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Alumina forming high temperature silicides and carbides

M. Sundberg[a,*], G. Malmqvist[a], A. Magnusson[a], T. El-Raghy[b]

[a] Kanthal AB, Hallstahammar S-73427, Sweden
[b] 3-ONE-2 LLC, Voorhees, NJ 08043, USA

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Abstract

Aluminium containing heat-resistant silicides and ternary carbides (Maxthal®), have been evaluated in terms of their high temperature behaviour in various atmospheres including vacuum. The novelty of these materials is in their ability to form a stable and adherent protective alumina scale at low partial pressures of oxygen as well as in air. Recently developed heating elements, for oxidising and reducing atmospheres, made of molybdenum aluminosilicide (Kanthal Super ER) have been evaluated by thermogravimetric analysis (TGA) studies in air and other atmospheres. The performance up to 1575 °C has been evaluated at vacuum levels down to 10^{-4} mbar. In addition to its remarkable thermal shock resistance, damage tolerance and machinability, Ti_2AlC (Maxthal®) showed a parabolic and stable oxide growth rate up to 1400 °C in air. Cyclic testing confirmed that the oxide layer is adherent to the bulk. It has been concluded that both Maxthal® and Kanthal Super ER are capable of operating in air, up to 1400 and 1575 °C, respectively.

Keywords: Ti_2AlC; $Mo(Si,Al)_2$; Alumina formers; High-temperature oxidation

1. Introduction

High-temperature oxidation and corrosion resistance are crucial for materials used in various industrial applications [1]. Electric heating elements are among the materials designed for optimal protection against degradation at elevated temperatures. The oxides providing a good oxidation resistance on electric heating elements of metallic alloys and intermetallics are Al_2O_3, Cr_2O_3 and SiO_2. Surface layers of chromia protect the NiCr alloys, alumina the FeCrAl alloys and silica the $MoSi_2$-based heating elements. Al_2O_3 is the most thermodynamically stable of these oxides and provides the best protection in reducing and oxygen deficient atmospheres. However, $MoSi_2$-based materials, such as Kanthal Super [2], have the highest maximum operating temperature in air, 1850 °C, due to its superior oxidation resistance and high melting point. On the contrary, due to the nature of the silica scale such materials will for example not be stable above 1300 °C at dew points below −20 °C in hydrogen or at vacuum levels below 10^{-1} mbar. A recently developed heating element that is a derivative of Kanthal Super where a fraction of the silicon has been exchanged for aluminium resulting in the intermetallic phase $Mo(Si,Al)_2$ which develops a protective scale of Al_2O_3 upon heating [3]. Potential applications for Kanthal Super ER are as heating elements in furnaces for firing of ferrites, electroceramics or powder metallurgy sintering. They can be applied to thermal processing in oxidising, inert and reducing atmospheres up to nearly 1600 °C [3].

The second class of compounds dealt with in this paper, Ti_2AlC, belong to the so called “MAX-phases”, a structurally related family of layered ternary carbides and nitrides with the general formula $M_{n+1}AX_n$ with $n = 1$–3, and where M is an early transition metal, A is an A group element in the periodic table and where X is carbon or nitrogen [4,5]. As a class, these ternaries possess an unusual combination of properties: they are readily machinable, good thermal and electrical conductors, relatively soft, thermal shock resistant, damage tolerant, stiff and have relatively low thermal expansion coefficients. The most studied of these phases is Ti_3SiC_2 (312) which has been extensively investigated by Barsoum et al. [4–8]. However, even though the oxidation resistance of 312 is acceptable at moderate temperatures the oxidation rate above 1000 °C is relatively fast in air and other

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[*] Corresponding author. Tel.: +46-220-21595; fax: +46-220-21191.
E-mail address: mats.sundberg@kanthal.com (M. Sundberg).

