Microstructure and Properties of Near-eutectic Mo-Si-B Alloys for High Temperature Applications

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Abstract

During the last 30 - 40 years molybendium-based alloys and molybdenum silicides had gained scientific and commercial interest since they combine excellent creep behavior and acceptable oxidation resistance at ultrahigh temperatures - properties, which makes this class of refractory materials potential candidates for structural applications in aerospace engines and the power-generating industry.

The present Ph.D. thesis deals with the development of near-eutectic Mo-Si-B alloys which were processed by arc-melting and directional solidification. Depending on the processing route the microstructure, mechanical properties and oxidation behavior at high temperatures were investigated. The ternary alloy compositions investigated were taken from the Mo-rich part of the Mo-Si-B system and consist of the molybdenum solid solution phase (Mo_{SS}) and the two intermetallic phases Mo_3Si and Mo_5SiB_2. Literature data of the liquidus projection and the cooling behavior were analyzed using the ALKEMADE theorem and compared with thermodynamic calculations in order to determine the ternary eutectic composition experimentally. The ternary eutectic Mo_{SS}-Mo_5SiB_2-Mo_3Si composition was determined to contain 17.5 at.% silicon and 8 at.% - 10 at.% boron and was further processed via directional solidification using a crucible-free zone melting technique. Regarding the mechanical properties, special attention was paid to the creep resistance at high temperatures. Besides this property the hardness of the ternary eutectic as well as the oxidation behavior of the near-eutectic ternary alloys were investigated. As a results of the present work, the near-eutectic alloys show outstanding creep behavior at temperatures between 1100 °C and 1400 °C as well as good oxidation resistance at temperatures higher than 1000 °C.

Kurzfassung

In den vergangenen 30 - 40 Jahren haben Molybdän-Basislegierungen und Molybdänsilizide an wissenschaftlichem und wirtschaftlichem Interesse gewonnen, da sie hervorragende Kriecheigenschaften mit aktzeptablen Oxidationseigenschaften bis hin zu sehr hohen Temperaturen kombinieren. Diese Eigenschaften machen Molybdän-Basiswerkstoffe zu potentiellen Kandidaten für Konstruktionswerkstoffe im Flugzeugturbinenbau sowie für stationäre Gasturbinen in der Energieversorgungsbranche.

Die vorliegende Dissertation befasst sich mit der Herstellung von naheutektischen Mo-Si-B-Legierungen mittels des Lichtbogenschmelzens und der gerichteten Erstarrung, der Chrakterisierung der Mikrostruktur in Abhängigkeit des Herstellungsverfahrens, sowie der Bestimmung der mechanischen und oxidativen Eigenschaften bei hohen Temperaturen. Die hier untersuchten ternären Legierungszusammensetzungen sind dem Mo-reichen Bereich des Mo-Si-B Phasendiagrammes entnommen und bestehen aus dem Molybdänmischkristall (Mo_{SS}) und den beiden intermetallischen Phasen Mo_3Si und Mo_5SiB_2. Für die experimentelle Bestimmung des ternären Eutektikums wurden zunächst Literaturdaten zur Schmelzflächenprojektion und dem Abkühlverhalten mittels des ALKEMADE-Theorems analysiert und mit thermodynamischen Berechnungen verglichen. Im Anschluss daran erfolgte die Herstellung von Testlegierungen in einem Lichtbogenofen und eine Analyse der Mikrostrukturen und Phasenzusammensetzungen im Guss- und wärmebehandelten Zustand. Die Legierungszusammensetzung des ternären Mo_{SS}-Mo_5SiB_2-Mo_3Si-Eutektikums konnte dabei auf 17.5 at.% Silizium und 8 at.% - 10 at.% Bor eingegrenzt werden, welche im nächsten Schritt mittels der gerichteten Erstarrung weiter untersucht wurden. Bei der Untersuchung der mechanischen Eigenschaften bestand ein besonderes Augenmerk auf den Hochtemperaturkriecheigenschaften der naheutektischen Legierungen. Neben dieser, für Hochtemperaturwerkstoffe wichtigen mechanischen Eigenschaft, wurde die Härte des ternären Eutektikums sowie das Oxidationsverhalten der naheutektischen Legierungen untersucht. Die in dieser Arbeit vorgestellten naheutektischen Mo-Si-B-Legierungen zeichnen sich dabei durch hervorragende Kriecheigenschaften bei Temperaturen zwischen 1100 °C und 1400 °C sowie durch eine gute Oxidationsbeständigkeit bei Temperaturen oberhalb von 1000 °C aus.

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Declaration of honor

I hereby declare that I produced this thesis without prohibited external assistance and that none other than the listed references and tools have been used. I did not make use of any commercial consultant concerning graduation. A third party did not receive any nonmonetary perquisites neither directly nor indirectly for activities which are connected with the contents of the presented thesis. All sources of information are clearly marked, including my own publications.

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Magdeburg, January 5th, 2017

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Abbreviations

$\dot{\varepsilon}$	Strain rate
$\dot{\varepsilon}_{\mathrm{DC}}$	Dislocation creep rate
$\dot{\varepsilon}_{\mathrm{II}}$	Creep rate
η	Efficiency
λ	Wave length
σ	Stress
σ_0	Initiale stress
σ_{true}	True stress
θ	Diffraction angle
ε	Strain
ε_0	Time independent strain
$\varepsilon_{\mathrm{true}}$	True strain
A	Material's constant
A_{HV}	Projected indenter area
A_{i}	Instantaneous cross-section area
b	BURGERS vector
D	Diffusivity or diffusion coefficient
d_{hkl}	Interplanar spacing
d_{HV}	Pryramide diagonal
E	Energy
G	Temperature gradient or shear modulus
HV	VICKERS hardness
k	BOLTZMANN's constant

k_l	Linear oxidation rate constant
l	Lenght
l_0	Initial length
n	Stress (or creep) exponent
P	Load
Q	Activation energy
Q_{SD}	Activation energy for self-diffusion
R	Ideal gas constant
T_m	Melting temperature
t_R	Rupture time
v	Solidification velocity
V_f	Volume fraction
ΔS	Entropy of fusion
AC	Alternating current
AM	Arc-melting
bcc	body-centered cubic
BDTT	Brittle-to-ductile transition temperature
BSE	Backscattered electrons
CFP	Carbon fiber reinforced polymers
CIP	Cold-isostatical pressing
CMC	Ceramic-matrix composites
DFT	Density-functional theory
DS	Directional solidification
DTA	Differential thermal analysis
EDM	Electrical discharge machining
EDS	Energy-dispersive X-ray spectroscopy
EPMA	Electron probe micro-analysis
FAST	Field assisted sintering technology
FIB	Focused ion beam

GA	Gas atomization
HIP	Hot isostatical pressing
HPC	High-pressure compressor
HPT	High-pressure turbine
IATA	International Air Transport Association
ICP-OES	Inductively coupled plasma optical emission spectroscopy
LPC	Low-pressure compressor
LPT	Low-pressure turbine
MA	Mechanicall alloying
MMC	Metal-matrix composites
MPT-AES	Microwave plasma torch atomical emission spectroscopy
PDC	Polymer-derived ceramic
PM	Powder metallurgy
PMC	Polymer-matrix composites
RT	Room temperature
SE	Secondary electrons
SEM	Scanning electron microscopy
T	Temperature
TBC	Thermal barrier coating
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
V_a	Vacancies
WDS	Wave length-dispersive X-ray spectroscopy
XRD	X-ray diffraction