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Report on the Doctoral Thesis entitled
Thermal stability of tungsten alloy

written by
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submitted to
Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering

Topic and relevance

The topic of the thesis submitted by Mr. Veverka is the manufacturing and thermal stability of tungsten alloys prepared by sintering, aiming on oxidation resistant composites. The development of oxidation resistant tungsten alloys in the case of a severe accident including vacuum breakage and cooling failure is of high relevance. First he introduces the necessity of other energy sources due to the increasing demand together with the need of reducing CO2 emissions. After that the concept of nuclear fusion, the tokamak structure and key parts of the inner wall (divertor and First wall) are presented. Then the aspects necessary for a safe operation including long lifetime of the plasma facing components are discussed with focus of a loss of coolant accident. Such an event combined with a vacuum leakage could indeed cause the escape of radioactive particles and molecules contaminating the surrounding area. A self-passivating alloy which forms a solid oxide layer and protects the rest of the wall for further oxidation and would reduce this contamination. The author focusses on W-Cr alloys as Cr forms a very stable oxide and is the most promising candidate in this field. He then discusses the advantages and shortcomings of pure tungsten as plasma facing material and some of the approaches, which are under investigation to improve on them, e.g. oxidation resistance. After that one of the major aspects of this thesis is discussed, the phase stability of W-Cr alloys including the kinetics and temperatures of forming precipitations. Field assisted sintering FAST was chosen as manufacturing exactly in order to prevent the decomposing by allowing high cooling rates. Then he discusses very shortly the basic principles of the powder metallurgic methods applied, i.e. mechanical alloying and subsequently consolidation by FAST. After describing the aims of the thesis, at a quite unconventional position, the main part of the thesis, chapter 8, follows with the four compiling papers. All of them are introduced with a short summary and motivation, embedding the paper in the broader scope of the thesis. It ends with a conclusion giving some practical lessons learnt to manufacture high quality composites with low amount of impurities. It also summarizes the results concerning the stability, i.e. long-term stability at 700°C; the finding of an additional stabilization element, i.e. tantalum, via the newly developed simulation model; and the indeed improved decomposition rate, i.e. factor of four. An outlook suggesting the possible steps for further improvement of the material or the next necessary steps for the development is unfortunately missing.

General remarks

The nine chapters of the thesis submitted by Mr. Veverka followed by references and three short appendices span over 72 pages and is based on four peer-reviewed papers, three of which he is first author. For twelve others he is co-author and which are not directly linked to this thesis, but it demonstrates that he has high interest in different topics and was intimately involved in the whole research area and the work of the group. Seven pages or roughly 10% of the main writing are devoted to the issue of climate change, CO2 concentration and the necessity of other energy sources, which is a bit long in my view, considering the quite narrow research topic and content of the thesis. However, the introduction of fusion, the structure of a future reactor and the materials in question afterwards (chapter 2 till 5) is nicely written and a good overview on the relevant aspects. It gives interesting details showing a deep understanding of the field, despite the fact that only now in 5.2. the material class and aim of this thesis is covered. It's a bit of a short coming that the complete part of oxidation of W and development of oxidation resistant alloys is discussed within only three pages. Here, more details about the oxidation process, properties of the oxides, the measurement techniques in question etc. and in particular, the context of the author's research approach compared to other e.g. W-Cr alloys would have been advantageous. Only eight references in total about oxidation and self-passivating W-alloys is a bit sparse and they are barely discussed.

Methods

Mechanical alloying by using rotating cylinders containing the powder mixture and balls was employed to form solid solution and reduce particle size. This is a very well established technique and suitable for the purpose. The same is true for the consolidation technique chosen, namely FAST. In his first article, consolidation behavior of pure W was investigated but not looking on the already thoroughly tackled parameters, pressure and temperature, but on other important aspects, namely sintering time, used atmosphere and the employed foil. Using a very efficient experimental plan, he was able to deliver important first insights on their effect on resulting microstructure, impurity concentration and temperature dependent tensile properties with only six samples. Microstructure was characterized using optical microscope and SEM including image analysis and dog-bone shaped samples for tensile testing. With XRF the elemental composition and impurity concentration was determined and XRD for analyzing the occurring phases and their aging.

