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# Effect of Ti content and nitrogen on the high-temperature oxidation behavior of $(Mo,Ti)_5Si_3$

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ABSTRACT

The binary intermetallic compounds $Mo_5Si_3$ (T1) and $Ti_5Si_3$ are prone to rapid oxidation below 1000 °C. Recent investigations on $(Mo,Ti)_5Si_3$, however, revealed that macro-alloying with 40 at.% Ti can result in a very good oxidation resistance in a wide temperature range (750–1300 °C) due to the formation of a duplex layer composed of a silica matrix with dispersed titania. Additionally, Ti decreases density making $(Mo,Ti)_5Si_3$ a promising key constituent of quaternary Mo-Si-B-Ti alloys considered for ultrahigh temperature structural applications. The aim of this study is to obtain an in-depth understanding of the influence of different Ti concentrations as well as of nitrogen on the oxidation behavior of $(Mo,Ti)_5Si_3$ at intermediate and elevated temperatures. The microstructure and oxidation mechanisms were analyzed using various experimental techniques. The experimental results were supported by ab initio and thermodynamic calculations.

## 1. Introduction

New materials which replace Ni-based superalloys are needed that fulfill different criteria: high melting point, adequate creep resistance and high temperature strength, sufficient oxidation resistance, acceptably (low) density as well as economic feasibility. Since this set of requirements is unlikely to be fulfilled by a single (phase) material, the development of composite materials is necessary [1,2]. Mo-rich Mo-Si-B alloys consist of a ductile $Mo_{ss}$ matrix with the embedded intermetallic phases $Mo_3Si$ and $Mo_5SiB_2$ (T2) [3–5]. However, those alloys suffer from catastrophic oxidation at temperatures below 1000 °C, because the phases $Mo_{ss}$ and $Mo_3Si$ do not possess passivation capabilities at any temperature.

Recently, Yang et al. showed that macro-alloying with (the light weight element) Ti can reduce density and stabilize a new ternary phase field including the Si-rich intermetallic phase $Mo_5Si_3$ (T1) by substituting the $Mo_3Si$ phase [6]. Through this alloying concept, it becomes possible to (i) get rid of the oxidation prone silicide $Mo_3Si$ and (ii) involve the Si-rich intermetallic compound T1 in the alloy design that exhibits a high melting point, a limited homogeneity range, and most importantly a high alloying potential. This allows adjusting materials properties, like the oxidation resistance.

In the phase T1, Ti atoms exclusively substitute Mo atoms leaving the positions of the metalloid Si and the tetragonal crystal structure up to concentrations of ~40 at.% Ti at 1600 °C unaffected [6]. Fortunately, only a negligible decrease of the melting point from 2180 to 2130 °C is associated with the alloying of up to 40 at.% Ti [6,7]. The addition of more than 40 at.% Ti stabilizes a two-phase field comprising additional hP-structured $(Ti,Mo)_5Si_3$ as demonstrated in Ref. [7]. An increase of Ti concentrations above 50% results in a single-phase field again with the hexagonal crystal structure $D8_8$ [7].

For investigating the oxidation resistance of the Ti containing T1 phase, Burk et al. [8] analyzed an arc-melted nearly single-phase material of composition $(Mo_{0.36}Ti_{0.64})_5Si_3$ (in at.%: Mo37·5Si40Ti), which, in contrast to binary $Mo_5Si_3$, revealed very good oxidation resistance in a wide temperature range from 820 to 1300 °C. Although this alloy has a Ti/Si ratio of > 1, the reason for the strongly improved oxidation protectiveness was found in the formation of a duplex layer mainly consisting of $SiO_2$ below an outer $TiO_2$ layer. Burk et al. [8], however, did not propose a mechanism, why macro-alloying with Ti – an element that forms a quickly growing and non-protecting oxide – can improve the oxidation behavior. Yanigahara et al. studied the effect of a third element on the suppression of the pest phenomenon observed in Mo-Si-X alloys [9] and concluded that alloying with X = Al, Ti, Zr forms oxides with a Gibbs free energy of formation lower than that of $SiO_2$. These oxides can suppress pesting in the temperature range from 400 to 700 °C, if the volume expansion during selective oxidation is small [9].

