fracture toughness and thermal shock resistance), other potential applications of these composites can be foreseen, such as high temperature structural components in heat exchangers and recirculation parts in exhaust gas systems for automotive engine, etc., propulsion and space thermal protection in aircraft, wear resistant parts in forming dies, non–structural applications like wall tiles in nuclear fusion reactors and coatings for wear– and corrosion–resistant components.

Metastability in Ti–Al_2O_3–TiC cermet system. Powders; Densified materials and Properties.

System Leader: **ICV-CSIC**

Staff: M. Jiménez, M.A. Rodríguez

Automotive and aeronautics the industrial sectors in which the use of Titanium alloys and composites are more widespread. The main potential applications identified for the Ti–Al_2O_3–TiC system were wear–resistant parts and thermo–mechanical components (valves, camshafts, etc. in the automotive industry, turbine blades, drums, blisks, blings, exhaust nozzles, compression links, etc. for aeronautical components, armor parts, etc.). Due to the excellent abrasive and friction wear resistance at high temperatures, Ti based can be used in engines and car components as shown in Figure 6 and Figure 7.

This summary involves a brief explanation about the metastable powders production and the consequent densification processes carried out to obtain bulk materials. The aim of the activity was achieved since the final materials exhibited improved properties and thus showing potential applications in the industrial fields above.

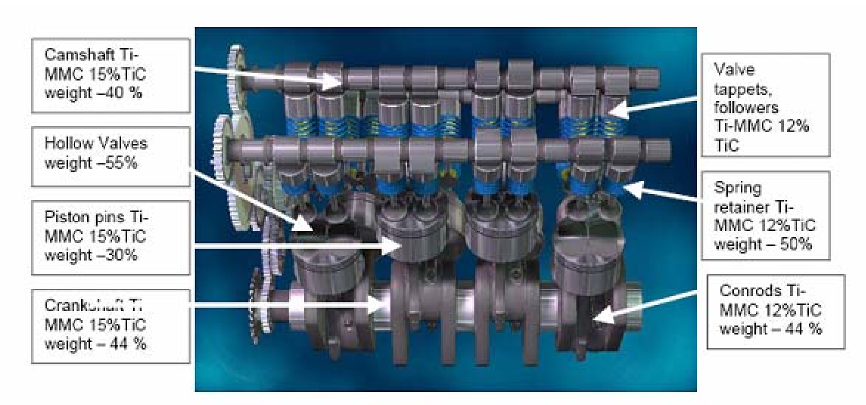


Figure 6. Application of Titanium-MMC-alloys for engine components.

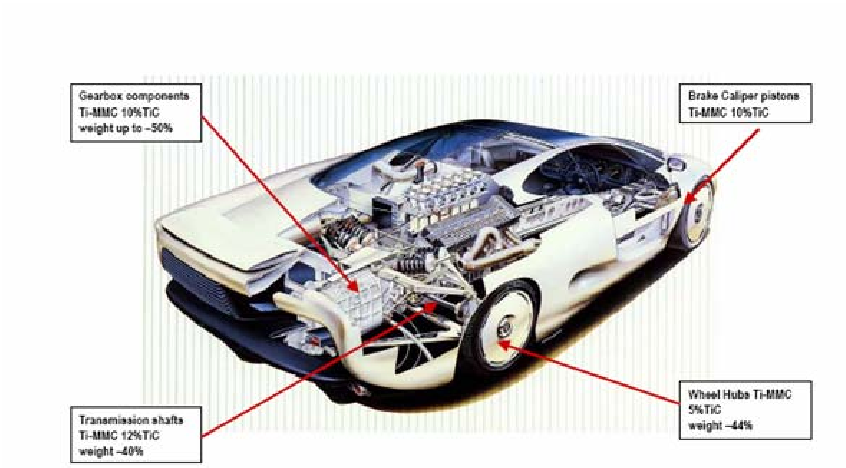
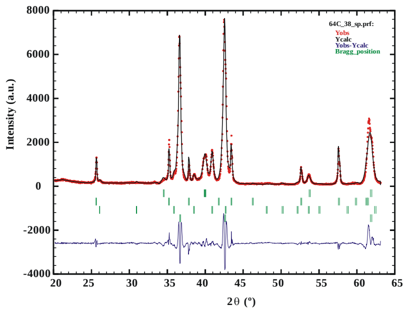


Figure 7. Potential application of titanium-MMC alloys for chassis components.

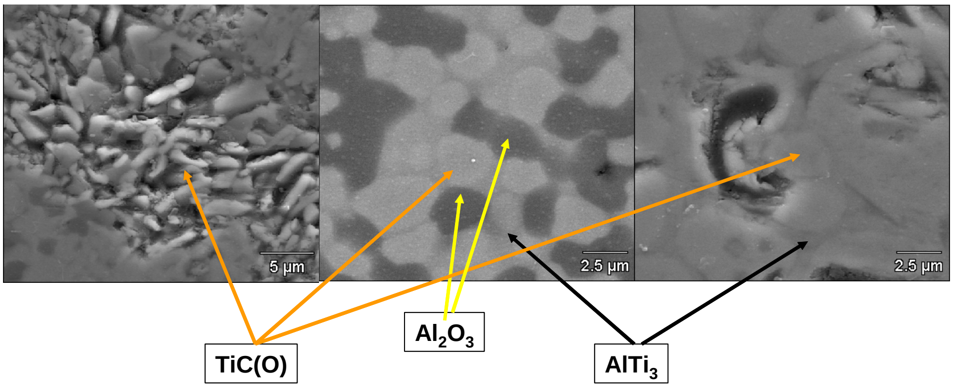
Powder Production: the selected composition was: 52Ti - 35Al_2O_3 -13TiC. This composition was obtained by FACS+ quenching in Liquid nitrogen. The characteristics of the as-obtained metastable powders are summarized in table I

Table 2. Characteristics of metastable powder.

Compos.	Final metastable powder
52Ti - 35Al_2O_3 -13TiC	see below



Phase	Percentage	R_f-adjust	Cell parameters(Å)	Crystallite size (Scherrer), nm
Hcp-Ti	12	1.68	a=b=3.000171, c=4.519409 α=β=90°, γ=120°	70
Al_2O_3	36	4.60	a=b=4.755447, c=12.980103 α=β=90°, γ=120°	27
$Ti_3Al(O)$	7	9.79	a=b=5.780717, c=4.676571 α=β=90°, γ=120°	21
TiC(O)	45	0.75	a=b=c=4.243447 α=β=γ=90°	38



The ***densification processes*** tested were the following: High Pressure-High Temperature (HPHT); Hot Press (HP); Pressureless Sintering (PS); Dynamic Compaction (DC) and Spark Plasma Sintering (SPS).

The best results in terms of density, reliability and properties were obtained by Hot Pressing, with values of final densities close to 100%.

The properties of the Hot Pressed materials are shown in Figure 8, together with a representative microstructure.

The high value of measured hardness can be explained by the presence of alumina and especially of the TiC phase. Also the measured toughness is high considering the kind of material. This was due to the presence of metal phase (Ti) acting as a bridge and thus hindering the crack propagation (Figure 9) through a crack–bridging toughening mechanism.

