Experimental report

17/11/2015

Proposal: 5-25-228 **Council:** 4/2014

Title: Ultra-rapid microwave materials synthesis in-situ; an investigation of the mechanism of formation of ternary transition metal carbides

Research area: Chemistry

This proposal is a new proposal

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Samples: Nb(1-x)Mo(x)C, Ta(1-x)Mo(x)C, Mo(1-x)W(x)C

Instrument	Requested days	Allocated days	From	To
D20	3	3	08/12/2014	11/12/2014

Abstract:

This proposal concerns the in-situ investigation of the mechanism of formation of ternary transition metal carbides. This experiment uses the novel microwave reactor developed for D20 to follow microwave synthesis reactions in-situ. The applicants seek three days of beamtime to study the systems Nb(1-x)Mo(x)C, Ta(1-x)Mo(x)C and Mo(1-x)W(x)C.
The samples will be prepared in-situ using novel microwave techniques, which offer a time- and energy-efficient alternative to conventional solid state synthesis. In-situ PND will enable us to identify all of the intermediate phases which arise during synthesis, including any metastable phases that would not be observed in an ex-situ measurement, and quantitatively analyse the evolution of these phases as the reactions progress. In addition, PND of the ternary carbide products will allow us to correlate metal and carbon stoichiometry with properties of the TM carbides, including superconductivity and catalytic activity.

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Introduction

In order to reduce energy consumption in industrial processes there has been an increase in research into alternative synthesis and processing methods to improve the green credentials of materials manufacture. Our previous work has shown that synthesis and processing times of structural and functional ceramics can be cut by orders of magnitude by switching from conventional to microwave (MW) heating processes. Carbides are excellent targets for MW synthesis and processing with carbon acting as both a starting material and MW susceptor. Further, there is only a very limited knowledge of the mechanistic and kinetic aspects of MW reactions in the solid state.

Three days of beam time were allocated on D20 to study, *in situ*, the microwave synthesis of ternary transition metal nitrides. The experiment made use of the novel microwave reactor developed specifically for D20 to follow such reactions as a function of time. This experiment concerned the $Nb_{1-x}Mo_xC$, $Ta_{1-x}Mo_xC$ and $Mo_{1-x}W_xC$ systems and their preparation from the metal oxide starting materials + carbon. *In-situ* PND presents us with a method to enable us to identify the intermediate phases which arise during synthesis, including any metastable phases that would not be observed in an ex-situ measurement, and quantitatively analyse the evolution of these phases as the reactions progress. Furthermore, PND of the ternary carbide products would allow us to correlate metal and carbon stoichiometry with properties of the TM carbides, including superconductivity and catalytic activity.

Sample preparation

Multiple samples from each reaction system were prepared prior to the neutron experiment. In each case, stoichiometric amounts of the respective oxide and carbon reactants were weighed, mixed and ground together. In each case, the reaction would be performed *in situ* with these mixtures applying a range of microwave input powers and reaction times. Hence, 5 samples of each of the intended reaction compositions below were prepared prior to the experiment on D20:

Nb-Mo-C system

1. $0.4\ Nb_2O_5 + 0.2\ MoO_3 + 3.6\ C \rightarrow Nb_{0.8}Mo_{0.2}C + 2.6\ C$

2. $0.325\ Nb_2O_5 + 0.35\ MoO_3 + 3.675\ C \rightarrow Nb_{0.65}Mo_{0.35}C + 2.675\ CO$

3. $0.25\ Nb_2O_5 + 0.5\ MoO_3 + 3.75\ C \rightarrow Nb_{0.5}Mo_{0.5}C + 2.75\ CO$

Ta-Mo-C system

4. $0.4\ Ta_2O_5 + 0.2\ MoO_3 + 3.6\ C \rightarrow Ta_{0.8}Mo_{0.2}C + 2.6\ C$

5. $0.325\ Ta_2O_5 + 0.35\ MoO_3 + 3.675\ C \rightarrow Ta_{0.65}Mo_{0.35}C + 2.675\ CO$

6. $0.25\ Ta_2O_5 + 0.5\ MoO_3 + 3.75\ C \rightarrow Ta_{0.5}Mo_{0.5}C + 2.75\ C$

W-Mo-C system

7. $0.8\ WO_3 + 0.2\ MoO_3 + 4\ C \rightarrow W_{0.8}Mo_{0.2}C + 3\ CO$

8. $0.65\ WO_3 + 0.35\ MoO_3 + 4\ C \rightarrow W_{0.65}Mo_{0.35}C + 3\ CO$

9. $0.5\ WO_3 + 0.5\ MoO_3 + 4\ C \rightarrow W_{0.5}Mo_{0.5}C + 3\ CO$

10. $0.4\ WO_3 + 0.6\ MoO_3 + 4\ C \rightarrow W_{0.4}Mo_{0.6}C + 3\ CO$

Experimental set up

In situ measurements were to be conducted on the D20 beamline with the bespoke single mode microwave reactor and sample environment. (Essentially, the reactor consists of a generator, tuner, quartz window, waveguide and an actuator for sample orientation). Our experimental plan allowed for reaction times of up to 1 h plus time for cooling and sample changes (~ 30- 40 min per sample). At the conclusion of the *in situ* measurements it was proposed to collect ambient temperature *ex-situ* data on the MW-synthesised samples (1 for each of the 10 compositions) to allow more detailed structural characterisation of the ternary carbide products.

Results

Unfortunately, it was not possible for us to investigate the above-mentioned MW syntheses and perform the experiment as we had planned. Serious problems with the microwave reactor were encountered, probably involving both the generator and the 3-stub tuner. As a result, the power transferred to the samples was not enough to see any visible change in the diffraction patterns of the precursors (**1**-**10**).

Several attempts were made to try and repair the single mode reactor with no success. These attempts also involved dismantling the reactor itself and also the 3-stub tuner. We discovered that the stubs in the latter were jammed in a fixed position which made it impossible to tune the field within the applicator. Therefore, as the impedance of the MW field could not be matched, we were not able to minimize the reflected MW power and, hence, maximize the forward power absorbed by the samples. Regrettably, therefore, the experiment was aborted with only diffraction patterns for the precursor mixtures (i.e. at time, t=0) collected.