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Self-Passivating Tungsten Alloys

Thomas Weissgaerber, Burghardt Kloeden, Bernd Kieback

Fraunhofer Institute Manufacturing Technologies and Advanced Materials,
Powder Metallurgy and Composite Materials Dresden,
Winterbergstrasse 28
01277 Dresden,
Germany

Abstract

Self-passivating tungsten-based alloys are an attractive material for application in future fusion reactors, because they combine the favourable properties of tungsten with an enhanced passive safety in the case of a loss of coolant accident. Powder metallurgical technologies have been used to prepare binary or ternary tungsten based alloys as a bulk material to improve the oxidation resistance. Silicon and chromium were chosen as the alloying elements. Elemental powder mixtures, pre-alloyed powders as well as mechanically milled powders were prepared with different alloying contents and consolidated by pressure assisted sintering technologies (hot pressing). The oxidation behaviour of tungsten alloyed with silicon and/or chromium was studied with respect to oxide growth kinetics, oxide phases and microstructure.

Introduction

Pure tungsten is presently the main candidate material for the plasma facing protection of future fusion power reactors. Compared with other materials, tungsten has the advantage of very low sputter erosion under bombardment by energetic deuterium, tritium or helium ions and atoms from the plasma. Thus a W-based protection material may provide a wall erosion lifetime of the order of five years which is a pre-requisite for economic fusion reactor operation [1-3]. A potential problem with the use of pure tungsten in a fusion reactor is the formation of radioactive and highly volatile WO_3 compounds and their potential release under accidental conditions. Figure 1 displays the temperature rise of in-vessel components in a reactor during a loss-of-coolant accident [1]. A loss-of-coolant accident in a He-cooled reactor would lead to a temperature rise to 1373 K after app. 10-30 days due to the nuclear decay heat of in-vessel component [1]. In such a situation intense air ingress into the reactor vessel would lead to the strong exothermic formation of WO_3 and subsequent evaporation of radioactive $(WO_3)_x$-clusters [4, 5].
To avoid the formation of WO_3 self-passivating tungsten alloys have to be developed. The selected alloying elements have to fulfil different criteria's, mainly the formation of a protective oxide layer as well as low neutron activation. Figure 2 displays the suitabilitiy of different alloying elements considering both properties. Chromium, silicon or yttria should be chosen. If a good oxidation behaviour can be expected (e.g. silicon) a low amount of alloying element can be used which is favourable because other properties of the base material remain unchanged.
W-Si and W-Si-Cr alloys were already produced by sputter deposition technique and the self-passivation mechanism could be shown [7]. The material behaviour is promising and an

application appears feasible since these materials can be produced as thick coatings or bulk materials.

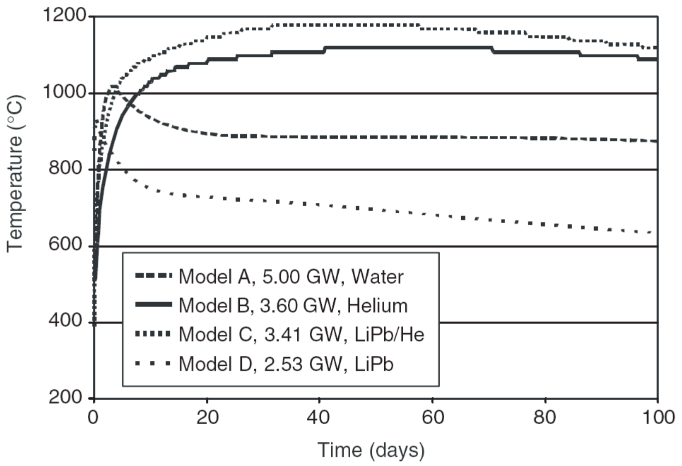


Figure 1 Temperature rise of in-vessel components in a reactor during a loss-of-coolant accident, taken from [1]