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oxidising atmospheres, forming a mixture of TiO_2 and SiO_2 [7,8]. On the other hand, as an engineering ceramic used for example at high temperatures in vacuum or hydrogen furnaces it can withstand up to about 1800 °C [9]. At present, 312 is also being evaluated in various low temperature applications as a replacement for graphite and SiC. Ti_2AlC, however, forms a passive surface layer of Al_2O_3 at high temperatures and provides a potential for MAX-phases to be used at very high temperatures in oxidising atmospheres. The oxidation behavior of Ti_2AlC has been studied by different groups. Barsoum et al. [10] reported on the formation of non-protective oxide while Wang and Zhou reported on the formation of an inner Al_2O_3 layer and a discontinuous outer layer of TiO_2 up to 1300 °C [11].

At Kanthal, single phase materials of Ti_3SiC_2 and Ti_2AlC (trade name: Maxthal) can be manufactured in a variety of shapes and sizes. Components made of these materials are at present being evaluated in various consumer and industrial applications. Ti_2AlC, for example, is being explored both as a gas-heated surface emitting heat radiation as well as a heating element.

This paper discusses the behaviour of these two novel alumina forming compounds in various atmospheres in order to establish an idea of the conditions under which these materials can be used as heating elements or as engineering ceramics for high temperatures. Although Ti_2AlC and $Mo(Si,Al)_2$ have the oxidation properties in common they differ substantially in many other respects. This is why the details of the experimental results are presented in two different sections.

2. Experimental

Table 1 shows some of the physical properties of the investigated materials produced by Kanthal. As well as having similar oxidation properties both materials are electrically conductive. However, the resistivity dependence on the temperature is much lower in these materials compared to standard $MoSi_2$ heating elements.

2.1. Kanthal Super ER

The electric heating element Kanthal Super ER comprises about 85 vol.% of hexagonal C40-phase, $Mo(Si,Al)_2$ [12,13]. An additional phase containing roughly 15 vol.% of alumina (Al_2O_3) provides a reinforcing phase as well as serving as a grain-growth inhibitor. In the case of standard $MoSi_2$-heaters, an aluminosilicate phase provides similar benefits. The heating elements from Kanthal AB are available either in two-shank or multi-shank configurations with dimensions 3/6, 4/9 and 6/12 (heating zone diameter in mm/terminal zone diameter in mm).

Table 1
A selection of physical properties of Kanthal Super ER and Maxthal 211

	Kanthal Super ER	Maxthal 211
Density (g/cm^3)	5.7	4.1
CTE ($\times 10^{-6}\,°C^{-1}$)	8	8
Electrical resistivity ($\Omega\,mm^2/m$), 20 °C	1.8	0.5
Electrical resistivity ($\Omega\,mm^2/m$), 1500 °C	3.3	1.8

SiO_2 formed on $MoSi_2$ heaters such as Kanthal Super 1800 is not stable under reducing conditions at high temperature since the oxide layer evaporates as SiO (g) thus exposing the bulk material to further attack leading to reduction of the silicon content in the material. Likewise, the alumina layer is of vital importance to protect the $Mo(Si,Al)_2$, since this silicide phase neither resists reducing conditions nor low oxygen partial pressures at high temperatures.

The 6 mm circular rods cleaned in acetone were used to investigate the stability and growth rate of the alumina layer on Kanthal Super ER. To provide a worst case scenario regarding corrosion the samples were unoxidised. New heating elements of this type are delivered in the pre-oxidised state to ensure the best possible performance. The short-term tests were done in a thermogravimetric analyser (Netzsch STA 409C). Long-term tests (1000 h) were performed in air in a box furnace and in a tube furnace for nitrogen and hydrogen atmospheres. Dew points and oxygen partial pressures were recorded during the experiments.

In the TGA runs the materials were held for 18 h at constant temperatures of 1300, 1450 and 1575 °C in air and of 1450, 1500 and 1575 °C in nitrogen and Ar/H_2. Atmospheres used were dry synthetic air ($80N_2/20O_2$, Dp −80 °C), nitrogen (Dp < -40 °C, $O_2 < 65$ ppm), 95/5 argon/hydrogen (Dp < -40 °C) and an (air) vacuum down to 10^{-4} mbar.

Long-term oxidation in air was performed at 1000, 1300 and 1575 °C for 1000 h in a box furnace with the samples placed in an alumina crucible with a perforated lid if there would be spallation of oxide. Sample weight was measured at room temperature after intervals of 0, 25, 100, 250, 500 and 1000 h.

