Experimental report

05/05/2022

Proposal: 5-21-1151 **Council:** 4/2020

Title: In-situ neutron powder diffractionstudies of phase decomposition in novel mixed carbide systems

Research area: Engineering

This proposal is a new proposal

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Samples: (Ti,Zr,W)C
(Ti,Zr,Nb)C

Instrument	Requested days	Allocated days	From	To
D20	4	4	11/06/2021	15/06/2021

Abstract:

Cemented carbides are composite materials manufactured via powder metallurgy. The excellent wear resistance, high hardness, and high toughness make them widely used materials in cutting and drilling tools. In order to develop cemented carbides with enhanced mechanical properties and reduced cost, our current research interests are oriented on the novel carbide mixtures for the replacement of WC. We have previously shown that the mixed transition-metal carbide phases, e.g. (Ti,Zr)C, with a miscibility gap decompose during the sintering. The formed lamellar structure enhances the hardness of the final product. Our ex-situ XRD results show that the addition of NbC affects the decomposition kinetics, allowing the control of microstructure evolution at sintering temperatures. In order for us and our industrial collaborators to gain a better understanding of the diffusion-driven microstructural evolution of NbC and WC doped novel (Ti,Zr)C mixtures, we propose the first in-situ neutron powder diffraction experiments of (Ti,Zr)C based carbide mixtures during the thermal treatments at 1600 °C.

Experimental report for:

In-situ neutron powder diffraction studies of phase decomposition in novel mixed carbide systems

(Proposal number: 5-21-1151)

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Experimental details and preparations prior to the beamtime:

The purpose of the proposed in-situ neutron diffraction experiments was to study the decomposition kinetics in (Ti,Zr)C-based novel carbide systems. Owing to the solid solution hardening effect, the binary (Ti,Zr)C system offers significantly higher hardness than tungsten carbide (WC), which is the primer choice of hard phase in cemented carbides, also known as hard metals. However, (Ti,Zr)C system also has a miscibility gap: it decomposes into TiC- and ZrC-rich phases at sintering temperatures of cemented carbides. Such phase separation proceeds through the formation of a lamellar structure. This on one hand can mean that possible increase in strength through boundary hardening, on the other hand, can cause a loss of solid solution hardening effect. The understanding and control of phase separation in (Ti,Zr)C system are thus critical for industrial utilization of this promising carbide phase.

For our in-situ experiments, we have designed transition metal carbide doped (Ti,Zr)C-based solid solutions using equilibrium thermodynamics calculations. The single-phase (Ti,Zr)C-based solid solutions were synthesized by spark plasma sintering. For our demanding in-situ experiments at 1600 °C, we have designed an alumina (99.9% Al2O3) sample holder. The sample performed well during the experiments and allowed the measurements of 7 different carbide samples during aging within the miscibility gap at 1600 °C for 10 h. Diffraction patterns were acquired in 5 min intervals. To determine phase fractions and crystal structure parameters, the Rietveld analysis of the ND patterns was performed in FullProf [1] software.

The experiments have already been used in: (i) PhD thesis [2], (ii) published article [3], and (iii) preprint in the submission process [4]. We foresee that performed experiments will bring further scientific contributions in terms of publications and conference presentations.

Results:

As an example, Fig. 1.a shows the diffraction patterns of binary (reference sample) (Ti,Zr)C and 1 mol% NbC-doped (Ti,Zr)C systems. Analysis of diffraction patterns, in Fig. 1.b, shows the amount of decomposed single-phase carbide solid solutions as a function of aging duration. Whilst the decomposition in reference (Ti,Zr)C initiates upon reaching the aging temperature. the addition of 1 mol% NbC strongly hinders the decomposition of (Ti,Zr)C. The system needs more than 3 h incubation period to initiate the decomposition. Besides the incubation period, scanning electron microscope (SEM) micrographs reveal that HfC- and NbC-doped systems have significantly lower number of decomposition sites, which accordingly results in sluggish decomposition kinetics. Only 11.1 wt% of the single-phase carbide solid solution is decomposed after 10 h aging. In Ref. [4], such strongly hindered decomposition kinetics by minor NbC-doping is attributed to the narrower miscibility gap and chemistry of moving interfaces and grain boundaries.