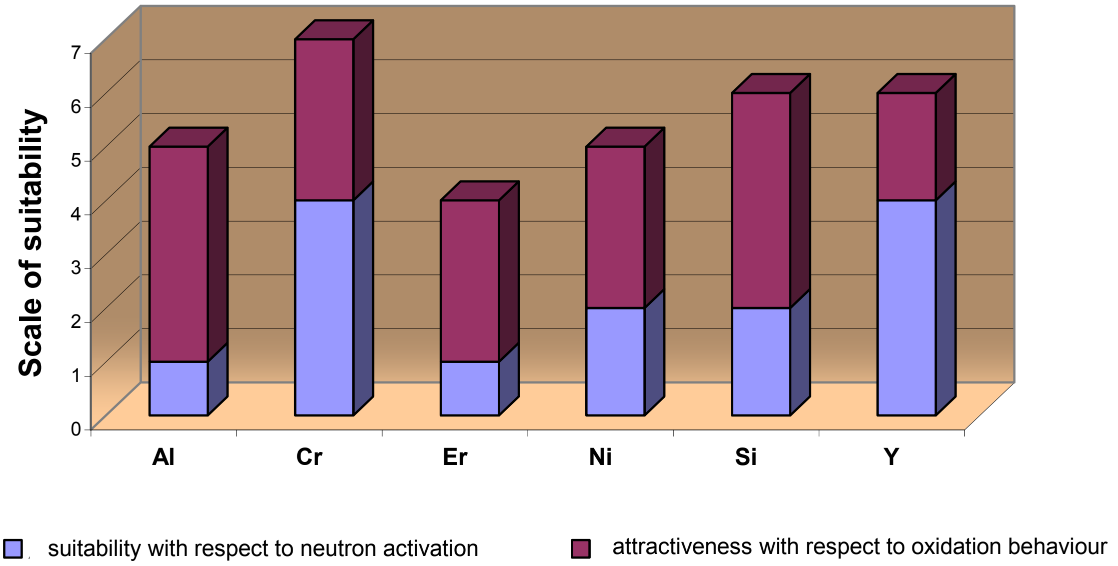


Figure 2 Scale of suitability of different alloying elements for tungsten [6]

Experiments

W, W-Si and W-Si-Cr alloys were synthesized by powder metallurgical methods. Elemental powders, shown in Figure 3, were used for mechanical milling in order to obtain a homogeneous distribution of the elements. Milling was performed with a planetary ball mill (300rpm, ball to powder ratio: 1:10, argon atmosphere, 5 hours). The milled powders were consolidated by hot pressing (1550°C, 1 hour, 35MPa, Ar/H_2). The following compositions (wt.-%) were prepared: W+0,3Si, W+1Si, W+10Si, W+10Cr, W+5Si+5Cr and pure tungsten as reference.

The microstructure of these samples was investigated by optical and scanning electron microscopy as well as x-ray diffraction. The oxidation behaviour was evaluated by thermogravimetry measuring the weight gain as a function of time at three different temperatures (800°C, 1000°C, 1200°C). Table 1 shows the temperature profile.

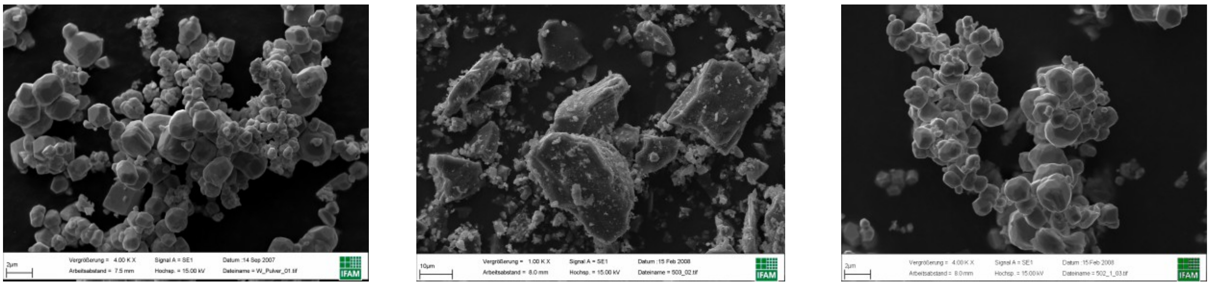


Figure 3 Powders, used for manufacturing of W-alloys (left: W-powder, d_{50}=4µm; middle: Si-powder, d_{50}=5µm; Cr-powder, d_{50}=8µm)

segment	temperature range [°C]	Heating /cooling rate[K/min]	Holding time [min]	atmosphere
Heating	20…800/1000/1200	10	-	Ar
Holding	800/1000/1200	0	240/120/120	synth. air
Cooling	800/1000/1200…20	-10	-	Ar