Hardness = 20,1 GPa

Toughness = 4,2 MPa·m$^{-1/2}$

σf = 202 ± 56 MPa
σcc = 1314 (2400 SPS) MPa

Toughness = 4,2 MPa·m$^{-1/2}$

High Temperature properties:
Hardness at high temperature (GPa):
7 (600ºC), 6 (700ºC), 5 (800ºC), 3(900ºC)
Deformation rates are extremely small:
Strain rate 10-5 s-1 (1000ºC)

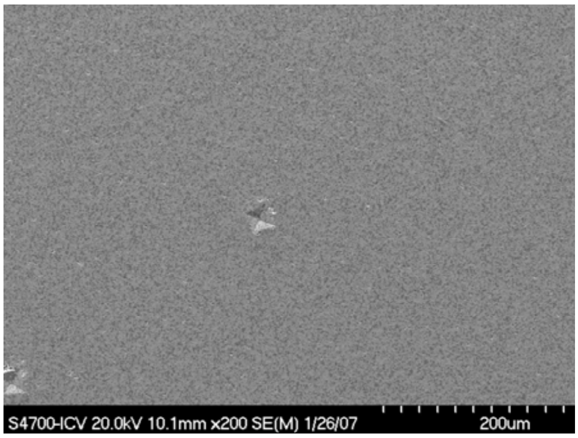


Figure 8. Properties and microstructure of the materials sintered at 1250°C for 1 h under 50 MPa.

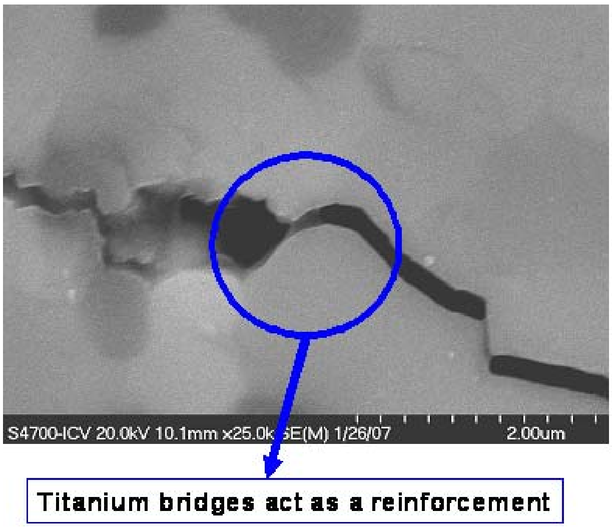


Figure 9. Image of the microstructure in the area of the crack for toughness measurements.

Hot Press is a well known technology to prepare materials in the ceramic-metal composite fields.

Several Ti–Al_2O_3–TiC samples were fabricated by hot pressing in order to evaluate the material and to test the capability to prepare different shapes (Figure 10).

The developed Ti–Al_2O_3–TiC cermet material showed wear rate much smaller than that exhibited by some commercial Ti–based alloys or superalloys.

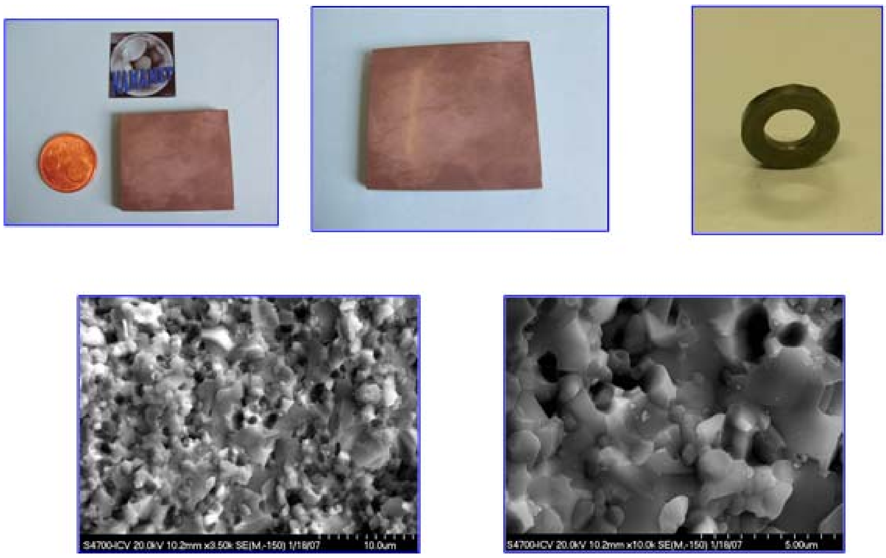


Figure 10. Examples of samples obtained by Hot Press for the metastable Ti–Al_2O_3–TiC.

Concluding remarks:

- Metastable and nanostructured Ti based powders were successfully obtained by FACS + quench.
- The metastable nanostructured powders have demonstrated their ability to be processed in standard ways.
- The powders were sintered to theoretical densities by different processes.
- The wear behaviour of the densified materials was much better in comparison with the data found in the literature for similar materials (Ti–48Al–2Cr–2Nb; Superalloy 718).

Metastability in $NbAl_3$ intermetallic system. Powders; Densified materials and Properties.

System Leader: **UNICA**

Staff: A. Locci, R. Licheri, C. Musa, R. Orrù, G. Cao

The feasibility of a process for the preparation of nanostructured $NbAl_3$ powders produced by SHS after activation of the elemental powders by ball milling, and subsequent mechanical treatment until reaching the desired crystallite size and powders size distribution is demonstrated. On the basis of the results obtained using a SPEX 8000 shaker mill, the condition t_M= 6h and CR=2 could be ascribed as the optimal one for the synthesis of $NbAl_3$ by mechanical activated SHS. In fact, a complete conversion to the desired niobium aluminide was reached as demonstrated by the XRD patterns of the corresponding final products reported in Figure 11.

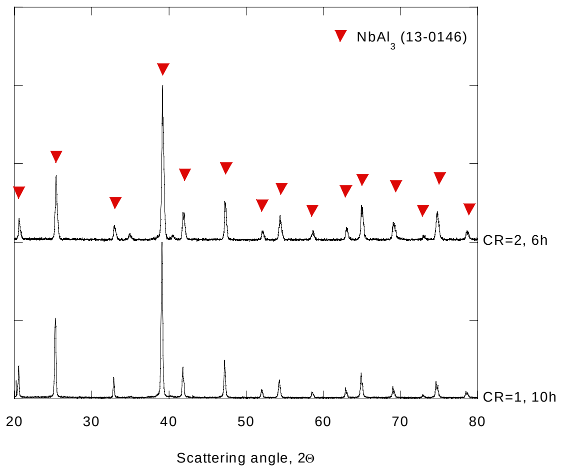


Figure 11. X-ray diffraction patterns of MASHS reacted powders, starting from different mechano-chemical activation conditions (SPEX 8000 shaker mill).

In order to obtain nanostructured powders, the comminution of SHS products is investigated using an attritor mill. The influence of the milling time on the powders dimension and crystallite size is shown in Figure 12 and Figure 13, respectively. In particular, it is seen that when considering the attritor mill and the condition CR=50 is adopted, the possibility to obtain $NbAl_3$ powders with crystallite size < 100 nm in less than 1 hour milling is demonstrated.

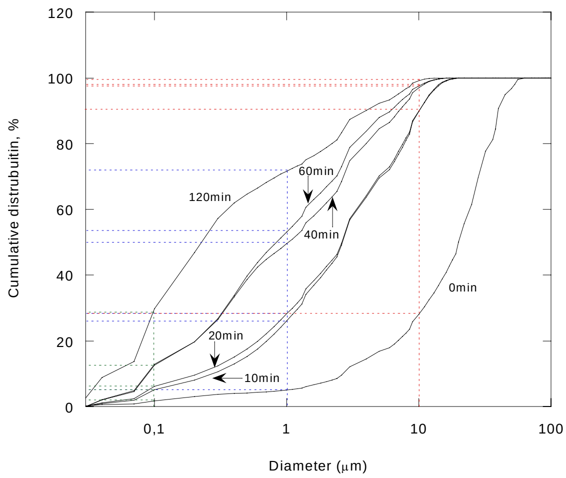


Figure 12. Size distribution (cumulative curve) of the $NbAl_3$ powders as a function of milling time (Attritor, Union Process 01-HD/HDDM, *CR* = 50)

