EPMA European Hard Materials Group

Project proposal: Kinetics of Multiphase Materials: Atomic Mobility in the Liquid Phase, Simulations and Experiments

"Kinetic 2"

Consortium Agreement

Issued June 2017

The Project – "Kinetic 2" as defined in Annex 1
The Contractors –

- Innomat AB, Movägen 21, 18249 Enebyberg, Sweden: **INNOMAT**
- KTH Royal Institute of Technology, Materials Science and Engineering Department, Brinellv. 23 S-100 44 Stockholm, Sweden: **KTH**

The Coordinator –

- The European Powder Metallurgy Association, Talbot House, 2nd Floor , Market St., Shrewsbury SY1 1LG, England: **EPMA**

The Members – Paid up corporate EPMA members funding the Project
The Participants – The Contractors and the Members

UV = unanimous vote of Members and Contractors; MV = majority vote of 2/3 members or higher

Heads

1. The Members and Contractors agree to cooperate in order to complete the Project according to Annex 1.
2. All information generated under the Project will remain confidential to the Members during the Project and for 5 years after delivery of the final written report to Members, and may only be disclosed to third parties (e.g. for dissemination purpose in PM Congress) with UV.

   For KTH: the contractor is obliged to publish in the usual scientific form the results of studies undertaken during performance of the project. The Member gives their fundamental consent to such publication. The contractor will inform the Member beforehand of any planned publication and will give them the opportunity of commenting on it within a reasonable period, at latest four (4) weeks after submission of the text intended for publication. A Member is entitled to refuse their consent to a publication if it is intended to publish company related data or, in connection with the granting of patent rights, if it is intended to publish any anticipatory information likely to constitute a bar to novelty. In such cases, the contracting parties will, without delay, seek to reach a special agreement governing the form and timing of rapid publication and taking due account of the legitimate interests of both parties.

3. The Contractors agree to not carry out or have previously carried out the same project or part of the same project on “Kinetics of Multiphase Materials: Atomic Mobility in the Liquid Phase, Simulations and Experiments” with organisations other than the Members until completion of the project (delivery of the final report). The aforementioned obligation shall not apply to other entities of KTH other than its performing entity research groups.
4. The Members agree **to share equally the cost of the Project** (EUR 50,500). The required minimum number of Members is **four** unless the Members agree to exceed the maximum Project Fee.
5. The Members who did not participate in the project “Kinetic simulations in Hardmetals – Evaluation of Mobilities by Coupling Experiments and Simulations” *Kinetic* may participate in the Kinetic 2 project by settling a “Kinetic results access premium” of **EUR 1,614** at the start of the Kinetic 2 Project. The premium less a 13% EPMA Management fee will be used to decrease the Kinetic 2 Project Fee for the Kinetic Consortium Members.
6. The KTH Royal Institute of Technology agrees to become or remain an associate Member (EUR 1,750 per year) of the EPMA once the “Kinetic 2” Project will have started. Mrs Karin Frisk from the Consulting Company Innomat AB agrees to become or remain an Individual Member (EUR 200 per year) of the EPMA once the “Kinetic 2” Project will have started.
7. **VAT**: The Project Fee is VAT exclusive if applicable. Non-UK participants do not pay VAT provided they give their VAT number to the EPMA. UK participants have to pay VAT regardless and then reclaim it.
8. The Members also undertake to provide the Contractors with the necessary materials (powders, specimen etc...) for the project. If no agreement on in-kind contribution between the industrial partners can be found or if the Consortium agrees to subcontract it internally or externally at additional costs, the EPMA will coordinate this task “Work Package 0” and charge equally each Member to cover the cost plus an administrative fee of 13%.
9. **Payment Schedule:**
   For Work Package 0: Full payment within one month of invoice if necessary.
   For “Kinetic” project:
   - **50% at the start**,
   - **50% after completion** of the “Kinetic 2” Project and delivery of the final report.
10. New paying members may be admitted during the Project by UV on payment of an additional reasonable premium (10%). The premium will be used to decrease the Project Fee for the Consortium Members.
11. Except for the deliverables of Annex 1, each Participant will retain the Intellectual Property for any other outcomes of the Project.
12. **Warranty**. The contractor's warranty extends solely to the use of due scientific diligence and to compliance with accepted engineering practice. The contractor does not guarantee that the desired objectives of the research and development project will be achieved.