Aim of this study is, thus, to understand, why the substitution of Mo

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atoms by Ti in the tetragonal structure of $(Mo,Ti)_5Si_3$ improves the oxidation resistance significantly. For this purpose, the effect of different Ti concentrations (20 and 40 at.%) on the oxidation of $(Mo_x,Ti_{1-x})_5Si_3$ is investigated. As poor oxidation resistance in air was reported for $Ti_5Si_3$ at 1000–1200 °C [10–13] due to the formation of an oxide scale with rutile being the major phase and subscales including TiN [14], the nitrogen effect was studied, additionally.

Density-functional theory (DFT) calculations were performed to calculate the migration barriers of Ti in $(Mo,Ti)_5Si_3$ alloys as well as the chemical potentials to explain the behavior of Ti in ternary T1.

## 2. Experimental procedure and computational details

Nearly single-phase $(Mo,Ti)_5Si_3$-type intermetallic compounds were manufactured with different Mo/Ti ratios using a powder metallurgical (PM) or arc-melting (AM) processing route. Alloys were prepared from elemental powder mixtures or bulk material of Mo, Si and Ti of 99.95%, 99.9% and 99.5% purity, respectively. PM was carried out under Ar atmosphere in a planetary ball mill (Retsch PM 400) with a rotational speed of 200 rpm and a ball to powder weight ratio of 13:1. Afterwards, the powder was compacted using Field Assisted Sintering Technique (FAST) at 1600 °C for 15 min using a heating and cooling rate of 100 K/min. During the entire compaction process a stress of 50 MPa was applied. Subsequently, a homogenization treatment was carried out at 1600 °C for 100 h in Ar atmosphere. For the AM processing route, the elemental bulk material was melted by arc-melting technique under a Zr gettered protective Ar atmosphere in a water cooled Cu mold. The so prepared buttons were flipped and remelted five times each to ensure homogenization. Finally the buttons were drop casted in an ingot mold of 12 mm diameter and 60 mm length. A subsequent heat treatment was carried out at 1600 °C for 100 h in Ar atmosphere.

Oxidation samples (dimensions: $10 \times 4 \times 3$ $mm^3$) were machined using a slow-cutting diamond saw and ground and polished with SiC paper down to 1200 grit and ultrasonically cleaned in ethanol prior to oxidation. The oxidation kinetics was studied under isothermal testing conditions in the temperature range of 750–1300 °C for 100 h in quasi-static laboratory air using a tailor-made Rubotherm magnetic suspension balance described in detail in Ref. [15]. The microstructure and the corrosion products were characterized by scanning electron microscopy (FEI dual beam system of type Helios Nanolab 600) in secondary-electron (SE) and backscattered-electron (BSE) mode. Phase identification and elemental distribution in the phases was investigated by energy-dispersive X-ray spectroscopy (EDX) and energy dispersive X-ray diffraction analysis (XRD). Transmission electron microscopy (TEM) lamellae from the affected zone underneath the oxide layer were prepared using the focused ion beam (FIB) of the Helios Nanolab 600 system. TEM analyses were performed on a Talos™ F200A by FEI Company.

The experimental studies were supplemented by electronic structure calculations of the tetragonal $(Mo_{1-x},Ti_x)_5Si_3$ using the plane-wave projector-augmented wave [16] DFT [17,18] code VASP [19–21] in conjunction with the GGA-PBE [22,23] exchange-correlation functional. $Mo_5Si_3$ silicide was represented in the body-centered tetragonal (tI32) unit cell containing 20 Mo atoms and 12 Si atoms. Ti atom was substituted for Mo atom and occupied one of the non-equivalent positions in the silicide, namely the 4b (chain) site or the 16k site. Details of the structure are given in Ref. [24]. Mo was represented by six valence electrons, Si and Ti by four valence electrons. The results were converged with respect to the energy cutoff and k-point mesh. We used an energy cutoff of 400 eV and a $10 \times 10 \times 20$ Monkhorst-Pack grid [25] for a $1 \times 1$ x 1 conventional (rectangular) unit cell. Using this computational setup the convergence of the Mo (Si) vacancy formation energy to ± 5 meV per vacancy is achieved for different cell sizes, constructed from a $1 \times 1 \times 1$ to a $2 \times 2 \times 2$ replication of the conventional $Mo_5Si_3$ unit cell. Structure optimization procedures were performed under zero pressure conditions and stopped after residual forces on individual atoms were smaller than 1meV/Å.

