Investigation the Oxidation Resistance of TZM Alloy Prepared by Spark Plasma Sintering Method
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Abstract
TZM is one of the most important molybdenum (Mo) based alloy which has a nominal composition containing 0.5–0.8 wt% titanium (Ti), 0.08–0.1 wt% zirconium (Zr) and 0.016–0.02 wt% carbon (C). It is a possible candidate for high temperature applications in a variety of industries. However, the rapid oxidation of TZM at high temperature in air atmosphere can be considered as a main drawback. In this study, TZM alloy was sintered with B4C addition by using spark plasma sintering (SPS) method. B4C was dispersed in the matrix in order to increase oxidation resistance by formation of Mo-B based phases during the sintering process. The effects of B4C addition was investigated in terms of oxidation resistance, densification behavior, Vickers hardness and microstructure.

1. Introduction
Molybdenum is significant refractory metals due to its high melting point, good thermal conductivity and low thermal expansion coefficient needed for many high temperature applications [1]. Since recrystallization temperature of Mo based alloys are higher than the pure one in most applications done above 1000 °C materials selection is made in the favor of Mo based alloys [2]. The beginning of recrystallization can be inhibited by the addition of fine particles dispersed such as carbides [3]. The fine particles added in to the TZM alloy form precipitates TiC and ZrC in the grain boundaries and through the grains of molybdenum. These precipitates contribute to solid-solution strengthening and behave as inhibitors in recrystallization [4-5]. Homogeneously dispersed carbides increase the recrystallization temperature of pure molybdenum approximately 500 °C. Besides the recrystallization temperature, higher creep and tensile strength are obtained by TZM alloy at temperatures above 1000 °C [4].

The major drawback of the Mo and Mo based alloys are low oxidation resistance at elevated temperatures [4]. TZM alloy can be used in air or oxidizing atmosphere without any restriction below 400 °C. However, mass gain observed between 400 and 650 °C due to the formation of oxidation products such as MoO2 and other oxides (MoO2), where 2 ≤ z< 3. Rapid vaporization of MoO3 results in mass loss and increase in oxidation rates above 650°C [6-8].

Mo is not suitable to be used in practical applications without protection system in oxidizing atmosphere at elevated temperature [9]. The protection systems applied to Mo and Mo-based alloys can be considered as two groups, mainly alloying and coating [10]. Alloying could provide a formation of protective layer on the surface of base metal during oxidizing conditions.

In this study, B4C powder in varying amounts was dispersed in the pre-mixed TZM powder in order to densify TZM alloys at relatively lower temperatures for shorter holding times compared to the conventional ones. A pulsed direct current passes through the graphite punch rods and dies simultaneously with a uniaxial pressure to sinter in SPS method. During the process grain coarsening can be suppressed by rapid heating and the densification of is accelerated at higher temperatures.

The sintered samples were investigated in terms of densification, phase analysis, microstructure, Vickers hardness and oxidation resistance.

2. Experimental Procedure
Pre-mixed TZM (H.C. Starck Corp.) and B4C (H.C Starck Corp. Grade HS) powders were used as starting materials. The raw materials were weighed in the quantities calculated and mixed by Turbula 8 h in order to get a homogeneous powder mixture. A graphite die with 50 mm inner diameter was filled with the powder mixture and then spark plasma sintering process (SPS-7.40 MK-VII, SPS Syntex Inc) was conducted. The powder was sintered at 1420 °C for 300 s with a heating rate of 100 °C/min. A uniaxial pressure of 40 MPa and a pulsed direct current (12 ms/on, 2 ms/off) were applied during the entire SPS process under vacuum. Sintered specimens were 50 mm in diameter and approximately 4 mm thickness. Then, the characterizations were performed. The bulk density of the specimens were determined by Archimedes' method.
Possible phases which could form during sintering process was calculated by FactSage© software. The crystalline phases were identified by X-ray diffractometry (XRD; MiniFlex, Rigaku Corp.) in the 20 range of 10-90° with Cu-Kα radiation (λ = 1.54 Å). Vickers hardness (HV) values were gathered (VHMOT, Leica Corp.) under a load of 9.8 N for 12 s and their average values were taken after 20 indentations. The microstructural characterization was carried out by scanning electron microscopy (FESEM; JSM 7000F, JEOL Ltd.). Energy dispersive spectroscopy (EDS) was used to investigate the surface elemental analysis.