13. **Liability**. The contractor is liable solely for wilful actions and gross negligence. Liability for proven damage is limited to the amount of the contractual sum. The Member is not liable for this project.
14. Coordination will be carried out by the EPMA, who will have responsibility for invoicing, day to day liaison with the Contractors and keeping Members informed. The EPMA will operate under the same confidentiality agreement as Members and the EPMA President will be arbitrator for unresolved disputes by the Members. Should the Parties fail to resolve a dispute, then such dispute shall be subject to the exclusive jurisdiction of the English Courts. The laws of England and Wales govern all matters arising out of or relating to this agreement, and all transactions contemplated hereby, including, without limitation, its validity, interpretation, construction, performance and enforcement.
15. All the terms of this agreement may be changed by UV, except for 4, 6,7, 12 & 13

Signatures: signed individually by all Members and Contractors

ORGANISATION:

VAT NUMBER:

NAME:

DATE:

SIGNATURE and STAMP:

Annex 1

Project proposal: "Kinetics of Multiphase Materials: Atomic Mobility in the Liquid Phase, Simulations and Experiments".

Karin Frisk (KF) and Joakim Odkvist (JO)

1. Background

Tough graded surface zones can be formed during sintering of hardmetals by altering the phase composition in the surface through the sintering atmosphere. Such graded surface zones are important for coated hardmetals, where differences in properties between coating and hardmetal can otherwise cause cracks. The mechanism of formation of the gradient zones can be understood by diffusion simulations as shown by Gustafson and Östlund [1], who applied a thermodynamic and kinetic model and could show that the surface zone is formed due to a coupled diffusion of N and Ti. Ekroth et al. [2] used a thermodynamic database that described the equilibrium situation in their alloy system, and coupled the thermodynamic description with diffusion simulations, and could reproduce the experimental information of gradient formation with simulations. Several other authors have later performed similar calculations for different compositions and conditions. The results depend critically on the models describing the phase equilibria (thermodynamics) and the diffusion (mobilities).

Reliable descriptions of the thermodynamics are available but for the mobilities more information would be useful. Since it is very valuable to be able to accurately simulate for example the gradient formation or other phase transformations during sintering, it is of interest to obtain better values for the mobilities. In a pre-study project "Kinetic Simulations in Hardmetals – Evaluation of Mobilities by Coupling Experiments and Simulations", a combined experimental and theoretical approach was applied to learn more about how to determine the mobilities for the selected application to surface gradients, and the feasibility of this concept was tested.

1. P. Gustafson and Å. Östlund, Binder-phase enrichment by dissolution of cubic carbides. Int J Refract Met Hard Mater 1994;12(3):129–36
2. M. Ekroth, R. Frykholm, M. Lindholm, H.-O. Andrén, J. Ågren. Gradient zones in WC–Ti(C, N)–Co-based cemented carbides: experimental study and computer simulations. Acta Mater 2000;48:2177.

2. Summary of results from the pre-study

In the pre-study a literature survey was performed to find reports where gradients in fcc phase had been studied by experiments and/or by computational techniques. New experimental determinations of gradients for samples with Co, Ni or Fe binders were also performed. The commercially available software DICTRA was used to simulate the gradient zone formation in different hardmetals. DICTRA is specifically designed to handle diffusion-controlled transformations in multicomponent and multiphase materials by solving the one-dimensional diffusion equation numerically.

The pre-study showed that the concept was feasible. However, the simulations were only tested on one alloy system, and it is thus of interest to continue the simulation work with more alloy systems and to validate the results with experiments. A question that was identified in the pre-study, but not addressed, is the influence of the microstructure on the diffusion in the liquid binder phase, both the grain size and the amount of binder can affect the diffusion.

3. Proposal for Stage 2

The mobilities of atoms in the liquid metal binders will be studied by experiments and modeling with DICTRA. The work will focus on the effect of chemical composition and the effect of microstructure on the gradient formation.

The effect of composition will be investigated by studying selected hardmetals with different compositions (WP1). The effect of microstructure on the mobility will be studied by investigations of alloys with different grain sizes and binder contents (WP2).

A combined experimental and modeling approach will be used, as applied in the pre-study.