Long time exposures were performed in a gas tight alumina tube furnace in nitrogen (Dp < -40 °C, $O_2 < 65$ ppm) and 100% hydrogen (Dp < -40 °C) at temperatures 1450, 1500 and 1575 °C. The sample weight was measured at room temperature after 0, 250, 500, 750 and 1000 h.

3. Results

The kinetics of the oxidation reaction are described by the parabolic rate constant for oxidation, k_n, and the power constant, n. The result of the short-term oxidation in air has been analysed from the rate equation [14]:

$$m^n = k_n t + C$$

where m is the specific weight in g/m^2 and C is set to zero. Following an initial exposure time of 3–6 h the oxidation rate changes from linear to diffusion controlled. In particular, for temperatures at 1450 °C and higher n equals 2–2.2

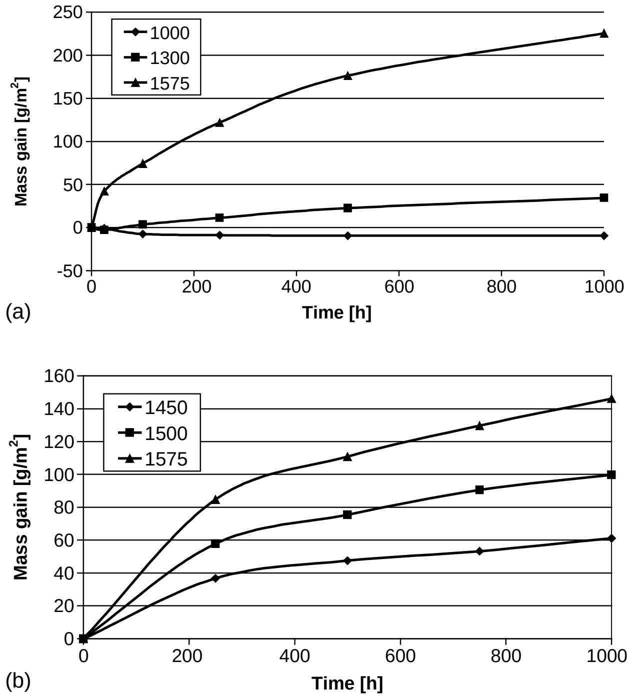

Fig. 1. Specific weight gain of Kanthal Super ER in: (a) air at 1000, 1300 and 1575 °C, and (b) hydrogen at 1450, 1500 and 1575 °C.

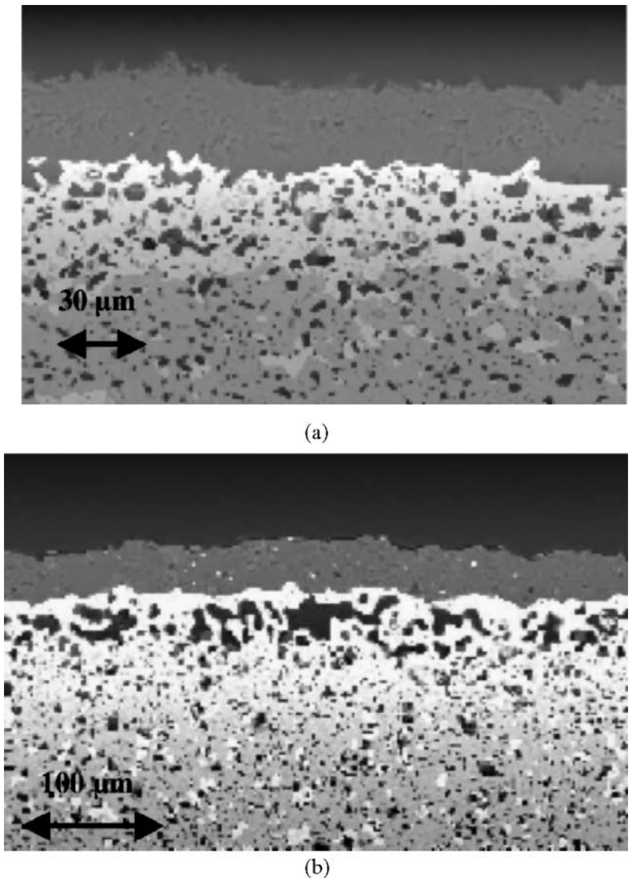

Fig. 2. SEM surface cross section image of sample in: (a) air (TGA), 30 μm oxide after 18 h at 1575 °C (TGA), Mo_5Si_3 intermediate layer with traces of Al, and (b) hydrogen, 35 μm oxide after 1000 h at 1450 °C, Mo_5Si_3 intermediate layer with traces of Al.

