



EMMC case study:

Grain boundary engineering on the atomic scale

Interview of Dr Lorenz Romaner, Materials Center Leoben Forschung GmbH (MCL)

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About the Company

MCL is an applied research institute offering competence in materials, process, and product engineering. MCL's key advantages lie in the combination of advanced experimental analysis with high level materials modelling and it comprises state-of-the-art technical facilities and wide-ranging specialist knowledge of materials. MCL combines this interdisciplinary expertise in its IC-MPPE (Integrated Computational Materials, Process and Product Engineering) approach to drive material based innovations. It performs long time cooperative projects together with universities where research topics are developed. Building on this expertise, the center offers targeted support in practical material, process and product development questions with a variety of industrial partners. 80% of the centre's R&D effort is related to developing, processing and applying advanced materials.

170 employees work at the centre and about 55 of them in simulation department which was initiated about 12 years ago. MCL's materials modellers can be found on all level of education, ranging from bachelor master and PhD students to post-doctoral and highly experience staff researchers. The educational background of the employees ranges from materials science, mechanical engineering, physics, mathematics and computer science. The majority of professional staff development happens internally, but training is out-sourced to 3rd parties if a member of staff requires it. In specific cases MCL actively hires staff for their modelling skill set to widen their expertise when needed. Young people are very attracted to MCL's activities and they are actively engaged with students.

About modelling – the nuts and bolts

MCL is familiar with electronic, atomistic, mesoscale, continuum and data driven modelling which are often integrated into multiscale approaches for deriving microstructure evolution and structure-property relationships. For example, as elaborated in more detail below, electronic models are linked with continuum thermo-kinetics models to estimate solute diffusion, the enrichment of solutes on grain boundaries and the associated ductilisation or embrittlement phenomena. Another example is the calculation of the coefficient of thermal expansion and elastic constants on the atomic scale which are coupled to finite element simulations to describe residual stresses as a function of heat treatments. To perform the calculations the centre uses commercial, in-house software and freeware on a daily basis. In addition, MCL also actively develops software for targeted purposes. See <https://www.mcl.at/software/>. In addition to physical-based modelling, more and more data-driven materials modelling approaches are being pursued. For this purpose, also databases of materials properties are hosted and developed at the center.

The computational expertise is applied to a variety of different applications or problems. As a first step, MCL's experts investigate an industrial problem and develop clear expectations and give a sensible time line and financial estimate to a client. They do not shy away from complex questioning

and will also start long-term projects involving one or more PhD students if required. MCL often embarks on collaborative programmes where partners bring in new knowledge or academics take over supervision of students. Materials modelling is often carried out with distinguished specialists in academia and in combination with advanced experimental analysis techniques.

About the Case Study

The case study is based on projects where MCL provided the modelling expertise and two Austrian companies, Plansee and Voestalpine AG, were involved as industrial partners. Plansee has expertise in refractory alloys and composite materials and Voestalpine AG is a steel-based technology and capital goods provider.

Metallic alloys can possess complex internal structures when zooming into the micrometer dimension. Typically, the materials are built up by many small grains that are connected by grain boundaries. These grain boundaries affect and often even determine numerous materials properties even on the macroscopic scale. MCL is using and developing simulation methods to learn which elements enrich at the grain boundary, how this enrichment can change the composition, and finally how a changed composition can affect the cohesion between the individual grains. Unsuitable compositions can lead to cohesion decrease which can make materials prone to grain boundary fracture which is undesirable. Examples include oxygen enrichment at grain boundaries in molybdenum or hydrogen enrichment in steels or nickel-based alloys which both represent major technological problems. Thus, it is pertinent to understand how diffusion of solutes and segregation to grain boundaries occurs to be able to counter-act this problem.

For this particular case, which were your objectives as an industrial provider of modelling?

We wanted to understand what type of chemical composition is beneficial for the cohesion at the grain boundary, as we aim to reduce the propensity of materials for intergranular failure and brittleness. For example, W and Mo are very weak at their grain boundary, so we were studying how alloying elements can help to reduce the weakness and work like glue to stick grain boundaries tighter together. For such calculations, we employ density functional theory which provides detailed insights into the atomistic processes in the grain boundary.