PROPOSED WORK PLAN:

- WP 1 Influence of Chemical Composition
- WP 2 Influence of Microstructure
- WP3 Reporting and Meetings

DESCRIPTION OF WORK PACKAGES:

<u>WP 1 Influence of Chemical Composition</u>

MATERIAL PREPARATION

ALLOY SYSTEMS

To study the influence of composition on the formation of gradients, alloy systems of interest have been selected and are listed below. The four first will be prepared as hardmetals, sintered in nitrogen free atmospheres, and the gradient will be evaluated. In addition, two types of model alloy diffusion couples will be prepared, where a pure metal is joined with a WC-Co hardmetal. The diffusion couples will be heat treated different times, and will be used to evaluate the in-diffusion of Fe and Ni into the liquid binder.

- W-C-Ti-N-Co
- W-C-Ti-N-Ni
- W-C-Ti-N-Co/Ni (50/50 by atom)
- W-C-Ti-N-Fe
- Model alloy diffusion couple: Fe/WC-Co and Ni/WC-Co

COMPOSITIONS

The compositions of the samples are defined by:

- Added Metallic Binder (Fe/Co/Ni): 7.5 wt%
- Ti content : 2% wt
- (Ti,W)(C,N)
- low-high C and N contents

SINTERING

The sintering time and temperatures will be fixed in the start meeting.

ANALYSIS

The bulk composition of all samples will be analyzed after sintering. The samples will be prepared for microstructural analysis, and the phase fractions in a section across the gradient zone will be analyzed in Scanning Electron Microscopy (SEM) by image analysis. The compositions across the gradient zone will be analyzed by GDOES.

SIMULATIONS

DICTRA simulations will be performed using the most recent commercially available thermodynamic database. Gradient thicknesses will be simulated, using the experimentally determined compositions, and the selected sintering conditions, using the same constant mobility in liquid Co for all the elements. The results will be analyzed comparing with the experimental results.

When all experimental and simulation data is available an analysis of the agreement/deviations between experiments and simulations will be performed. An optimization of the mobilities will thereafter be made to obtain the best agreement to the experiments. The values for the mobilities should be kept within reasonable limits considering what is known from theoretical simulations.

The final optimization will be performed after the work package 2 has been finalized.

WP 2 Influence of Microstructure

The influence of microstructure on the formation of gradients will be studied in this work package. Only one system will be investigated. The same sintering conditions as used in WP1 will be used. The objective is to investigate experimentally if/how the amount of binder and the grain size of the carbide affects the gradient. The simulations can take the microstructure into account through the labyrinth factor, and this parameter will be assessed using the results from the experiments.

MATERIAL PREPARATION

ALLOY SYSTEM

- W-C-Ti-N-Co

COMPOSITIONS

- Added Metallic Binder Co: 6 and 15%.
- Ti : 2% wt;
- (Ti,W)(C,N);
- C, N selected from WP1
- WC: extremely coarse and fine

SINTERING

The sintering time and temperatures will be fixed in the start meeting. The same choice as for WP1 will be made.

ANALYSIS

The bulk composition of all samples will be analyzed after sintering. The samples will be prepared for microstructural analysis, and the phase fractions in a section across the gradient zone will be analysed in Scanning Electron Microscopy (SEM) by image analysis. The compositions across the gradient zone will be analysed by GDOES.

SIMULATIONS

DICTRA simulations will be performed using the most recent commercially available thermodynamic database. Gradient thicknesses will be simulated, using the experimentally determined compositions, and the selected sintering conditions, using the same constant mobility in liquid Co for all the elements. The results will be analyzed comparing with the experimental results with respect to the labyrinth factor. An assessment of the labyrinth factor will be made based on the experimental results.

WP3 Reporting, Training and Meetings

Reporting of the results will be made at each project meeting through presentations, and the material from the presentations will be distributed together with the minutes.

In connection to the final meeting there will be a half-day training session for the project partners on the computational tools that are used in the project. The applications that are addressed in the project will be demonstrated.

A final report will be written, describing the background, the methods and all experimental and simulation results.

SUGGESTED TIME PLAN (to be fixed in start meeting)

Activity	Year 1				Year 2			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
WP1								
Material Preparation	x	x						
Analysis		x	x	x				
Simulations				x	x	x		
WP2								
Material Preparation		x	x					
Analysis			x					
Simulations				x	x	x		
WP3								
Meetings	x			x				x
Report				x			x	

Schedule :

Total project duration: ca. 24 Months

Budget for project:

KTH: 22,500 EUR

Innomat AB: 22,500 EUR

EPMA: 5,500 EUR

Total: 50,500 EUR