for all tested atmospheres up to 18 h, i.e. close to parabolic. At lower temperatures and shorter times the evaporation of MoO_x has to be accounted for to explain the behavior more in detail. However, on the actual heating elements the surfaces are pre-oxidised to eliminate the effect of the initial evaporation to ensure a protective film. After 18 h at 1575 °C the thickness of the oxides is of the order of 30 ± 5 μm. This might seem somewhat unexpected but even in the N_2 and the $Ar/5H_2$ there is sufficient O_2 and H_2O to oxidise the samples.

In Fig. 1(a) the results of the long-term exposures in air are shown. After an initial minor weight loss at 1000 °C due to MoO_x evaporation, an Al_2O_3 layer forms after about 250 h and passivates the surface. This weight loss was also confirmed in the TGA run up to 18 h.

After completing the heat treatment in air at 1575 °C for 1000 h the oxide thickness had grown to about 120 μm.

The corresponding data for long time exposure in pure hydrogen are given in Fig. 1(b). In this case, the overall growth rate is also close to parabolic at the tested temperatures. For comparison, exposing the silica former Kanthal Super 1800 ($MoSi_2$-base) to hydrogen at 1575 °C results in a substantial weight loss after just a few hours due to reduction of the silicon in the base material [3].

Fig. 2(a) and (b) show the oxide and the bulk region next to the interface on two samples after heat treatment in air 18 h at 1575 °C (TGA) and after 1000 h in H_2 at 1450 °C. Noteworthy is the thicker section of Mo_5Si_3 which is a result of long time exposure and consumption of aluminum which is the source for oxidation at the bulk to oxide interface. In the photo it is also clear that some voids have been created in the aluminum depleted Mo_5Si_3 layer beneath the oxide, possibly as a consequence of the decomposition of $Mo(Si,Al)_2$ [15]. However, an adherent dense alumina layer has grown on the surface.

The 1000 h exposures in dry nitrogen were partially affected by a reaction between the sample and the carrier resulting in a higher weight gain than expected with a parabolic growth rate. This is confirmed by the fact that the oxide thickness after 1000 h at 1575 °C was measured as about 110 μm by SEM. A further quantitative analysis of the exposure data and a detailed SEM investigation of the heat-treated samples are underway and will be published elsewhere [16].

A basic study was made to establish the stability of unoxidised samples of Super ER under vacuum at approximate pressure levels of 10^{-2} and 10^{-4} mbar. It was concluded that a maximum of 1575 °C was tolerated to grow a thin alumina layer at 10^{-2} mbar in the TGA equipment, whereas there was a weight reduction at 10^{-4} mbar. On the other hand, in the presence of CO in a graphite furnace the alumina was only capable of forming up to 1350 °C at 10^{-2} mbar. This is not surprising since CO acts as a reducing agent destabilising the alumina layer at elevated temperatures. A more thorough study is needed in more detail to map the stability range of alumina on Mo(Si,Al)$_2$-based materials in vacuum as well as to explain and quantify the mechanisms. The purpose of this study was to get some guidelines regarding the feasibility of using Super ER in, for example, heat treatment furnaces operating under carburising conditions in a low vacuum which is common for heat treating steel parts. The pre-oxidised surface of new heaters will however improve the performance.

3.1. Ti$_2$AlC (211)

Single phase, dense samples of Ti$_2$AlC, Maxthal®, (denoted 211 onwards), were made at Kanthal AB. The average grain size was found to be about 100 μm.

