# Thermogravimetric Measurements on High-Temperature Oxidation of Molybdenum-based Alloys

Keywords: High temperature oxidation, Thermogravimetry, Corrosion, Mo-based alloys

TA402

## ABSTRACT

To reduce fuel consumption in air traffic, airplane turbines are required to be operated at higher combustion temperatures. For this purpose, new high temperature resistant materials are necessary. Mo-Si-B alloys could be suitable materials because at temperatures around 1100 °C, protective borosilicate layers are formed by oxidation. Depending on temperature and composition, it is also possible that corrosion occurs due to evaporation of volatile molybdenum oxides. Using thermogravimetry, the oxidation behavior of various molybdenum-based alloys can be measured at 900 °C – 1330 °C, and the alloy composition for technical applications can be optimized.

## INTRODUCTION

In the interest of climate protection as well as for economic reasons, it is desirable to reduce the fuel consumption in air traffic. Further increasing the efficiency of modern airplane turbines requires higher combustion temperatures, because many other possibilities have already been exploited. The materials used to date, e.g. nickel based alloys, are reaching their limits at 1100°C.

Therefore, there is a demand for the development of new high temperature resistant materials that allow an increase of combustion temperaures, ideally without the need for cooling. Mo-Si-B based alloys could be suitable for this application range because at high temperatures, borosilicate layers that protect the material are formed. It is also possible that extreme corrosion could occur due to evaporation of volatile molybdenum oxides.

Using a TA Instruments DynTHERM system, the oxidation behaviour of various alloys can be investigated. Optimizing the composition of Mo-Si-B based alloys with regard to oxidation resistance can make them a suitable material for future airplane turbines.

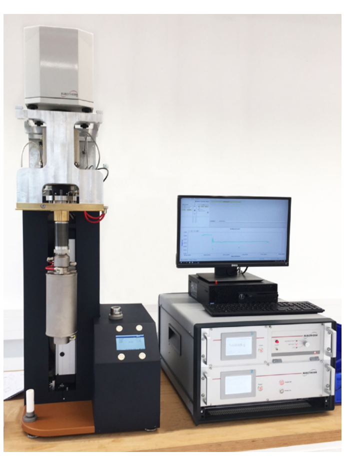

*Figure 1: Operating unit and balance head of a DynTHERM instrument with a bellows-type cover for rapid sample heating.*

## EXPERIMENTAL

Maximum operating conditions of this instrument are 1550 °C at 1bar. The experiments described later were done at max. 1300 °C. The DynTHERM system is based on the principle of the magnetic suspension balance: by magnetic coupling of the sample to the balance through the wall of a measuring chamber, a spatial separation of balance and measuring chamber is achieved. This way, thermogravimetric measurements in air at 1550 °C are possible. This setup can be used to reliably measure small weight changes on comparably large samples over a period of several days at the relevant temperature.

By means of a bellows-type metal cover that connects the balance head with sample holder and the oven, it is possible to move the sample into the hot oven where it can be immediately heated to the measurement temperature. This is important, because for the investigation of the oxidation behaviour at a given measurement temperature, reactions during the heating process have to be minimized.

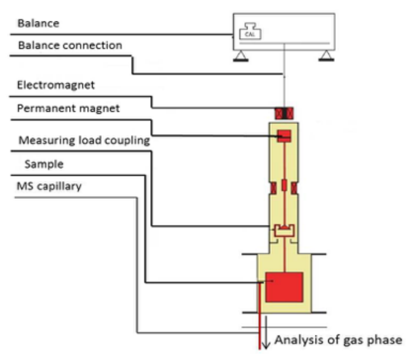


*Figure 2: Schematic of the thermogravimetric measurement chamber.*

Mo-9Si-8B was used as the reference material and starting point for the investigations. The aim of the study was to find an alloy that is as stable as possible in the technically relevant temperature range up to 1300 °C. It is also required that no damages occur to the operating temperature of the turbine during the heating process.

## RESULTS AND DISCUSSION

At 900 °C in air, Mo-9Si-8B is destroyed fast by catastrophic oxidation (Figure 3). No protective borosilicate layer is formed in this temperature range, so the mass loss by evaporation of volatile molybdenum oxide $MoO_3$ leads to a status that no longer allows the use of the material within short periods of time.

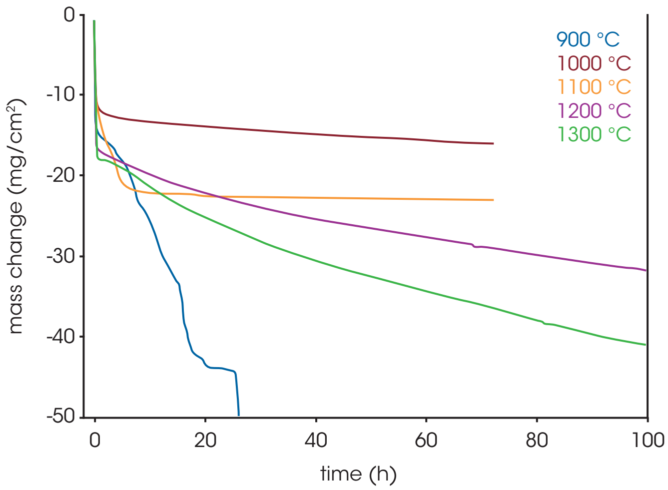


*Figure 3: Oxidation behaviour of Mo-9Si-8B in air at various temperatures.*

In contrast to these findings, at temperatures of 1000 and 1100 °C a complete surface layer is formed that provides long-term protection for the material. But at 1200 and 1300 °C, the surface layer is again less stable and a continuous mass loss is observed.