Table 1 Temperature profile for oxidation experiments

Results and Discussion

XRD investigations on W+10Si powder mixtures as a function of milling parameters (Figure 4) have shown peak broadening and a reduction of the intensity of W-peaks. The Si-peaks disappears as a consequence of grain refinement or partial amorphization but no phase reactions between W and Si could be obtained. Si is homogeneously distributed in the tungsten particles and a typical lamella structure is visible (Figure 5).

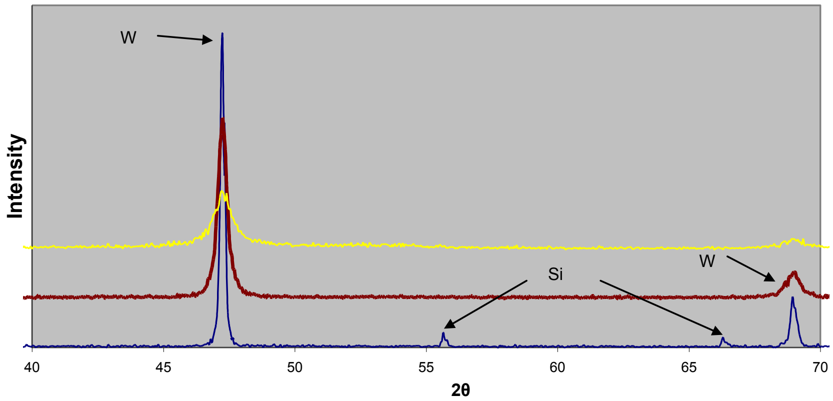


Figure 4 XRD measurements of W+10Si powder mixtures (blue – elemental powder mixture,red – after milling for 1h/300rpm, yellow – 5h/300rpm)

The formation of W-silicide phases can be obtained during heating. In the case of elemental powder mixture exothermic reaction at 1100°C can be detected by DSC. With increasing milling time the phase formation temperature is reduced and the reaction takes place over a broader temperature range (Figure 6). After consolidation by hot pressing a theoretical density >95% could be obtained. Figure 7 displays the microstructure of W-10Si, W-1Si and

W-10Cr as an example. In case of W-10Cr a tungsten solid solution as well as a chromium solid solution was detected. Some chromium oxides are visible as impurities. For the W-Si system intermetallic phases can be detected, W-1Si material contains a tungsten matrix with incorporated W_5Si_3 intermetallic phases. If the silicon content is higher (W-10Si) the microstructure is in accordance with the phase diagram characterized by a mixture of W_5Si_3 and WSi_2.