In the case of 211, it is basically the oxidation behaviour in air that is interesting to study. Under conditions resulting in an unstable alumina layer such as at high vacuum levels and in dry atmospheres the 211 phase itself will resist and stay intact as Ti$_3$SiC$_2$ (312) does. However, in many oxidising environments environmental attack from various volatiles could be detrimental to the 211. An inert layer of alumina would in many cases be beneficial to prolong service life of the component.

This work was performed on samples produced in equipment intended for fairly large scale production. That was done in order to verify that the data are valid when it comes to real components in real applications. A dense plate of 211 with dimensions 15 mm × 150 mm × 200 mm intended for a high-temperature application was used to machine samples for oxidation testing. Additionally, it is worth noting that samples from the same plate also were used to conduct thermal shock experiments. It was concluded that the thermal shock resistance was excellent when quenching even from 1400 °C to room temperature. This is comparable to what has been measured previously for 312 with a corresponding grain size of about 100 μm.

In this case, the short-term oxidation tests were also conducted using the Netzsch thermogravimetric analyser. Fig. 3 shows the time dependence of the specific weight gain during oxidation at 1100, 1200 and 1300 °C for 8 h at each temperature. The oxide growth rates were found to follow parabolic rate law with *n* close to 2 for all temperatures tested. Fig. 4 shows a BSSEM micrograph of the oxide formed as a result of the oxidation experiment discussed in Fig. 3. The 5 μm thick oxide is dense and adheres to the base material.

To verify the stability of the oxide after long time exposure, a sample was placed in an alumina tube furnace at 1200 °C in air for a total of 1000 h. A continuous Al$_2$O$_3$ was covering the surface after completing the test. At present, a corresponding heat treatment has been running for about 500 h at 1400 °C and the surface is also in this case covered by continuous alumina. Preliminary data show that this material is even capable of resisting 1500 °C due to the formation of a pure alumina scale.

3.2. Cyclic oxidation

Al$_2$O$_3$ formers sometimes exhibit spalling of the oxide due to the build up of thermal stresses that result from the thermal expansion mismatch between the oxide and bulk during cycling. The sample, which is subject of this study,

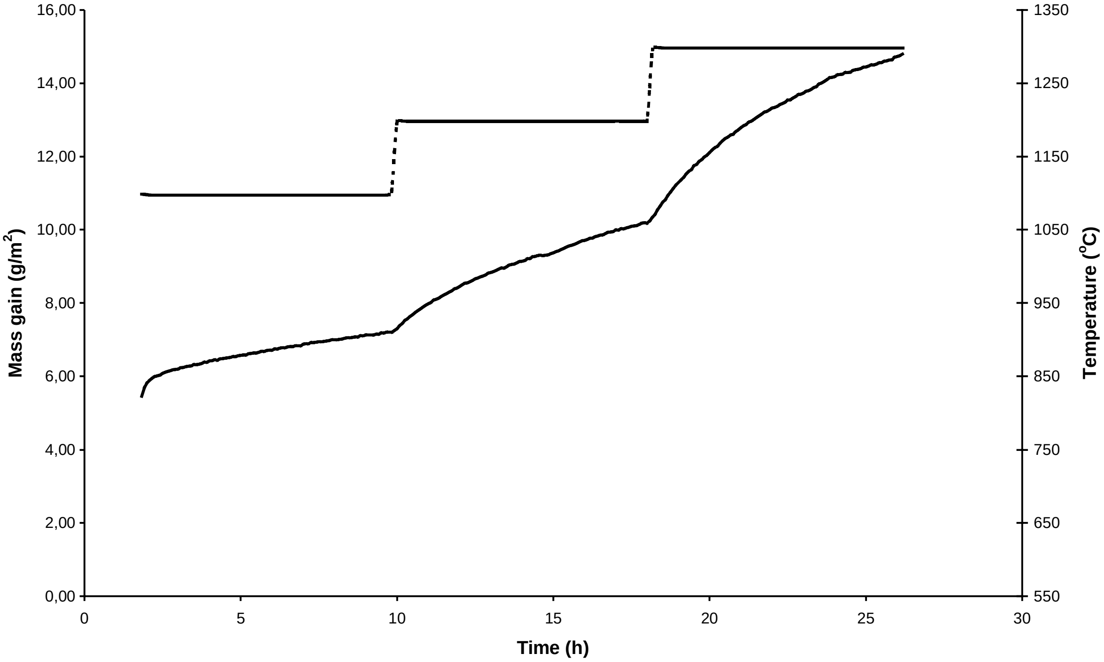

Fig. 3. Time dependence of the specific weight gain during oxidation of Ti$_2$AlC (211) at 1100, 1200 and 1300 °C for 8 h at each temperature showing parabolic growth.