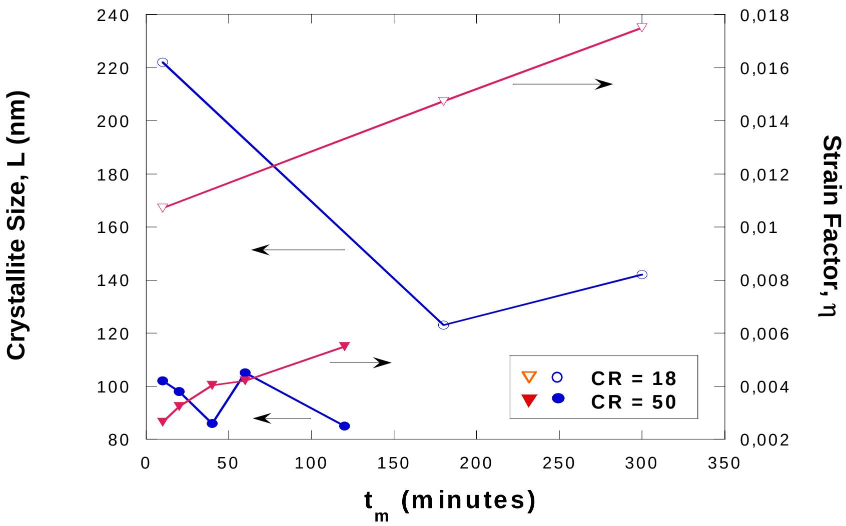


Figure 13. Dependence of $NbAl_3$ crystallite size and internal strain on milling time at different charge ratios (Attritor mill, Union Process 01-HD/HDDM).

Densification of nanostructured $NbAl_3$ powders by Spark Plasma Sintering

As shown in Figure 14, the production of $NbAl_3$ bulk samples by Spark Plasma Sintering (SPS) has been performed following two different routes.

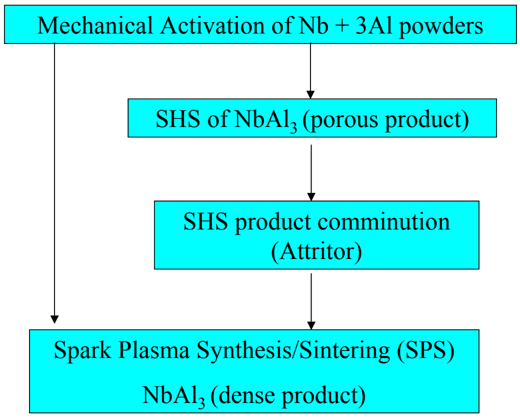


Figure 14. Schematic representation of the two possible routes for the obtainment of $NbAl_3$ bulk samples by SPS

It was found that when powders obtained after comminution of the MASHS product were densified by SPS according to the route reported on the right side of Figure 14, the resulting dense sample contained significant amount of corundum and other intermetallic phases formed during the densification stage. This result was also obtained when consolidating by SPS the $NbAl_3$ powders prepared by the other synthesis techniques adopted in the framework of the NAMAMET Project.
Thus, the synthesis and consolidation of the $NbAl_3$ intermetallic phase was also investigated following the route reported on the left side of Figure 14, when starting directly from co-milled (Nb+3Al) powders. The SPS apparatus was used under temperature controlled mode as shown in Figure 15. Specifically, the first step of the temperature cycle, consisting in increasing the temperature from the ambient value to 600°C in 600 s and maintaining this value for additional 300 seconds, was followed by a second thermal stage. During the latter one, the temperature was changed from 600 to 1000°C in 300 s and the sample was maintained at 1000°C for 300 more s. In addition, the applied mechanical load was changed during the SPS process as reported in Figure 15.

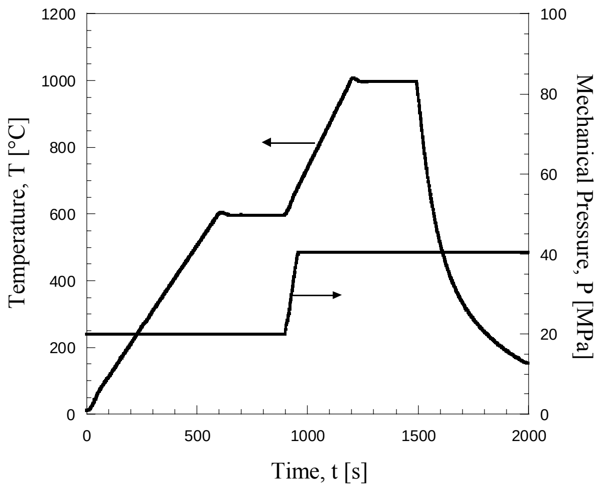


Figure 15. Two steps temperature and mechanical load temporal profiles during the SPS of $NbAl_3$.

A near fully dense (97.5 ± 2.5% of the theoretical density) single $NbAl_3$ phase product (cf. Figure 16) with a crystallite size below 100 nm was obtained.

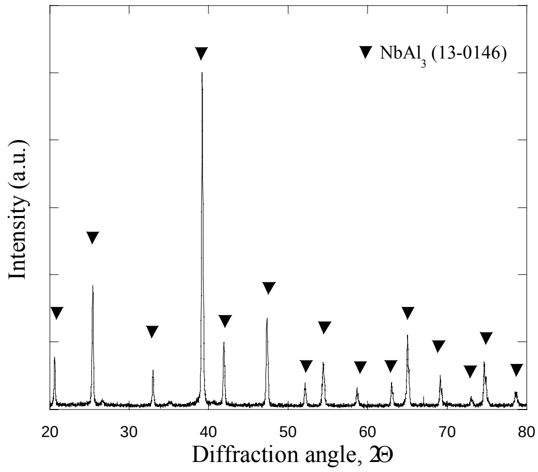


Figure 16. XRD pattern of the Nb-Al product obtained by SPS after ball milling (t_M=35 h) when adopting the two steps temperature and mechanical load temporal profiles (cf. Figure 15).

The results of the mechanical characterization performed on the different $NbAl_3$ bulk samples are reported in Table 3.

Table 3. Mechanical properties of the densified $NbAl_3$ material.

Powder Production Route	E [GPa]	H_{KI} [–]	$H_{V0.3}$ [–]	H_{V1} [–]	H_{V5} [–]	σ_f [MPa]	σ_{cc} [MPa]	K_{Ic} [MPam$^{1/2}$]	Wv*10–6 [mm3/Nm]	µ [–]
MA	232	820	~~~~	986	840	~~~~	~~~~	2.69	203	0.65
MA+SHS+Attritor	255-293	1120	849	1194	1170	67	1531	3.86	209.2	0.64

Although materials with properties comparable or slightly higher than those of the state–of–the–art materials were obtained in NAMAMET, in the case of the $NbAl_3$ system several problems were connected with the achievement of a single phase pure $NbAl_3$ intermetallic.

Concluding remarks:

The following considerations can be drawn:

- $NbAl_3$ single phase powders have been obtained only by MASHS while oxides contamination has been found in the powders produced by APS + quench.
- $NbAl_3$ powders have been consolidated by different techniques, but consolidation gave rise to a multiphase product.
- $NbAl_3$ single phase bulk samples have been obtained only when starting from mechanically activated blend of elemental powder (Nb + 3Al) and consolidating them by the Spark Plasma Sintering method (SPS).

In the case of the $NbAl_3$ material densified during the NAMAMET project, the high amount of aluminium oxide formed during the densification had a major influence on the mechanical properties. The alumina content was 65 wt. % in the case of the hot pressed sample and only 29 wt. % in the SPS samples.

Therefore as a final conclusion, the $NbAl_3$ material developed in the NAMAMET project did not show a clear progress beyond the state of the art.

However the nanoscale microstructure of the material developed by SPS, HPHT and Hot Pressing is encouraging enough, also considering the very large potential market for this family of materials. Nevertheless, the many problems encountered during the powders consolidation will have to be overcome for the exploitation of the developed intermetallic for the foreseen applications.