It is known from literature that the addition of zirconium has a positive effect on mechanical properties. Therefore, small amounts of Zr were added to the base alloy and the resulting alloy Mo-9Si-8B-1Zr was investigated.

Compared with the reference material, the mass loss in the temperature range from 1000 °C to 1200 °C is substantially reduced (Figure 4). However, at temperatures above and below, the oxidation is too strong for a technical use of the alloy Mo-9Si-8B-1Zr. Additional investigations show that during the preparation of the alloy, $ZrO_2$ is formed at the grain boundaries, which leads to a considerably finer microstructure of the alloy. This different microstructure contributes to a faster formation of the protective oxide layer.

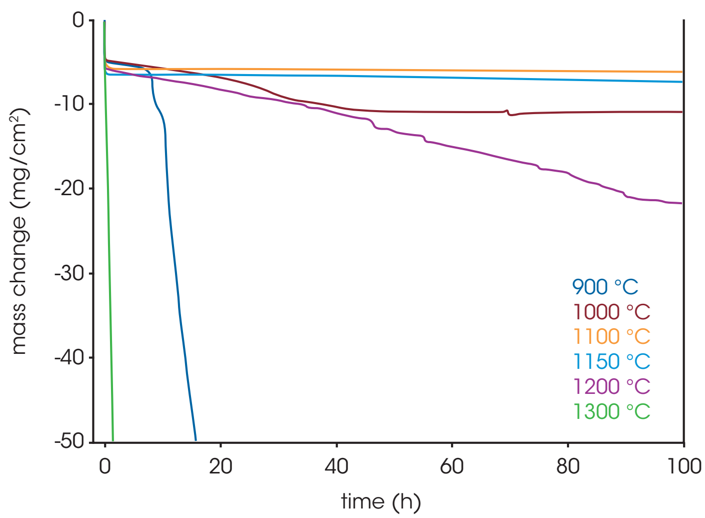


*Figure 4: Temperature dependent oxidation behaviour of Mo-9Si-8B-1Zr.*

From the addition of yttrium (Figure 5), improvements of the mechanical properties are known as well. As with zirconium, oxides are formed at the grain boundaries that lead to smaller grains and a smoother structure. Measuring the alloy Mo-9Si-8B-0.2Y at 1000 °C, this results in a considerably lower mass loss from the starting period until the complete formation of the oxide layer. At 1200 °C, a higher mass loss can be observed at the beginning, but as the experiment continues, the mass loss rate is lower, so that again, a slightly lower total mass loss can be seen in comparison with the reference material.

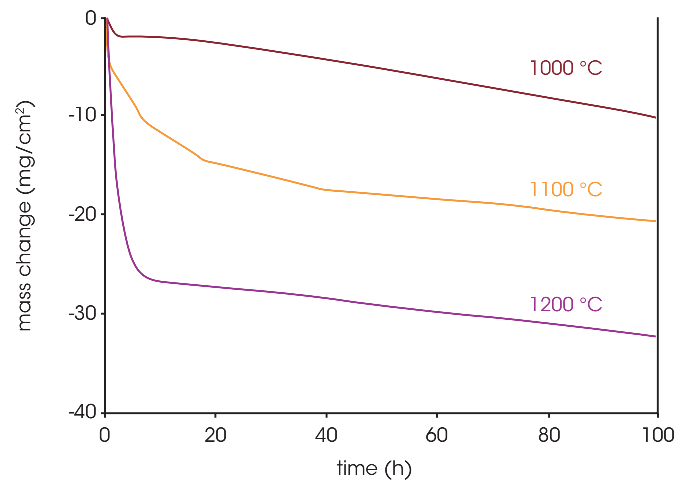


*Figure 5: Oxidation behaviour of Mo-9Si-8B-0.2Y*

## CONCLUSION AND OUTLOOK

The results show that alloying the reference material with additional elements can improve the thermal stability, sometimes to a large exent. As a result, applications in technical areas are becoming more likely. Further investigations can prove that the mechanical properties could be improved considerably.

The DynTHERM TGA system by TA Instruments is very well suited for long and continuous TGA measurements in oxidizing atmospheres.

## REFERENCES

1. S. Burk: *Hochtemperaturoxidation Molybdän-basierter Legierungen unter Berücksichtigung von Einflüssen aus Umgebungsatmosphäre und legierungstechnischen Maßnahmen*, Ph.D Thesis University of Siegen, June 2011

2. B. Gorr, . Wang, S. Burk, M. Azim, S. Majumdar, H.-J. Christ, D. Mukherji, J. Rösler, D. Schliephake, M. Heilmaier: *High-temperature oxidation behavior of Mo-Si-B-based and Co-Re-Cr-based alloys,* Intermetallics 48 (2014) 34-43

3. M. A. Azim, S. Burk, B. Gorr, H.-J. Christ, D. Schliephake, M. Heilmaier, R. Bornemann, P. Haring Bolivar: *Effect of Ti (macro-) alloying on the high temperature oxidation of ternary Mo-Si-B alloys at 820-1300 °C,* Oxidation of Metals, 80, 2013, 231-241

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