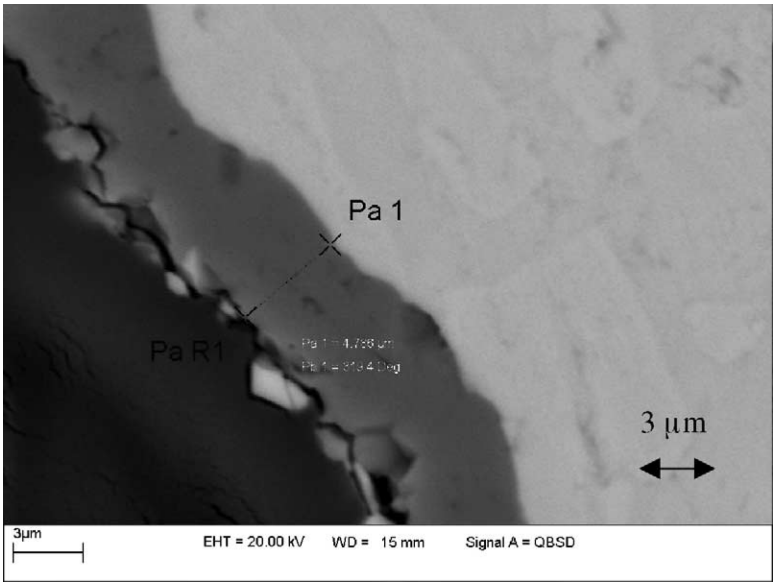

Fig. 4. SEM micrograph with a 5-µm oxide after oxidation at 1100, 1200 and 1300 °C for 8 h at each temperature.

was cycled in air at 1200 °C for 10 cycles. Each cycle consisted of heating the sample at 10 °C/min to 1200 °C followed by a holding period of 4 h before the sample was cooled down at 10 °C/min to room temperature. Fig. 5 represents the cyclic oxidation run in the TGA. The sample did not exhibit any weight loss at any stage. This is a conclusive evidence that the oxide layer is adherent. This is neither surprising from the fact the the thermal expansion coefficient of 211 and Al_2O_3 are matching, $8 \times 10^{-6}\,°C^{-1}$, resulting in negligible thermal stresses during heating and cooling.

As mentioned in the introduction a potential application for 211 is as a resistance heater. A heating element was manufactured and energised to be tested under cyclic conditions. Fig. 6 shows the heating element glowing at 1350 °C. After about 8000 on/off cycles from ambient temperature up to 1350 °C surface temperature the heater was still in operation. The effective time at operating temperature had been 260 h and only a minor increase of the electrical resistivity was measured. Furthermore, cross sections of the shanks were investigated by SEM and confirmed that a