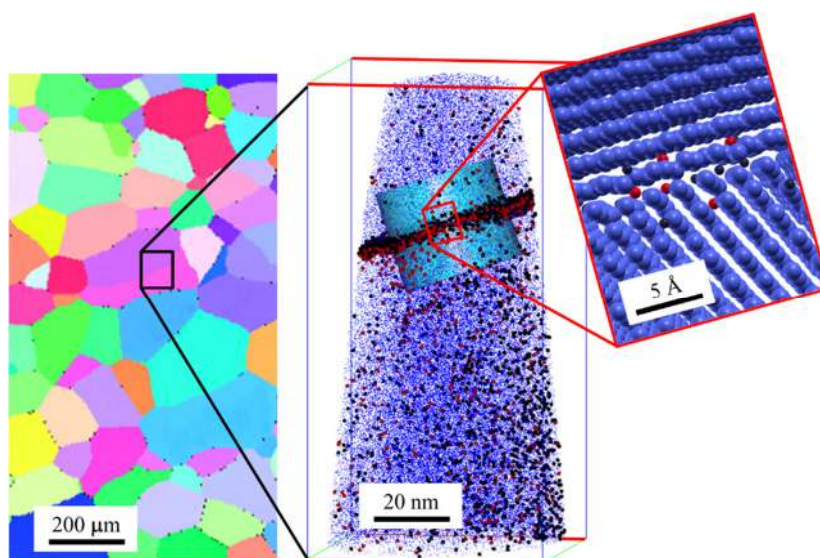


Figure 1: Segregation at grain boundary illustrated by atom probe tomography (center) and atomistic simulation (right). Different grain orientations as found in Mo are revealed by electron backscatter diffraction (left). For details see Ref. [3]



For Mo we scanned the periodic table and established that alloying with elements highlighted in green strengthen the grain boundary, while elements highlighted in orange decrease the cohesion. Elements highlighted in yellow only show negligible effects on the grain boundary.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

Figure 2: Periodic table where cohesion enhancing elements are shown in green while cohesion weakening elements are shown in red.

Similar investigations were carried out to learn how we can avoid hydrogen embrittlement in steels. For example, the automotive industry would be very keen to work with high and ultra-high strength steel grades which enable considerable weight reduction of vehicles. However, over a certain strength limit these steel grades are particularly prone for hydrogen embrittlement where hydrogen is introduced during processing or corrosion. It is of great importance to understand how the microstructure of such advanced steels grades can be changed to make them insensitive against embrittlement.

How did materials modelling play a key role in problem solving?

The analysis and characterisation of grain boundaries is experimentally demanding. There are methods such as Auger spectroscopy, transmission electron microscopy (TEM), or atom probe tomography which can provide such insights. However, these methods require highly specialized staff and a prohibitive amount of time and resources for many research projects. These methods are not routinely accessible and a decent characterisation could still be the topic of a thesis. In certain situations, it can be also practically impossible to perform an experiment, as for example, hydrogen would out-diffuse too quickly to be measured. Thus, modelling is often the only way to get an insight into what happens at grain boundaries.

What tools and methodologies have been applied?

We used electronic DFT models implemented in the VASP code to calculate the segregation and cohesion energies. We created models for grain boundaries, by creating vacuum slabs comprised of two surfaces mimicking the grain boundaries. We worked with periodic boundary conditions and cells comprised up to 500 atoms. By calculating the segregation energies, we could estimate at the electronic level what happens when an atom enters the grain boundary. We are now confident with the way we build grain boundaries using electronic models and can apply it to any element of the periodic table. The obtained segregation energies are fed into a database and thermokinetic models (developed in-house) so we can estimate how much segregation of a particular element can happen at the grain boundary. Finally, we can provide quantitative information on the concentration of



alloys at the grain boundary as function of time. This serves to estimate the enrichment of solute elements at the grain boundary at the end of a heating or cooling process.