We would like to thank our local contact Dr. Thomas Hansen and sample environment responsible Frédéric Marchal and Sébastien Turc for their support before and during the beamtime.

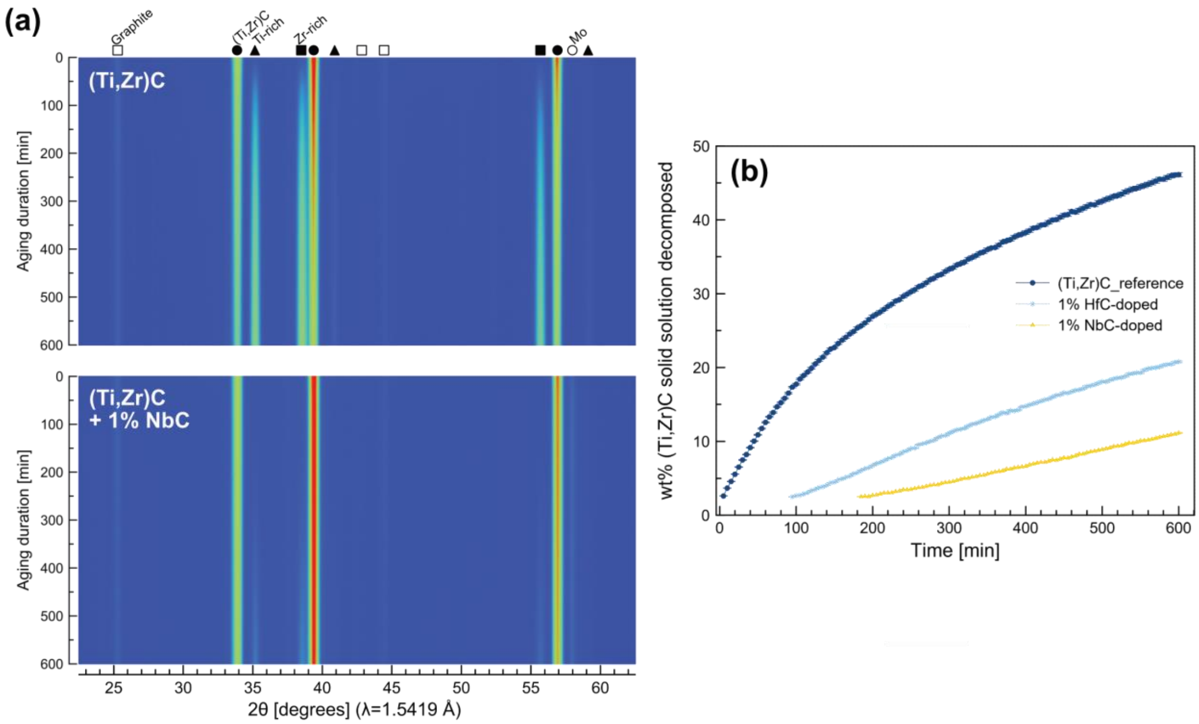

Fig 1 *Investigations of reference (Ti,Zr)C and 1 mol% HfC- or NbC- doped systems. (a) In-situ neutron diffraction patterns. (b) Amount of decomposed solid solution during 10 h aging at 1600 °C. Results are from Refs. [2, 4].*

References:

[1] J. Rodríguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, Physica B: Condensed Matter. 192 (1993) 55–69.

[2] A.B. Yildiz, Neutron scattering studies of hard metals, KTH Royal Institute of Technology, 2021.

[3] A.B. Yildiz, H. Yixuan, R.P. Babu, T.C. Hansen, M. Eriksson, K.M. Reddy, P. Hedström, Design, synthesis, structure, and stability of novel multi-principal element (Ti,Zr,Hf,W)C ceramic with a miscibility gap, J Eur Ceram Soc. (2022). https://doi.org/https://doi.org/10.1016/j.jeurceramsoc.2022.04.029.

[4] A.B. Yildiz, R.P. Babu, T. Hansen, P. Hedström, Manipulating the decomposition kinetics in a mixed carbide through small compositional adjustments, Preprint. (2021).