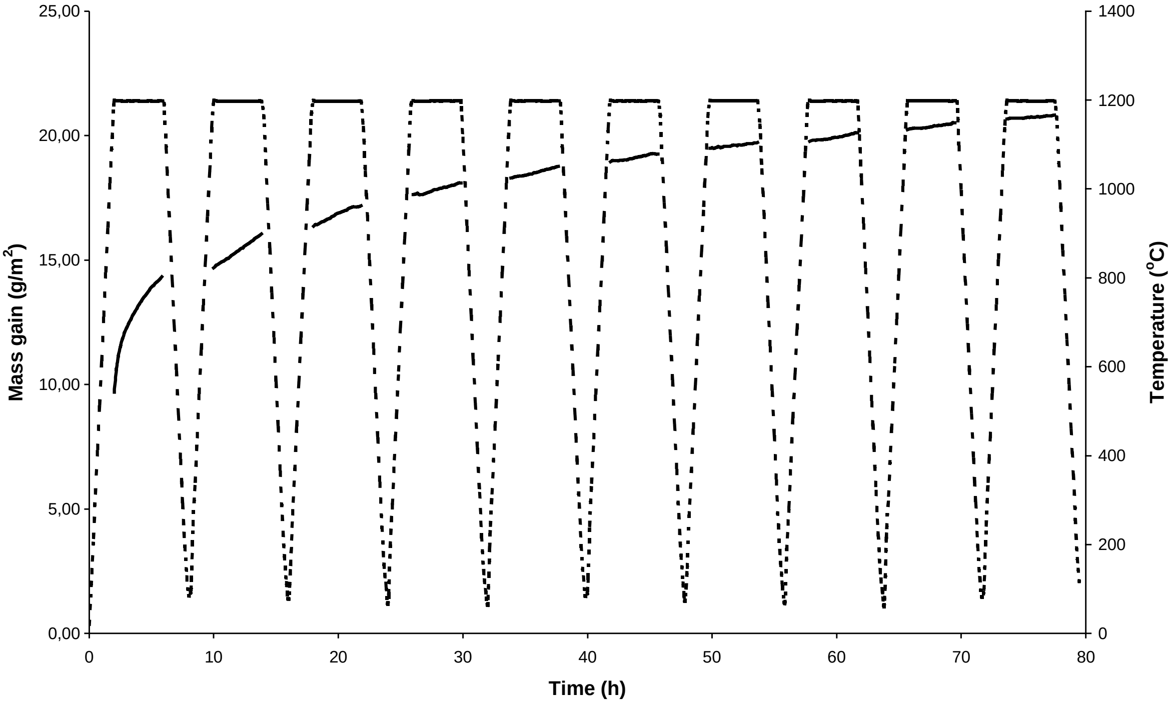

Fig. 5. Cyclic oxidation of 211 at 1200 °C with a heating and cooling rate of 10 °C/min suggesting an adherent oxide scale.

Fig. 6. Heating element of 211 glowing at 1350 °C.

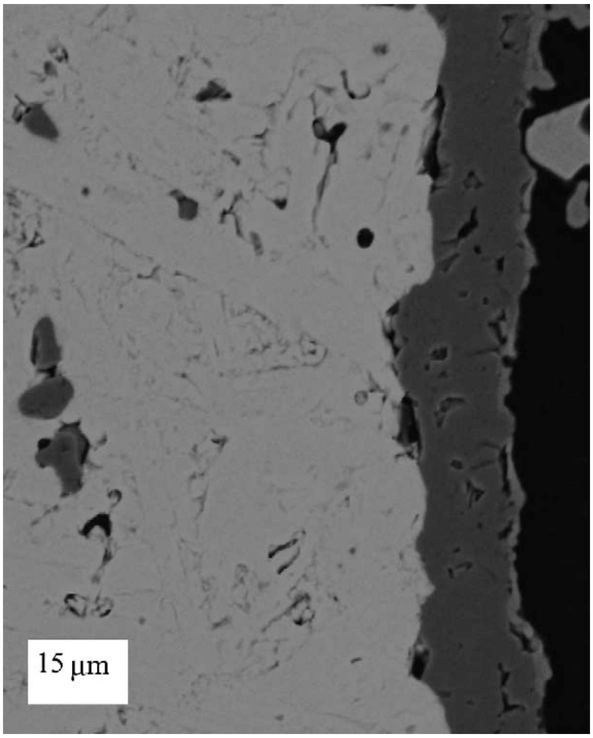

Fig. 7. SEM micrograph with a 15-μm thick oxide after 8000 heating cycles up to 1350 °C.

dense 15 μm thick α-Al_2O_3 adhered to the base material (Fig. 7).

On all samples mentioned above a scale of α-Al_2O_3 was detected by XRD after high-temperature oxidation. Any presence of rutile or a mixed oxide as previously reported have not been detected.

4. Conclusions

Two different aluminium containing compounds form stable, adherent and protective alumina surface layers upon oxidation up to 1400 and 1575 °C. Both the 211-Maxthal and the Mo(Si,Al)$_2$-based Kanthal Super ER show promise at providing new features for heating elements in various atmospheres and engineering ceramics for high temperatures.

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