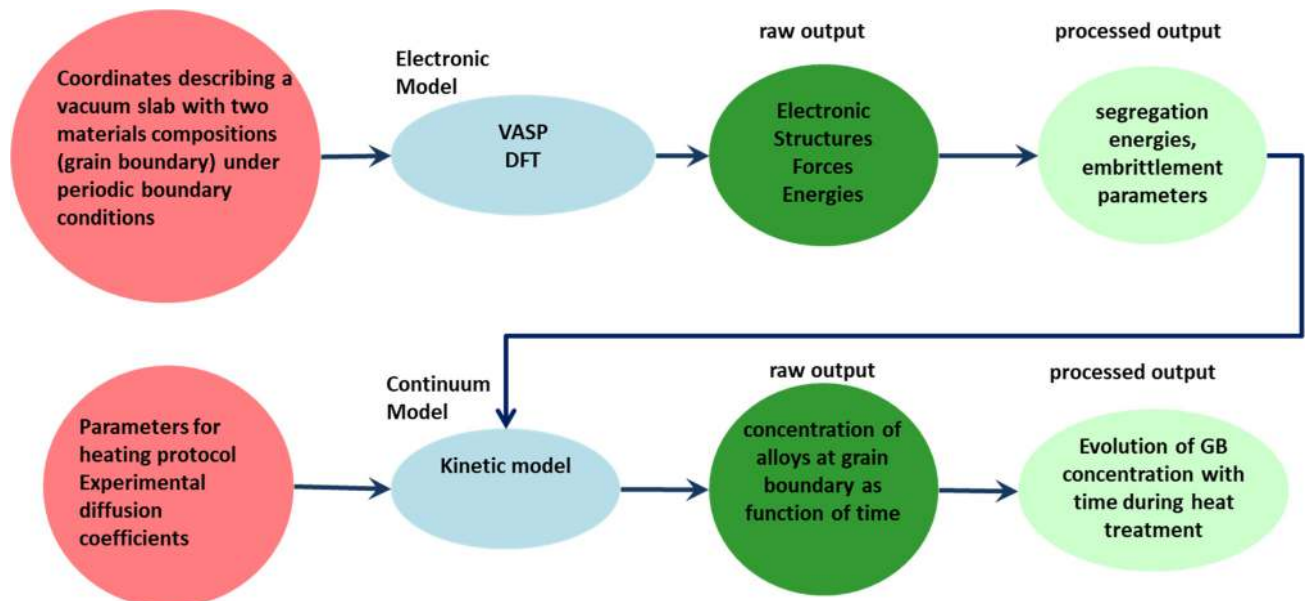


Figure 3: MODA diagram of the simulation approach

More details can be found here:

[1] D. Scheiber, R. Pippan, P. Puschnig, L. Romaner, Ab initio calculations of grain boundaries in bcc metals, *Model. Simul. Mater. Sci. Eng.* 24 (2016) 035013. doi:10.1088/0965-0393/24/3/035013.

[2] D. Scheiber, R. Pippan, P. Puschnig, A. Ruban, L. Romaner, Ab-initio search for cohesion-enhancing solute elements at grain boundaries in molybdenum and tungsten, *Int. J. Refract. Met. Hard Mater.* 60 (2016) 75–81. doi:10.1016/j.ijrmhm.2016.07.003.

[3] K Leitner, D. Scheiber, S. Jakob, S. Primig, H. Clemens, E Povoden-Karadeniz, How grain boundary chemistry controls the fracture mode of molybdenum L. Romaner *Materials & Design* 142 (2018) 36-43. <https://doi.org/10.1016/j.matdes.2018.01.012>

[4] S. He, W. Ecker, R. Pippan, Vi. Razumovskiy, Hydrogen-enhanced decohesion mechanism of the special $\Sigma 5(0\ 1\ 2)[1\ 0\ 0]$ grain boundary in Ni with Mo and C solutes, *Comp. Mater. Sci.* 167 (2019) 100-110. <https://doi.org/10.1016/j.commatsci.2019.05.029>

What were the expected improvements of the material behaviour simulation?