Metastability in NiTi SMA system. Powders; Densified materials and Properties.

System Leader: **INETI**

Staff: B. Correia, I. Martins, M. Oliveira, E. Gaffet

NiTi Shape Memory Alloys (SMAs) have undergone detailed studies for their potential use as functional materials in many engineering applications, such as active, adaptive or smart structures, as well as certain biomedical applications. Shape memory effects and pseudoelastic behaviour are associated with the reversible martensite-austenite phase transformation and the reorientation of martensite variants. The reversible and diffusionless martensite/austenite transformation takes place in the temperature range from -50 °C to 110 °C as a function of the Ni content of the matrix (usually 49 – 51 at.%).
The aim of NAMAMET project was to investigate the viability of the "metastability route" for bulk materials and coatings synthesis. In the Ni-Ti system the main objective was to produce nanostructured NiTi SMAs by using metastable processing. Starting from various kinds of nanostructured powders, bulk materials were prepared with a range of consolidation techniques:

- Powders
  - MA (Mechanical Activation – CNRS)
  - APS (Atmospheric Plasma Spray) + quench process (UNIBA)

- Bulk materials
  - High Velocity Forging/Extrusion (INETI)
  - SPS (Spark Plasma Sintering – UNICA)
  - Hot-Pressing (ICV-CSIC)
  - Dynamic Compaction (CNR-IENI)

The high velocity forging/extrusion experiments carried out on mechanically activated Ni-Ti powders have been designated as:

- MARFOS - Mechanically Activated Reactive FOrging Synthesis
- MARES – Mechanically Activated Reactive Extrusion Synthesis

According to the Ni – Ti phase diagram (Figure 17), the equiatomic composition has been selected in order to check the various processing methods. Attention has been paid to identify the pertinent processing parameters in order to optimise the SMAs properties for the given composition.

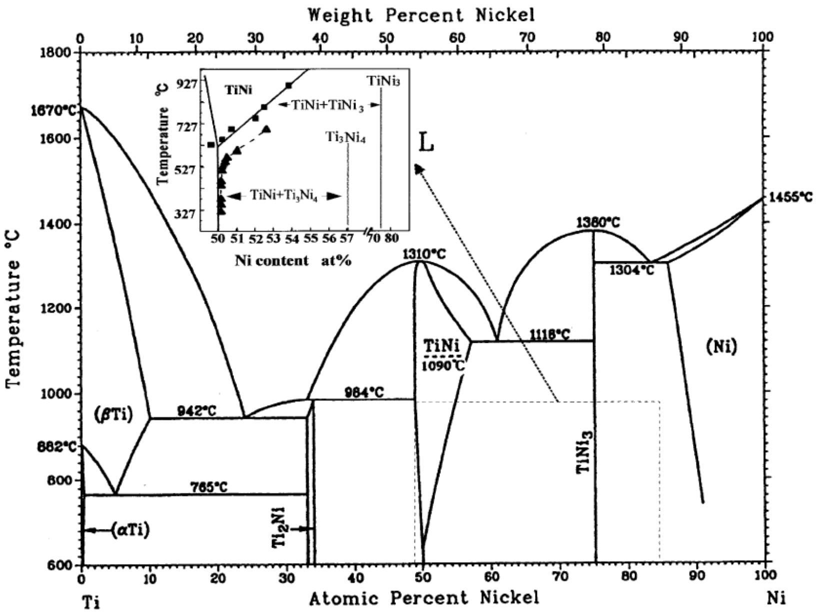


Figure 17. Phase diagram of Ti–Ni [K. Otsuka].

Results

Table 4 shows the highest values of density and relative density attained for the Ni-Ti alloys produced by the different densification processes. It can be concluded that virtually all the densification processes used can yield a high densification. The relative density values range from 98 to 100%.

However, since the shape memory effect is only enabled by the NiTi phase, the percentage of this phase should be maximized in the final product. Thus, the density is not the only factor that should be taken in consideration when comparing the processes. As a range of compounds was obtained with the various densification processes, only the main phase obtained with each type of processing is listed in Table 5.

Table 4. Higher densities and relative densities of the Ni-Ti bulk materials.

Powder production methods		Densification processes				
		High velocity forging (INETI)	Extrusion (INETI)	SPS (UNICA)	Hot-pressing (ICV-CSIC)	Dynamic compaction (CNR-IENI)
MA (CNRS)	Density (g/ cm³)	6.43	6.33	6.38	6.39	6.45
	Relative density* (%)	99.7	98.1	98.9	98.4	100
APS + quench (UNIBA)	Density (g/ cm³)	6.39	–	6.41	6.79	6.45
	Relative density* (%)	99	–	99.3	100	100

*using the theoretical density of NiTi (6.45 g/cm³).

Table 5. Main phase obtained for each densification process.

Powder production methods		Initial powder	At 900 °C	High velocity forging (INETI)		Extrusion (INETI)		SPS (UNICA)		Hot-pressing (ICV-CSIC)		Dynamic compaction (CNR-IENI)	
				as-densified 700 °C	HT* 950 °C	as-densified 700 °C	HT* 950 °C	as-densified 950 °C	HT* 1000 °C	as-densified 950 °C	HT* 1000 °C	as-densified	HT*
MA (CNRS)	Main phase	Ni, Ti	NiTi	Ni_3Ti	NiTi	Ti_2Ni	NiTi	Ni_4Ti_3	Ni_3Ti	NiTi	Ni_3Ti	Ni	–
APS + quench (UNIBA)	Main phase	NiTi, NiO	Ti_2Ni, Ni_2Ti_4O	Ti_2N	–	–	–	NiTi	–	–	–	NiTi	–

*Heat-treated.

It can be concluded that the MARES and the MARFOS processes provide the highest NiTi content, respectively 69 and 76 wt%, after heat treatment at 950ºC. The hardness values somewhat mirror these results as the highest values were again obtained by MARES and MARFOS processed samples, after heat treatment at 950ºC, respectively 682 and 708 HV.
As attested by Figure 18, rods of superior quality were obtained. After can removal the Ti-50Ni extruded products showed no surface cracks. Typical microstructures of the extruded and heat-treated materials are also illustrated in Figure 18.

