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High-energy synchrotron X-ray *in situ* observation of ternary eutectic growth in a directionally solidified Mo-Si-B alloy

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Introduction

Molybdenum-based alloys such as molybdenum silicides and Mo-Si-B alloys are seen as very promising candidates for the next generation turbine blade material beyond the capability of state-of-the-art Ni-based superalloys and are therefore studied extensively over the last two decades. Mo-Si-B alloys in particular, combine excellent creep properties and acceptable oxidation resistance at high and ultrahigh temperatures. However, the microstructure formation and the materials' properties strongly depend on the processing route of Mo-Si-B alloys. Thus, a holistic approach considering the alloy composition (affecting the phase distribution and volume fraction of phases) and the alloys microstructure has to be pursued to achieve the desired mechanical and oxidation properties to tailor alloys for specific applications.

Directional solidification (DS) offers the possibility to directly control the growth morphology of the microstructure basically by two parameters: the temperature gradient over the solidification front, G, and the growth rate, v. In general, G is determined by the DS system. It depends on technical parameters such as the design and cooling of sample chucks and/or thermal conductivity of the sample material and is therefore difficult to control actively. However, v can be easily manipulated and adjusted during the DS process.

The present study focuses exclusively on the ternary eutectic growth, microstructure and texture formation during directional solidification of the eutectic alloy Mo-17.5Si-8B. The unique "FlexiDS" sample environment [1] has been used to directly investigate crystal growth of a ternary eutectic Mo-17.5Si-8B alloy. During the *in situ* diffraction experiments at the German synchrotron source at DESY, Hamburg special interest was paid to the liquid-solid transformation and the eutectic decomposition of the liquid phase into the three (eutectic) phases Mo_{SS}, Mo_3Si and Mo_5SiB_2. The microstructure perpendicular and parallel to the solidification direction was analyzed and the DS textures obtained by *in situ* synchrotron high-energy X-ray diffraction (HEXRD) with a photon energy of 100 keV and SEM-EBSD analysis were compared. The results provide strong evidences for a coupled ternary eutectic growth of the phases Mo_{SS}, Mo_3Si and Mo_5SiB_2, which could be directly observed during *in situ* experiments for the first time.

Materials and Methods

Prior to directional solidification a master alloy of Mo-17.5Si-8B (at.%) was produced using arc-melting and a cold-crucible furnace. Directional solidification was performed using the FlexiDS zone melting device [1], a worldwide unique sample environment that was specially designed to be used for DS *in situ* experiments at the P07 High Energy Materials Science (HEMS) beamline operated by Helmholtz-Zentrum Geesthacht at PETRA III (Deutsches Elektronen-Synchrotron (DESY); Hamburg, Germany). A growth velocity of 60 mm/h and a synchronized rotation speed of 20 rpm for the feed and seed axis was used. For the *in situ* high-energy X-ray diffraction (HEXRD) experiments, a monochromatic beam with a photon energy of 100 keV ($\lambda = 0.124$ Å) and a narrow cross section of 1 x 0.5 mm² (width and height) was used in transmission mode. A Perkin Elmer XRD 1621 flat panel detector was used to record the Debye-Scherrer diffraction patterns. The software Fit2D was used for azimuthal integration of the recorded 2D-diffraction patterns. For the Rietveld refinement, the upper right quarter of the detector images was used. Thus, the diffraction patterns were integrated from 0° to 90°. Furthermore, the integrated data was normalized to the background intensity. The resulting data files were analyzed by Rietveld and an additional texture analysis refinement using the software MAUD. The DSed microstructures were investigated by SEM (BSE and EBSD) and TEM.

Results and Discussion

Fig. 1 shows the determined phase fractions of the melt and of the three eutectic phases during the following states: in the liquid state (red region), during directional solidification (yellow region) and after entire (directed) solidification (blue region). With respect to experimental scatter, the volume fractions of the ternary eutectic are consistent with previous literature findings [2,3]. During the liquid-solid transition via directional solidification, all three solid phases simultaneously form out of the liquid phase. The fraction of the liquid phase is decreasing afterwards. Independently

from the fraction of the liquid phase that is present in the actually observed sample volume, the Mo_{SS}, Mo_3Si and Mo_5SiB_2 phases grow with an almost constant ratio of their volume fractions relative to each other. This *in situ* observation is a strong experimental evidence for a coupled ternary eutectic growth in the Mo-rich Mo-Si-B system.