The simulations indicate how to produce materials with reduced or absent cracking along grain boundaries under different, for the specific material critical, loading conditions. They also improve our understanding about fracture behaviour of metallic alloys and assess which elements should be added to a material. In this way we expect to improve toughness in-service of the materials, to render alloys less susceptible against intergranular embrittlement caused e.g. by hydrogen. Our results also provide hints how to steer processing of materials to avoid damage already during production.



For this particular case, did modelling affect your value chain?

By using modelling, we were able to screen through a selection of elements and investigate their influence on the grain boundary, which is a great starting point for the manufacturers. This information can then be put into a greater context to take into account that some solutes may be beneficial for the grain boundary, but have other undesirable effects on other material properties. The in-house kinetic model does allow to look into the forming of a grain boundary and can inspire experimental workflows needed to form these in real life.

For this particular case, what was the quantitative value of materials modelling?

Materials modelling was a great enabler for the manufacturers to get an idea on which alloying elements they should look into first. They had to rely on modelling as screening experiments are either not possible or time consuming. Thus, the material development process happened much faster and unusual solutions could be found.

What investments were made during the project?

We had to undergo a learning process as we had to develop the workflows. A common effort is typically 1 PhD student per material class together with the computational resources which are around 1 Million core hours per year.

For this particular case, how did you measure the impact of Materials Modelling as a tool to assist in problem solving, process optimisation, product development?

We do have well defined KPIs to report to our managements. One KPI, for example, is the number of projects that can be generated from an activity. Our gained knowledge can be offered to other clients, ideally in short term projects. We are also encouraged to publish our results, so we report the number of publications. The manufactures we work with are encouraged to give us feedback and their satisfaction level is a KPI for our centre. For the material producer the number of new and improved materials grades and the reduction of scatter in the properties are relevant measures. The generated insights are used by company partners to improve processing steps and materials concepts.

What technical and technological benefits resulted from the project?

We developed workflows on how to simulate grain boundaries and have now expertise to do it accurately. The benefits for our industrial partner was that with our help they could harness materials modelling to progress to knowledge-based materials design. With the knowledge of materials modelling the material producers are able to link a part of scatter in material properties to physical based reasons and, hence, they were able to reduce these variations.

What were the economic benefits/impacts when you did use modelling?

The economic benefit for us is that we have now sophisticated workflows to embark on follow-up service projects, and we can serve a wider range of clients who need similar answers but have no budget for a full workflow development. The economic benefit for our clients is that by sharing our joint competences and providing our knowledge in form of software tools they are able to stand out from the international landscape of materials producers by offering a knowledge-based material to the market.



What was the business impact versus previous approach?

Involving modelling delivered ideas for a more structured and streamlined materials design which led to producing better and novel alloys, which can create new IP. With addition knowledge about underlying physical mechanisms the quality of materials could be improved and the scatter in quality could be reduced. At MCL the activities were the core for building a group on Computational Materials Design with currently 20 researchers and numerous research projects and direct assignments from industry.

Did modelling improve your competitiveness/innovation power?

Due to papers and success stories we got more visibility which will distinguish ourselves as the go-to partner for similar projects. By taking on these industrial challenges we are pushing ourselves to be innovative. The activities initiated four follow-up PhD project and the software package SEGROcalc <https://www.mcl.at/en/software/segrocalc/> was developed.

What sort of obstacles or barriers did you have to overcome to use modelling?

The barrier in our case is to find opportunities and the right timing to offer modelling to our clients. It is pertinent to look at contemporary problems and offer suitable modelling solutions. Even though our clients and partners are realising more and more that simulations are important, we still need to show what a calculation means to a particular manufacturing process. Thus, translation is very important – if we manage to understand the concepts of our experimental clients, we can translate modelling to a language they are familiar with and work together on new materials challenges.