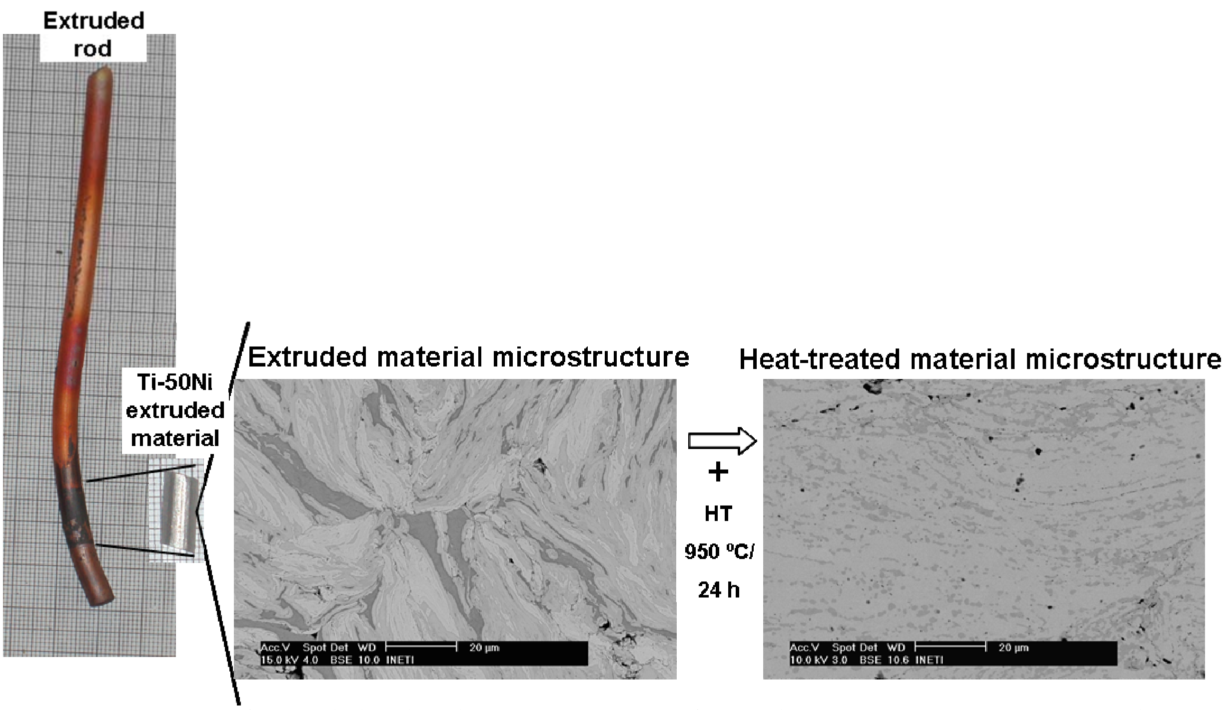


Figure 18. Typical extruded rod and microstructure evolution during MARES of Ti-50Ni powders.

Concluding remarks:

- The densification processes used enabled the production of fully dense materials;
- Multiphase compounds were always obtained after densification;
- By X-ray diffraction analysis it was found that the crystallite size was less than 100 nm for all the phases indicating that the materials are nanostructured;
- The synthesis of Ni-Ti intermetallics was achieved at lower temperatures through a controlled synthesis reaction, instead of the usual strong exothermic reaction between elemental titanium and nickel powders;
- The results of this R&D project suggest that mechanically activated reactive extrusion synthesis (MARES) may be a suitable and promising PM route for producing dense intermetallics compounds based on other metallic systems.

Metastability in Coatings and direct bulks. Processes and Properties.

System Leader: **UTBM**

Staff: G. Bertrand, E. Tresso, I.G. Cano, S. Dosta, J.R. Miguel, J.M. Guilemany, R. Alexandre, A. Gonçalves, L. Comas

Since more than one decade, nanostructured materials are the focus of intensive research in the thermal spray field. In conventional atmospheric plasma spraying, which is a rapid heating, cooling and solidification process, powders in the size range 10-100 µm produce lamellar structures. These lamellae are between 1 and 3 µm in thickness and tens to hundreds µm in diameter. The coatings present numerous and large defects: micro and macro-cracks, unmelted particles and globular pores. Unfortunately in thermal spraying injection of particles below 5 µm is impossible. The momentum that can be imparted to the particle by the carrier gas is limited.

The aim of the NAMAMET project was to investigate a new route implementing a high speed quenching process to the conventional APS technique that could lead to fully metastable or amorphous coatings that could be further recrystallized by an appropriate thermal treatment. A second solution was also investigated that consists in spraying reconstituted powders from mechanically activated particles. The as-sprayed coatings could contain both nanostructured grains and metastable or amorphous zones that could be further recrystallized by an appropriate thermal treatment.

Several ceramic binary systems (Al_2O_3-TiO_2, ZrO_2-Al_2O_3, TiC-TiB_2) and metallic alloys (NiTi as SMA and $NbAl_3$ as an intermetallic) have been manufactured as coatings or direct bulks using Thermal Spray technology. When rapidly quenched from the solid state, these materials often give rise to a metastable or amorphous structure that, upon recrystallisation by medium temperature treatments, converts into a stable nanocomposite structure. These structures were achieved using

- Atmospheric Plasma Spray technique with a cryogenic quenching device from commercially available powders (cryo-APS) (UNIBA, TMC),
- Conventional Atmospheric Plasma Spray technique from mechanically activated[†] spray dried powders (MA-APS) (UTBM, TEandM),
- Unbalanced DC Magnetron Sputtering (dc-PVD) was also implemented to produce coatings of TiC-TiB_2 ceramic (TEandM).

For Al_2O_3-TiO_2 system, the use of the cryogenic cooling device leads to coatings only composed of the spinel-Al_2O_3 phase whereas the spraying from MA powder leads to coatings with the metastable phases γ-Al_2O_3 and β-Al_2TiO_5. For Al_2O_3-40TiO_2 system, using the cryogenic device or the MA powder as feedstock material allows to manufacture coatings composed of a mixture of the metastable α-Al_2TiO_5 and β-Al_2TiO_5 phases. Decreasing the plasma energy promotes the β-Al_2TiO_5 phase versus the α-Al_2TiO_5 phase.
After a thermal treatment the metastable phases have been changed into nano stable phases α-Al2O3 and rutile TiO2 that lead to higher mechanical properties (E increases by 350% and σ increases by 230%)

For ZrO_2-Al_2O_3 system, whatever the APS route (either cryogenic or MA powder) the resulting crystallographic coating characteristics are very similar. From the ZrO_2-60Al_2O_3 mixture, the t-ZrO_2, m-ZrO_2, α-Al_2O_3 and γ-Al_2O_3 phases were identified in the plasma sprayed coatings. The latter phase was evidenced using the cryogenic cooling system. For the ZrO_2-20Al_2O_3 mixture, the t/c-ZrO_2 phases were identified and the alumina was no more observed. A dissolving of alumina into zirconia may be

[†] The ceramic and metallic particles have been mechanically activated by CNRS.

assumed.
The heat treated coating appears to be nanostructured with α-Al_2O_3 and t+c/m-ZrO_2 and grain size below 100 nm. The mechanical properties seem to be maintained.

For TiC-TiB_2 system, the metastability seems to be difficult to evaluate although a deformation of the peaks is always observed. However, high porosity and nitridation of the titanium is observed in the coatings obtained through the different tested conditions. This nitridation is reduced for the best tested spraying conditions. The viability of producing coating of TiC-TiB_2 by APS has been demonstrated although the results are not completely successful.
Using PVD process, difficulties are encountered to achieve the targeted compositions because of the oxygen content of the coating.

NiTi coatings have been produced through the APS + quench process from initial commercially micron-sized powders.
The oxidation of the coating has been highly reduced when compared with a Ni-Ti coating produced through a conventional APS route.

For Nb-Al system, the metastability seems to be difficult to evaluate although a deformation of the peaks is always observed.
However, it was shown that the coatings obtained have low porosity with a combination of phases homogeneously distributed. These phases correspond to different Nb-Al percentages that have been analysed by EDS. In this case, the XRD seemed to show a higher metastability rate.

Concluding remarks:

- Several ceramic binary systems (Al_2O_3–TiO_2, ZrO_2–Al_2O_3, TiC–TiB_2) and metallic alloys (NiTi as SMA and $NbAl_3$ as an intermetallic) were manufactured as **coatings or direct bulks** using Thermal Spray technology or Physical Vapour Deposition Process.
- Two processes, namely cryo–APS and MA*–APS were successfully set up for the production of coatings and bulks for the Al_2O_3–TiO_2 and Al_2O_3–ZrO_2 systems.
- Both processes enable the production of coatings or bulks in a metastable state that could be further converted into a **nanostructured material** by an appropriate thermal treatment (1h @ 1200 or 1400°C). High-temperature (α or β–Al_2TiO_5, γ–Al_2O_3, t or c–ZrO_2) or amorphous phases have been achieved in these binary ceramic systems by spraying.
- The **evolution of the mechanical and wear behaviour** of the coatings after thermal treatment was a valid confirmation of the metastable approach. The mechanical properties were **drastically increased** which is interesting in term of applications. The good thermal resistance as well as biocompatibility of these compounds render interesting their application in turbine hot zones, as prostheses (hip joint), …
- The APS + quench process has proved to be a valid forming technique for obtaining **metastable and nanostructured bulk materials with complex shapes** that can be converted into stable fine–grained microstructures by annealing treatments at moderate temperatures.