**Table 1**
Processing route, phase composition, theoretical and experimental density as well as porosity of the alloy compositions Mo37.5Si20Ti, Mo37.5Si30Ti and Mo37.5Si40Ti.

| | Mo37.5Si20Ti | Mo37.5Si30Ti | Mo37.5Si40Ti |
|---|---|---|---|
| Processing route | PM | AM | AM |
| phase composition | T1 | T1 | 97% T1 + 1.4% $Mo_{ss}$<br>1.6% $Ti_5Si_3$ |
| theoretical density [$mg{\cdot}cm^{-2}$] | 7.04 | 6.52 | 5.88 |
| experimental density [$mg{\cdot}cm^{-2}$] | 6.8 | 6.5 | 5.8 |
| porosity | 4% | negligible | negligible |

For calculating of the migration barriers for Mo, Ti and Si atoms we have used the climbing-image nudged-elastic-band method [26,27] with a number of intermediate images equal to five and a spring constant equal to 5 eV/$Å^2$.

## 3. Results

### 3.1. Microstructure

Table 1 gives an overview of the processing route, phase composition as well as theoretical and experimental density of the alloys investigated. All compositions are denoted in at.%.

The theoretical density was calculated using the crystallographic information (occupancy sites and preferences etc.) gained from full pattern Rietveld analyses. The density was experimentally determined by pycnometer and the Archimedes' principle. It can be observed from Table 1 that arc-melted compositions do not show any porosity and Ti addition significantly reduces the alloy density.

Fig. 1 shows the BSE-SEM images of the microstructures of the different alloys. Micropores are only visible in the PM processed alloy Mo37.5Si20Ti (see Fig. 1 (a)). There, the pores are homogenously distributed throughout the whole substrate. The alloy compositions Mo37.5Si20Ti and Mo37.5Si30Ti are single-phase T1 (see Fig. 1 (a) and (b)) which was confirmed using XRD and EDX. Mo37.5Si40Ti additionally contains traces of hexagonal $(Ti,Mo)_5Si_3$ (see Fig. 1 (c)).

### 3.2. Oxidation behavior of $(Mo,Ti)_5Si_3$ at 750–900 °C in air

Fig. 2 shows the specific weight change vs. time for single-phase Mo37.5Si20Ti in comparison with Mo37.5Si40Ti in the temperature range from 750 to 900 °C. Weight gain kinetics and steady state oxidation is observed. All curves follow a parabolic rate law. Passivation occurs almost immediately after a short period of transient oxidation of only few minutes. The absolute mass gain after an exposure time of 100 h is as low as 0.178 $mg/cm^2$ at 750 °C and 0.509 $mg/cm^2$ at 820 °C for Mo37.5Si20Ti, respectively. The oxidation isotherms of Mo37.5Si20Ti and Mo37.5Si40Ti are almost congruent at the same temperatures indicating that the course of oxidation is neither affected by the 4% porosity of Mo37.5Si20Ti nor by the increased Ti concentration of Mo37.5Si40Ti.

The macroscopic inspection of all samples after oxidation for 100 h revealed that the samples retained their shape and contours indicating the formation of thin, dense and adherent oxide layers.

EDX analyses show that the cross-section of Mo37.5Si20Ti oxidized for 100 h at 820 °C consists of a duplex oxide layer (thickness of 2.5 µm) composed of a $SiO_2$ matrix with embedded $TiO_2$ particles of $< 300$ nm size (see Fig. 3 (a)). The modification of Ti-oxide is rutile, which was identified by XRD analyses of the surface of the oxidized samples. Small amounts of Ti are also dissolved in the silica scale. After Ricker et al. up to 10 wt.% Ti can be dissolved in cristobalite and an even higher