In the chapter 6 only a short general description of mechanical alloying and FAST has been given but no details of the process and parameters used in the cause of this work. Naturally, they are mentioned within the publications, which follow later on, however, specifics about the processes and things to keep in mind could have been discussed here even more thoroughly than it is typically done in an article and would have been valuable for any reader wanting to adapt and continuing the process.

Goal achievement

First mandatory milestone was the achieving of the desired phase composition in the starting powder and to preserve a solid solution during the FAST process, as the thermal stability of these alloys should be investigated afterwards with long term annealing experiments. The very time-consuming preparation and long-term stability tests reduced the possible number of compositional variations for investigation. With the help of chemical simulations done by partners, the efficiency of the experiments could be increased, by down selecting the number of possible auxiliary elements for reducing the decomposition rate, to one - tantalum. The validity of the developed model and the increased solid solution lifetime of W-Cr by adding Ta should then be experimentally verified.

The main objectives have been achieved.

Scientific value and overall evaluation

This thesis and the embedded papers make significant contribution to the area of manufacturing self-passivating W-Cr alloys with minimum amount of impurities, determination of their thermal stability against decomposition and its increase by minor alloying with Ta.

Mr Veverka has demonstrated the ability to perform high quality experimental research, analysis and publish the gathered scientific results. I, therefore, **recommend this Ph.D. thesis for defense** without any reservation with the aim of receiving the degree of Ph.D.

Detailed remarks / Questions for discussion

1) On page 32, the necessity of a low DBTT around 200°C due to the baking is stated. However, why focusing on the baking? The high DBTT of tungsten is anyhow the necessity of using a structural material or heat sink.
2) DBTT is indeed a complex topic with many different and contrary factors. However, few remarks are, as far as I know, not correct. Recrystallization causes grain growth and reduces hardness and yield strength as stated but increases the ductility for bulk W if grain boundaries don't get to much weakened. The reference cited in the first paper is in fact not investigating recrystallization W but sintered and rolled. Mechanical deformation is done to increase the hardness by introducing many dislocations and reduce/shape the grains but this reduces the ductility.
3) Why has the alloy to be stable against precipitation in case of a LOCA for months (p. 35)? The formation of an oxidation barrier happens in seconds or minutes after the LOCA, being the reason for the reduced oxidation rate right from the start, and after the layer is there, it is stable.
4) Would forming precipitations at this temperatures even be an issue? They are finely dispersed and could still form a barrier, after a very limited amount of W has been oxidized. Are there experiments/values how the oxidation rate changes when W-Cr has started to decompose?
5) As the first paper deals with sintering and resulting properties of pure W, what differences can be expected using W-Cr? Cr has completely other chemical, thermal and mechanical properties thus introducing high amounts of it seem to change quite a lot in terms of optimal sintering properties and impurity concentrations.
6) Fig 4 in the second paper shows clearly a lower amount of carbides despite the fact that in the first paper it was stated that the W-foil is not as efficient as the graphite foil to hinder carbide formation, any idea why this was the case?
7) The intensity of the XRD signals in Fig 3 in the second paper are very different from each other, most likely due to varying integration times. The reflexes under question are barely larger than the noise and seem to be at nearly the same positions thus, the stated differences in phase composition etc. seem not particularly reliable.
8) What purpose in the second paper or in general has the Hf, as it was not discussed in the paper and later on with the comparison of Ta it seems only a worsening effect, or? What about the comparison to the W-Cr-Y system, other people investigate?
9) "Ultrafine-grained W-Cr composite" is a bit misleading as it seems to me, that only the occurring precipitations are indeed small, but this is not what is meant by ultrafine-grain structure.
10) The assessment of the quality of the DFT prediction of the elastic modulus by stating it is within 10% range is not proper as the differences of all measurements and phases are in this regime. The model predicted higher differences and also sometimes in another direction than measured. So yes the model predicts values in this range for this material class but the gain of knowledge for the specific issue of the influence of precipitations is very limited and I wouldn't dare to state that this work proves that a disentanglement of the influences of the phases can be done by the model. So what have been the insights in the system you gain by the DFT model?

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