Dissemination and Use

Exploitation:

The outcomes of the activities carried out in *WP5 – Assessment of the developed technologies and prospects* represented an effective starting point for the assessment of possible routes and strategies for the exploitation of the research results, and will constitute a valid and ready–to–use basis for possible start up, spin–off or take–up actions to be realised through the involvement of non–participant actors interested in the research outcomes.

The Consortium intends to evaluate the possible products that can be commercialized. At present, commercial contacts have been taken with industries interested in the commercialization. This action will be further investigated after the end of the NAMAMET project. Commercial partners have been recognized, and the transfer of non–exclusive licences will be evaluated, as well as the creation of possible joint–ventures to be set up after the end of the project.

The exploitable results achieved during the project are mainly constituted by the developed nanostructured materials in the form of powders, bulk composites and coatings.

The following exploitable results were identified by the NAMAMET Consortium:

N°	Topic	Status
1	APS + quench	Validated on 2 materials $ZrO_2 - Al_2O_3$ $TiO_2 - Al_2O_3$
2	SHS + quench	Validated on TiC, TiB_2 and Ti – Al_2O_3 - TiC
3	PVD coatings	Validated for TiC and TiB_2
4	APS + quench for coatings	Validated on 2 materials $ZrO_2 - Al_2O_3$ $TiO_2 - Al_2O_3$
5	Bulk materials	POLITO is evaluating the launch of a spin–off about cutting tools and appropriate binders using TiC–TiB_2
6	Correlation between microstructures and bulk properties of the resulting materials	Fundamental knowledge gained
7	Complex shapes	Obtained for: $Al_2O_3 - TiO_2$ $Al_2O_3 - ZrO_2$ Ni – Ti
8	Shape memory alloys	Ni–Ti as shape memory alloy

Concerning the bulk materials, several techniques have been employed in this project to densify a large variety of materials and classes. It was shown that these materials can be successfully densified to fully dense samples with nanosized grains. The microstructure and the resulting mechanical properties were in many cases superior to the values that are reported in the literature.
The **successful evolution of the metastable condition exhibited by the powders into nanostructures** during the densification activities of NAMAMET was a very encouraging result. The *exploitation of this evolution to obtain nanocomposites* has been definitively confirmed after the characterisation and assessment activity carried out during the last period.

Therefore, the developed materials and methods resulted very promising for the fabrication of a class of nanostructured materials with outstanding properties. These results were successfully obtained for most of the investigated materials, and particularly will be immediately exploitable for the TiO_2–Al_2O_3 and ZrO_2–Al_2O_3, TiC–TiB_2 and Ti–Al_2O_3–TiC systems.

The main issues are reported below for each identified exploitable result.

Results No. 1 and No. 2

Nature of exploitable result: Innovation

Powders in metastable state represent the first exploitable product of the NAMAMET Project. In the Consortium opinion, the demonstration that metastable powders are potentially breakthrough "raw materials" to obtain high quality nanocomposites can stimulate a possible market spread of these powders. In this case the protection of the knowledge collected in the NAMAMET Project will be evaluated by means of a proper patenting activity. Concerning this, the evaluation of patent possibility will regard mainly the operative processes, particularly for the APS route and for the developed quenching methods.
As the economical viability of the investigated technological routes was demonstrated (by feasibility study and business plan), the production route by SHS + quench turned out to be a competitive way to produce metastable nanocomposite powders.

Results No. 3

Nature of exploitable result: Innovation

Unbalanced DC Magnetron Sputtering (dc-PVD) was implemented by TEandM to produce ceramic coatings of TiC-TiB_2.
The PVD coating showed a low friction coefficient (0.55) and also a low wear rate ($6.6 \cdot 10^{-6}$ mm^3/Nm). These properties render these coatings very interesting for application as anti-sticking materials for high temperatures (up to 1200°C), high hardness, high wear and high corrosion/oxidation application for air, land and sea turbines components, for automotive (recirculation engine exhaust gas systems) and moulds for die– casting.
However, the exploitation at industrial level needs a further process optimisation in order to limit the formation of oxides during PVD.

Results No. 4

Nature of exploitable result: Innovation

Coatings were successfully produced by cryo–APS and MA–APS for the Al_2O_3–TiO_2 and Al_2O_3–ZrO_2 systems. Cryo–APS was implemented by UNIBA and TMC based on Atmospheric Plasma Spray technique with a cryogenic quenching device from commercially available powders. The second process used by UTBM and TEandM is based on Atmospheric Plasma Spray technique from mechanically activated spray dried powders.
Both processes enable the production of coatings or bulks in a metastable state that could be further converted into a **nanostructured material** by an appropriate thermal treatment (@ 1200 or 1400°C). High-temperature or amorphous phases were achieved in these binary ceramic systems by spraying.

The **evolution of the mechanical and wear behaviour** of the coatings after thermal treatment was a valid confirmation of the metastable approach. The mechanical properties were **drastically increased** which is interesting in term of applications. The good thermal resistance as well as biocompatibility of these compounds render interesting their application in turbine hot zones, as prostheses (hip joint), …

Results No. 5

Nature of exploitable result: Innovation

The TiC–TiB_2 materials developed by both HPHT and SPS resulted to be a valid candidate for cutting difficult–to–cut materials like titanium alloys as they were **wear resistant** and showed **thermal shock resistance comparable or superior to other competing commercial (Al_2O_3 – 30wt.% TiC) cutting tool materials.**
It can be anticipated that the application can be extended to other difficult–to–machine materials, such as nickel–based alloys, and may lead to much improved performances and test the potentiality of the developed nanostructured TiC–TiB_2 composites for cutting a wide range of materials. In the view of limiting the coolant use in cutting operations (ideal conditions of dry cutting), the addition of a metal binder (like e.g. Ni) to the TiC–TiB_2 hard material can be anticipated.
In the view of possible exploitations, the fact that no actual application of TiC–TiB_2 materials is commercially available is due to the lack of a cost–effective and reliable processing route allowing an accurate control of the microstructure for this class of materials. Regarding this, the SHS process seems to offer a promising way provided an accurate control of the process parameters is achieved.
According to the properties reported in the literature and those measured on the NAMAMET TiC–TiB_2 materials (good fracture toughness and thermal shock resistance), other potential applications of these composites can be foreseen, such as high temperature structural components in heat exchangers and recirculation parts in exhaust gas systems for automotive engine, etc., propulsion and space thermal protection in aircraft, wear resistant parts in forming dies, non–structural applications like wall tiles in nuclear fusion reactors and coatings for wear– and corrosion–resistant components.

Regarding the Ti–Al_2O_3–TiC system the final material exhibited improved properties with respect to the state-of-the-art. The developed Ti–Al_2O_3–TiC cermet material showed wear rate much smaller than that exhibited by some commercial Ti–based alloys or superalloys (Ti–48Al–2Cr–2Nb; Superalloy 718), thus showing interesting potential applications in the automotive and aeronautics industrial sectors for wear–resistant parts and thermo–mechanical components (valves, camshafts, etc. in the automotive industry, turbine blades, drums, blisks, blings, exhaust nozzles, compression links, etc. for aeronautical components, armor parts, etc.). Due to the excellent abrasive and friction wear resistance shown at high temperatures, the sue of the developed Ti–Al_2O_3–TiC system materials can be used in engines and car components.
In the case of the $NbAl_3$ material densified during the NAMAMET project, the high amount of aluminium oxide formed during the densification had a major influence on the mechanical properties. The alumina content was 65 wt. % in the case of the hot pressed sample and only 29 wt. % in the SPS samples. However the nanoscale microstructure of the material developed by SPS, HPHT and Hot Pressing is encouraging enough, also considering the very large potential market for this family of materials. Nevertheless, the many problems encountered during the powders consolidation will have to be overcome for the exploitation of the developed intermetallic for the foreseen applications.