In addition, the pole figures calculated from the texture analysis of the HEXRD data are shown in Fig. 2. Here it must be noted that, in comparison with the usual methods used to determine texture by HEXRD, only a single image acquired during a 180° sample rotation was analyzed. In addition, only a 1 mm wide sample volume in the center of the rotating bar was analyzed, resulting in a much sharper preferred orientation compared to a "normal" texture measurement. The Mo_{SS} phase shows a weak <001> texture along the growth direction with low intensity. Whereas the texture intensities of Mo_3Si and Mo_5SiB_2 were relatively high. The pole figure of the Mo_3Si phase demonstrated a strong preferred orientation of the <001> direction along the growth direction. The Mo_5SiB_2 phase showed a strong texture formation and grew preferentially in the <100] direction with the {001} planes parallel to the growth direction, which is consistent with the microstructure reported by Uemura et al. [4,5]. The eutectic phases had the preferential growth of <001>Mo_{SS}//<001>Mo_3Si//<100]Mo_5SiB_2 along the temperature gradient and the result agrees with texture recently evaluated [6].
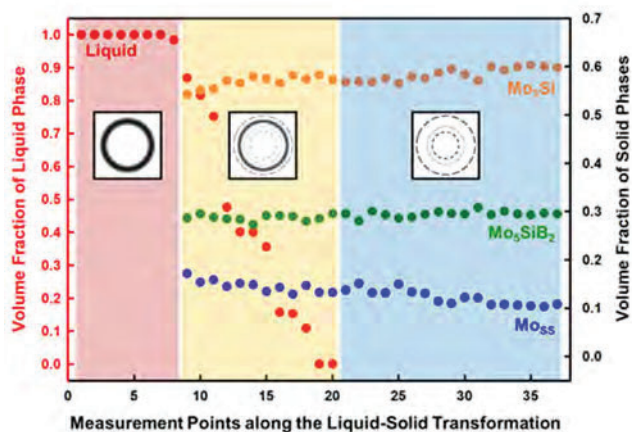

Fig. 1: Fraction of the liquid and solid phases measured along the phase transformation and the eutectic solidification front during DS. Schematic Debye-Scherrer rings as detected during the *in situ* DS measurements are additionally illustrated.
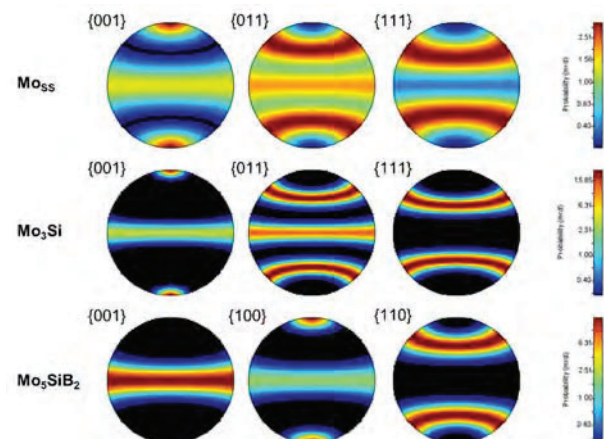
Fig. 2: Pole figures of Mo_{SS}, Mo_3Si, and Mo_5SiB_2 in a 1 mm sample volume obtained during the *in situ* HEXRD measurements of the directionally solidified alloy Mo-17.5Si-8B.

Conclusions

The results of the present study can be summarized as follows:

– During the liquid-solid transition, all three eutectic phases simultaneously form out of the solidifying liquid phase.
– Independently from the fraction of the liquid phase that is present in the actually observed sample volume, the Mo_{SS}, Mo_3Si and Mo_5SiB_2 phases grow with an almost constant ratio of their volume fractions relative to each other.
– The *in situ* observation during DS provides an experimental evidence for a coupled ternary Mo_{SS}-Mo_3Si-Mo_5SiB_2 eutectic growth in the Mo-Si-B system.
– Analyzing the DS texture formation by in situ HEXRD diffraction experiments could confirm EBSD texture analysis of the present experiments and recent work [6] showing preferential growth of the ternary eutectic of <001>Mo_{SS}//<001>Mo_3Si//<100]Mo_5SiB_2 along the solidification direction.

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