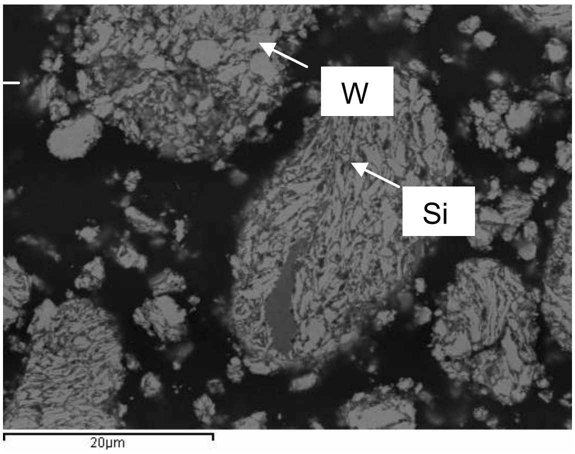


Figure 5 SEM micrograph of W+10Si powder mixtureafter milling for 5h/300rpm

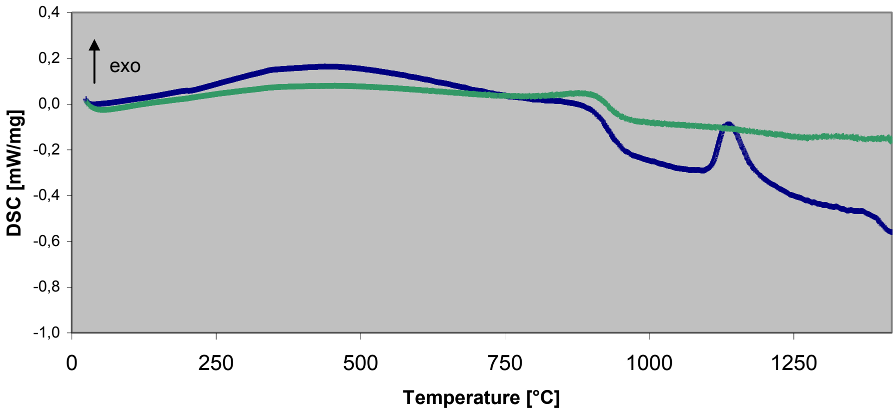


Figure 6 DSC scan of an W-10Si elemental powder mixture (blue curve) as well as an mechanically milled one (green curve)

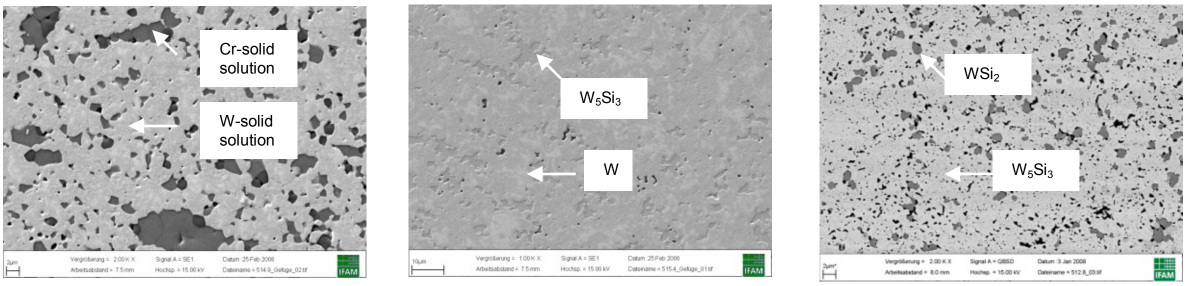
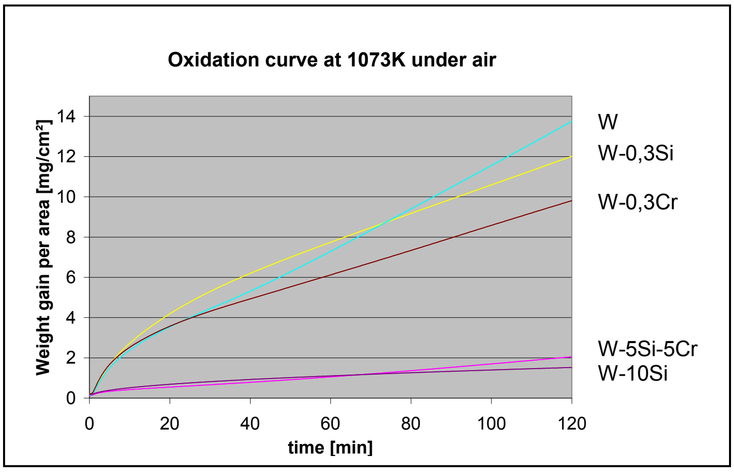


Figure 7 SEM micrographs of three different W-alloys (left: W-10Cr, middle: W-1Si, right: W-10Si)

Different samples containing silicon or chromium were used to study the oxidation behaviour. The temperature profile is displayed in table 1. Figure 8 shows oxidation curves at 1073K and 1273K. As expected the highest weight gain is obtained for pure tungsten and with increasing alloying content the weight gain can be reduced and the oxidation resistance is improved. In case of W-10Si the lowest weight gain was measured but it is visible that there is still an oxidation reaction connected with a weight gain. That means that a dense and protective SiO_2 layer is obviously not formed. Figure 9 displays the oxidation rate at three different temperatures for different alloys. The higher the alloying content the lower is the oxidation rate. The alloying element chromium is obviously less effective then silicon.