Results No. 6

Nature of exploitable result: **Basic knowledge**

The highly advanced knowledge gained during the project will be crucial for the long–term exploitation of the new class of materials developed. The understanding of the role played by the interfaces and by the grain boundary diffusion in the determination of the behaviour of nanostructured materials is a key factor for the full exploitation of these materials, and was studied in the last project period.
However the exploitation of this result appears to be more long-term oriented than the other exploitable results.

Results No. 7

Nature of exploitable result: **Functionality**

The production of nanostructured direct bulks by APS + quench was also successfully achieved during the project. Two ceramic systems (Al_2O_3 – TiO_2 and ZrO_2 – Al_2O_3) and the NiTi alloy were chosen as coating materials.
The APS + quench process has proved to be a ***valid forming technique*** for obtaining metastable and

nanostructured bulk materials with complex shapes. The metastable materials obtained by APS + quench could be converted into stable fine–grained microstructures by annealing treatments at moderate temperatures.

Results No. 8

Nature of exploitable result: **Innovation**

An innovative process named Mechanically Activated Reactive Extrusion Synthesis (MARES) was successfully set up for the Ni–Ti alloy. The synthesis of Ni–Ti intermetallics was achieved at lower temperatures through a controlled synthesis reaction, instead of the usual strong exothermic reaction between elemental titanium and nickel powders.
The results of this task suggested that the MARES process may be a suitable and promising PM route for producing dense intermetallics compounds potentially extendable to many other metallic systems.
Also in this case the protection of the knowledge generated in NAMAMET will be evaluated by evaluating the possibility of patenting the innovative developed process by the owners, i.e. CNRS and INETI.

The exploitation results address the following issues:

- New materials such as nanostructured powders, coatings and densified materials can be developed for future market needs by employing the ***metastability approach*** successfully set up during the NAMAMET project.
- The partners involved in the exploitation activity of powders, coatings and bulks are those carrying out the development and coordination of activities regarding the set up of the products to be industrialized. Therefore an information passage will not be necessary. A key role on coatings will be played by **TEandM** and **TMC**, as industrial partners interested in:
    - Anti sticking materials for low or medium temperatures (up to 500°C) and high corrosion resistance applications like moulds for plastic injection, food and pharmaceutical industries;
    - Anti sticking materials for high temperatures (up to 900°C) and high corrosion / oxidation applications for automotive (recirculation engine exhaust gas systems) and moulds for die–casting;
    - High hardness, high wear, high temperatures (up to 1200°C) and high corrosion / oxidation application for air, land and sea turbines components.
- During the 3rd period of the Project, the knowledge generated by each partner and the nature of the developed products allowed a group of partners to evaluate the possibility of transferring manufacturing licences for metastable powders and coatings to industrial companies interested in this field.
- Concerning the technical and economic considerations, it can be stated that the current period is very favourable for a possible commercialization of metastable powders, since the related market is currently in a formation phase and the production rate of the market leaders is still very limited. Consequently the appearance of new producers with new–generation powders (as metastable powders can be considered) represents a good business opportunity, obviously after the phase of presentation of the new products.
- The technologies investigated for the products preparation are original and no competing technologies are identified at present. For these reasons no obstacles or barriers to commercialization of the developed metastable powders, nanostructured coatings and bulks were identified, provided three appropriate identified actions are undertaken (*decide to patent or not the process knowledge, sign a consortium agreement for exploitation of all the project results, look after two exploitation routes - large scale powder manufacturing and value added applications involving such powders).*

- Regarding the further additional work, including further collaborations, once NAMAMET project was concluded, the results were acquired and the knowledge of the products was complete, the most promising applications were identified for each material system, both at bulk and coating level and the performance of the developed materials was compared with that of commercial ones. The products validation was carried out prior to commercialization both at laboratory testing and operative conditions level. It was a demanding and expensive activity, but in this way the most interesting exploitable results were identified.
- The Consortium is still evaluating the possibility to patent the products or procedures showing an originality trait after the end of the densification activity and the evaluation of the bulk materials. The intellectual property of discovery will be owned by the developer partner, according to the Consortium Agreement. The Consortium will continue to push activities addressed to upgrade the gained knowledge into commercial products also after the end of the project.
- The Consortium has identified the possible products that can be commercialized as the following: *bulk **$TiC–TiB_2$ material for cutting tools; $ZrO_2–Al_2O_3$** and **$TiO_2–Al_2O_3$** bulks and coatings by **APS + quench** and **$TiC–TiB_2$ PVD coatings**.* At present the first commercial contacts have been taken with industries interested in commercialization. This action will be completed after the end of the NAMAMET project. If commercial partners are recognized, a non–exclusive licence will be transferred to them. Possible joint–ventures will also be evaluated. Finally, if new enterprises are set up, they will benefit by Incubator facilities, like i.e. that available in Politecnico di Torino, that help the starting activity of new enterprises.
- The social–economic impact plays a key role for the following considerations:
  - The developed products are high added value.
  - The developed products can be realized by high–tech industries.
  - The developed products don't require high investments in terms of equipments and plants. Quality control equipments, generally expensive, can be supplied by means of joint–ventures with academic structures/research centres.

In conclusion the particular nature of products developed in the NAMAMET Project can have a relevant socio–economic impact, requiring high qualified personnel.

Dissemination:

A project website (www.polito.it/namamet) was managed and updated by the coordinator POLITO (responsible E. Tresso). The section with access restricted to the project contractors was used in order to effectively exchange documentations and communications among the partners, and was periodically updated with the main outcomes and decisions derived from the various project meetings. A public section of the website was designed at the end of the 2nd year in order to disseminate the most interesting scientific, technological and dissemination results.

Regarding the publication activity, many papers and contributions were prepared in collaboration between two or more partners as a result of the good cooperation and integration of the participants within the project Consortium. Furthermore, most of the Conferences and Congresses were of international level, with audience size of more than 1000 participants. As is reported in Fig. 1 the first period (2004-2006) of the NAMAMET project was mostly devoted to participation to conferences, in view of having scientific exchanges of ideas concerning the project with the scientific community of nanostructured materials. In the next periods (2006-today) the submission of scientific papers to International Journals for publication of the results obtained in the project became predominant.

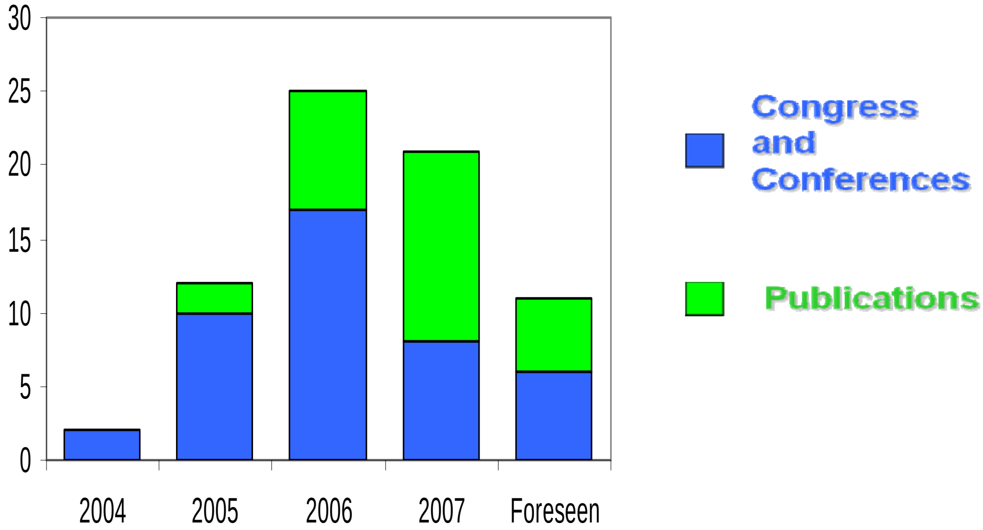


Fig. 1. Evolution of publications and participations to Congress and conferences during the entire project (2004-2007) and after its conclusion (2008)

Concerning the dissemination activity, 3 dedicated Seminar were organised during the overall project duration in order to disseminate and discussion the main experimental results on the developed nanomaterials inside the international scientific/technical community.
The organised Seminars were the following:

- **"Nanomaterials: Synthesis, Processes and Properties"**, held in Brussels at Casa de Asturias, on 28 November 2005. In order to enlarge the dissemination outside the NAMAMET Consortium, the interaction with another project was identified on the basis of a common interest topic. The project was the Integrated Project NANOKER, FP6–515784–2 (Structural ceramic nanocomposites for top–end functional applications), coordinated by Consejo Superior de Investigaciones Científicas (CSIC). After the contacts, the organisation of a joint Seminar was decided. The outcome of the Seminar was the deliverable "D24 – Proceeding of the technical seminar organised after 1st year of the project", which was delivered at month 12.
- **"Nanostructured coatings obtained by a metastability approach"**, held in Krakow on 8 September 2006 during the 24 months progress meeting at IOS. The outcome of the Seminar was the deliverable "D39 – Proceeding of the technical seminar organised after 2nd year of the project", which was delivered at month 24.
- **"Processing of Nanostructured Materials through Metastable Transformations"**, held as a satellite seminar of the *47th Annual Congress of the Spanish Society of Ceramics and Glasses* (XLVII Congreso Anual de la Sociedad Española de Cerámica y Vidrio – SECV, 24 – 26 October 2007) and held in Toledo, Spain, on 26 October 2007. Dr. M.A. Rodriguez, the scientific responsible of ICV–CSIC in NAMAMET, organised the seminar as member of the Organising Committee of the Annual Congress. The outcome of the Seminar was the deliverable "D45 – Proceeding of the dissemination seminar organised after the 3rd year", which was delivered at month 41.

GENERAL CONCLUSIONS

The experimental densification activities carried out have highlighted that samples with **nanocrystalline grains** were obtained in all cases. Fully dense materials were achieved by spark plasma sintering (SPS), high pressure–high temperature (HPHT) sintering, and hot pressing. In these cases the nanosize of the grains was retained during sintering.

The activity of the project have confirmed the **feasibility of fabrication of bulk nanostructured materials** starting from **metastable powders obtained by means of both APS and SHS followed by quench** and of **coatings by processes based on metastability**.

This **corroborated the basic idea of the project**, i.e. the **effectiveness of the metastability in the retention of the nanostructure** during densification.

Also another key objective of the project was successfully demonstrated, i.e. the **successful evolution of the metastable condition into nanostructures**. The *exploitation of this evolution to obtain nanocomposites* has been partially started and will be completed after the end of NAMAMET.

The developed materials and methods resulted **very promising** for the fabrication of a broad class of nanostructured materials with outstanding properties. Only the results obtained on the $NbAl_3$ intermetallic and the Ni–Ti alloy didn't prove a clear progress against the state of the art, mainly due to the problems of contamination connected with the processing of these materials through the selected technologies.

The following achievements can be pointed out for the various investigated systems:

ZrO_2 – 20%wt Al_2O_3 (powder by APS + quench):

- the material developed by SPS exhibited very low wear rate and good thermal shock resistance. Therefore it is a valid candidate for the target applications identified at the beginning of the project, i.e. both **wear–resistant parts** (wiring machine components, ceramic/clay extrusion moulds, cement and coal powdered piping, pharmaceutical components, etc.) and **components subjected to thermal shock and thermal fatigue**.

Al_2O_3 – 13%wt TiO_2 (powder by APS + quench):

- the material developed by SPS exhibited rather low wear rate and very good thermal shock resistance. Therefore it perfectly fits the requirements of the target applications identified at the beginning of the project, i.e. both **wear–resistant parts** (textile machine components, food/beverage machine components, sealing zones moving parts, etc.) and **components subjected to thermal shock and thermal fatigue**.
- the material developed by HPHT exhibited very good thermal shock resistance. Therefore it is especially suitable for applications like **thermo–mechanical components subjected to thermal shock and thermal fatigue**.

TiC – 33%mol TiB_2 (powder by SHS + quench):

- the material developed by HPHT successfully passed the bench tests as **cutting material** for turning of Ti–based alloys. The material showed very low wear rate when turning with a coolant and moderate wear rate under hard dry turning conditions. Therefore it perfectly fitted the requirements for the previously foreseen main application as a very interesting candidate for cutting difficult–to–cut materials, like titanium alloys and nickel–based alloys. It also exhibited good fracture toughness and thermal shock resistance that allows to foresee its application for the fabrication of thermo–mechanical components subjected (heat exchangers, recirculation parts in exhaust gas systems for automotive engine, etc.).

- the material developed by SPS exhibited very low wear rate and average thermal shock resistance. Therefore it is suitable for application in wear–resistant parts (moulds for plastic and die casting, punches and dies in the pharmaceutical industry, etc.).
- the coatings developed by Magnetron sputtering starting form composite targets fabricated by SHS + densification showed very good microhardness at both room and high temperature and good adhesion to the substrate. Therefore the material is a valid ultra high–temperature ceramic for the realization of wear–resistant coatings for thermo–mechanical components (propulsion and space thermal protection in aircrafts, etc.) as well as for corrosion resistant components.

On the overall, the developed $TiC–TiB_2$ composites showed **a very good combination of properties** in terms of Young modulus, hardness, toughness, wear rate and thermal shock resistance, which are generally **comparable or superior to** those of available state–of–the–art materials or **other competing commercial cutting tool materials.** The NAMAMET $TiC–TiB_2$ resulted thus to be **an excellent candidate for cutting tools applications,** especially for cutting difficult–to–cut materials.

Concerning a possible exploitation, it can be anticipated that the potentiality of the developed nanostructured $TiC–TiB_2$ composites can be positively extended to cutting a wide range of materials. In the view of limiting the coolant use in cutting operations (ideal conditions of dry cutting), the addition of a metal binder (like e.g. Ni) to the $TiC–TiB_2$ hard material can be anticipated.

$Ti – Al_2O_3 – TiC$ (powder by SHS + quench):

- the cermet developed by hot pressing exhibited very good hardness, low wear rate considering the content of metal (53%wt Ti) and average/good thermal shock resistance. Therefore it is a valid candidate for the target applications identified at the beginning of the project, i.e. both wear–resistant parts and thermo–mechanical components (valves, camshafts, etc. in the automotive industry, turbine blades, drums, blisks, blings, exhaust nozzles, compression links, etc. for aeronautical components, armor parts, etc.).

$NbAl_3$ and Ni–Ti systems:

The results obtained on the $NbAl_3$ intermetallic and the Ni–Ti alloy didn't prove a clear progress against the state of the art, mainly due to the problems of contamination connected with the processing of these materials through the selected technologies.

A possible reason to explain this result is that no evidence of metastability has been found in the powders produced for both systems.

In the case of the NiTi system the largest amount of NiTi phase was the achieved by dynamic consolidation and high velocity forging/extrusion techniques. In both cases, very high densities and small grain sizes have been obtained.

Small grain sizes have also been obtained in the case of SPS and hot pressing, but these techniques suffer in the formation of undesired intermetallic nickel–titanium phases. Though these phases are undesirable for shape memory alloys, these materials can be utilized as structural materials due to their high hardness because of the nanocrystalline intermetallic phases.

Dynamic consolidation turned out to be a promising technique to obtain very small grain sizes because of the short time in which a very large amount of energy is brought into the system. Although the final densities did not reach values higher than 90 %, the characteristics of the starting powder were maintained to a larger extent by this technique.