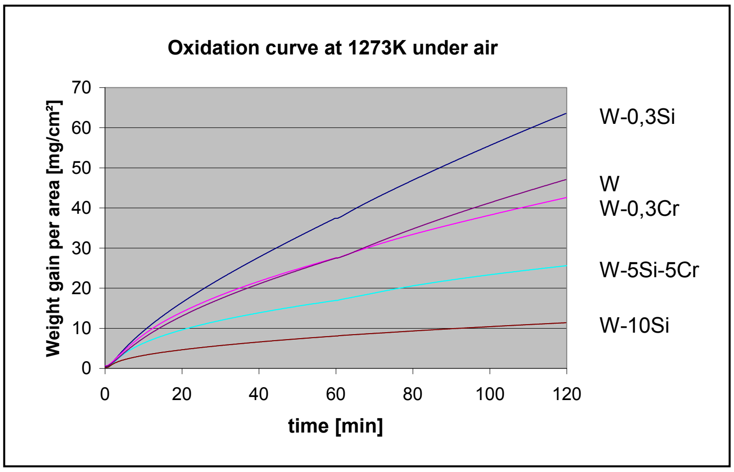


Figure 8 Oxidation curves measured at 1073K and 1273K for different tungsten alloys

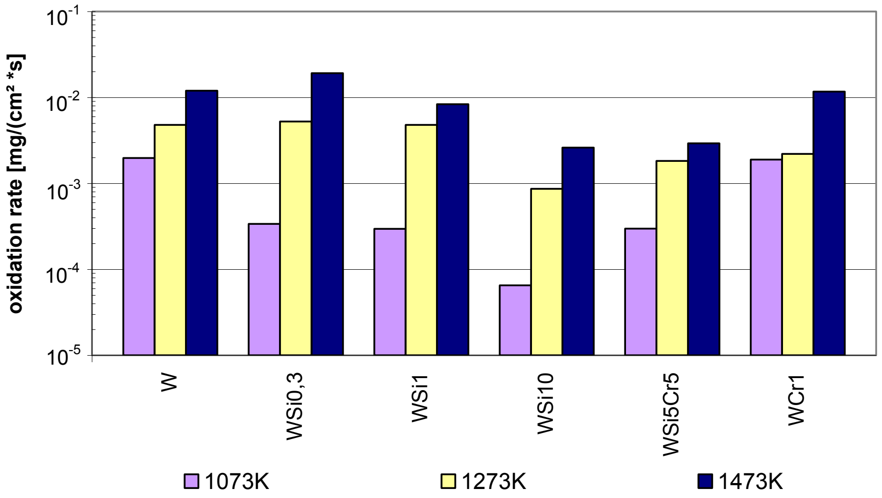


Figure 9 Linear oxidation rate of different tungsten alloys at different temperatures

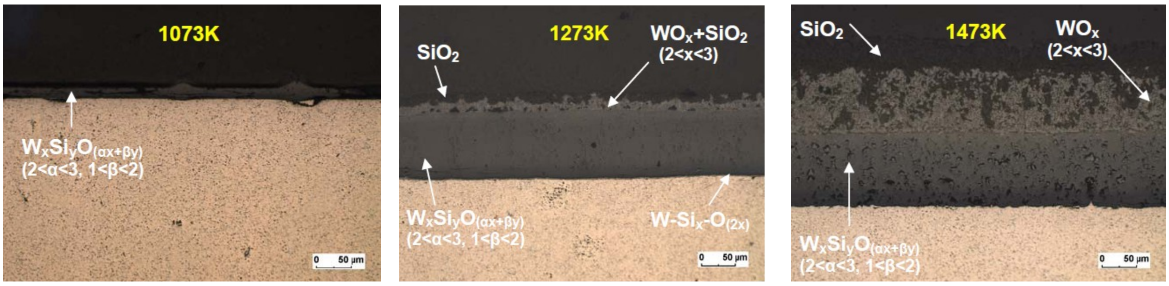


Figure 10 Optical micrographs of oxidized W-10Si samples at different temperatures

Figure 10 shows optical micrographs of W-10Si samples oxidized at 1073K, 1273K and 1473K. In general, during oxidation of silicides a selective oxidation of Si or simultaneous oxidation of metal and Si can be observed. Which reaction is liable to occur would depend on thermodynamic (affinity of metal and silicon for oxygen) and kinetic (diffusivity of oxygen in oxide scale and silicon in silicides) factors. In the case of W-Si alloys the affinity of Si for oxygen is much higher than of the metal. In such materials, it can be speculated that Si tends to be selectively oxidized, leading to the formation of a SiO_2 layer. Additionally, diffusivity of Si in a silicide phase and oxygen in the oxide layer must be considered. Sufficient supply of Si from the W-Si substrate comparing with that of oxygen trough the SiO_2 layer is required for continuous growth of SiO_2 layer. Consequently, in silicides which have a diffusivity of Si in the silicide phase and low affinity of metal for oxygen, steady growth of a SiO_2 scale is liable to occur. Conversely, in silicides which have low diffusivity of Si in the silicide and high affinity of metal for oxygen, simultaneous formation of metal oxide and SiO_2 is liable to occur. As shown in Figure 10 for W-10Si alloys a mixed oxide scale is obtained consisting of SiO_2 and WO_3 or also a mixed $W_xSi_yO_z$ scale which cannot be clarified clearly with our investigations. At oxidation temperature of 1073K the oxide scales consist of mixed oxides SiO_2 and WO_3 or $W_xSi_yO_z$. In the intermediate temperature range a double layer structure is formed. The outer layer consists of SiO_2, but porosity is visible. The inner layer contains the mixed oxide. At the temperature of 1473K the double layer structure is still visible with the significant difference of a thicker porous SiO_2 layer. As proposed in [8] a dense SiO_2 layer should be formed at oxidation temperatures >1573K taking into account the relationship between vapour pressure of a metal oxide and the formation of a SiO_2 scale [9]. Based on these calculations a complete SiO_2 scale can be formed when the vapour pressure reaches 10Pa. This value is reached at an estimated temperature of 1500K in case of pure WSi_2. Further oxidation experiments on W-10Si alloys at 1573K as well as at 1773K couldn't form a dense SiO_2 scale. The layer still consists of SiO_2 and WO_3 which could be verified by XRD measurements. Form thermodynamic reasons a reduced oxygen partial pressure has to be realized in order to avoid oxidation of tungsten and to oxidize silicon selectively.

Another point is that all alloys have a relatively small silicon concentration. Therefore the concentration of silicon at the surface could be to low in order to form a dense SiO_2 scale. As shown in the microstructure (Figure 7) pure tungsten or the W_5Si_3 phase (low silicon concentration) is available at the surface thus the silicon concentration at the surface is low. Obviously, beside a low oxygen partial pressure, which is a prerequisite to form a dense SiO_2 scale, higher silicon concentrations are necessary (pure WSi_2 phase).

Summary

The oxidation resistance of tungsten is low which can be a problem for different applications. Oxidation of tungsten starts already at low temperatures. The aim of this work was to develop tungsten alloys containing alloying elements like silicon or chromium to improve the oxidation resistance. The alloying content was kept relatively low because the typical properties of tungsten necessary especially for the fusion application should be maintained. Elemental powder mixtures were used for high energy milling in order to get a homogeneous distribution of the alloying elements. During milling silicon was distributed in tungsten. The grain size was reduced and a partial amorphization can be assumed based on XRD analysis. The high energy milled powders were consolidated by hot pressing getting a density of >95%. Depending of the alloying content the microstructure consists of pure tungsten with the embedded intermetallic phase W_5Si_3 or a mixture of intermetallic phases (WSi_2 and W_5Si_3) as it can be expected from the phase diagram.

Oxidation experiments have shown that the alloying elements lead to an improved oxidation resistance. Nevertheless a dense SiO_2 scale couldn't be formed due to thermodynamic and kinetic reasons. A mixed oxide scale with an outer porous SiO_2 layer was observed. The thickness of the different layers depends on the oxidation temperature. In order to obtain a dense SiO_2 scale higher silicon concentration or special condition for oxidation should be necessary taken into account that high silicon concentration lead to the formation of intermetallic phases connected with an embrittlement.

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