Oxidation behaviors of the specimens were studied in air condition at 600, 800 and 1000 °C. The samples were placed into alumina crucible and put in a laboratory muffle furnace after surface area of them were measured in order to calculate mass change in mg/cm². The samples were weighed before and after heat treatment. They were heated from room temperature (RT) to determined temperature by a heating rate of 10 °C/min then exposed to 60 min dwell time and cooled to RT inside the furnace.

3. Results and Discussion

Particle size of TZM and B₄C powders were measured by laser particle sizer (Malvern Mastersizer 2000). Average particle size of TZM and B₄C powders were obtained as 20.3 ±0.06 μm and 1.78 ±0.04 μm, respectively. The morphology of the TZM powder and the particle size distribution were given in Fig. 1(a) and (b). Although in the SEM image the particle sizes were seemed to be around 2μm, the average particle size distribution was determined to be around 20μm. This could be due to the cold welding of particles in the preparation of pre-mixed powders. The morphology of the TZM powder and the particle size distribution were given in Fig. 1(a) and (b).

Thermodynamic calculation was performed by FactSage© software which is able to calculate free energy of the system and give a result of chemical equations by a wide integrated database. Depending the temperature, the reaction products was calculated over the temperature range of 100-2000 °C for addition of 5 wt% B₄C in Fig. 2. Mo₂B phase was observed in all temperatures. The amount of Mo was reduced slightly by the increase in temperature up to 1225 °C. Then, a sudden decrease in the amount of Mo was seen and some impurities was formed such as Ti, Zr, C and B which resulted in a decrease in the purity of Mo. Moreover, Mo₂C formed and its amount was increased by rising temperature. Added to this, TiC and ZrC phases were found in a complex compound over the temperature of 1250 °C.

Displacement of the punch rods due to the shrinkage of the powders during the SPS process was measured in micron sensitivity. The data were used to determine the starting and ending temperature of the densification. Ending temperature of the densification also referred as the sintering temperature of samples. Fig. 3 shows the densification behavior of the samples at 800-1420 °C and isothermal displacement at 1420 °C for 300 s. The shrinkage of monolithic TZM powders started at 1020 °C and stopped at 1420 °C. The addition of B₄C increased the starting temperature of the shrinkage.

A density of 9.93 g/cm³ was measured for monolithic TZM (theoretical density: 10.16 g/cm³) which was equal to relative density of 97.7%. The density values decreased by an increase in the amount of B₄C. With the addition of 5 wt% B₄C into TZM the density was decreased from 9.93 g/cm³ to 9.41 g/cm³.

Theoretical hardness of TZM was given as 2 GPa in the literature [11]. In present study, the hardness of monolithic TZM measured as 1.9 GPa was compatible with literature. The values increased by addition of B₄C into TZM. The hardness value was increased from 1.9 GPa to 7.8 GPa with addition of 5 %wt B₄C.
The X-ray diffraction analyses of the monolithic TZM and TZM-B₄C specimens with variable amount of B₄C were shown in Fig 4. The characteristic peaks of molybdenum (JCPDS: 42-1120) were observed for all compositions. The peaks for α-Mo₂C (JCPDS: 31-0871) started to be apparent by the addition of 1 wt% B₄C, while Mo₂B phase (JCPDS: 25-0561) could be detected after 2 wt% B₄C addition. Almost all of the characteristic peaks of Mo₂B and Mo₂C were determined for TZM-5B₄C specimen. Moreover, the intensities of the peaks also showed that the amount of Mo₂B was increased by the addition of B₄C, eventhough the pure Mo was decreased in the structure. These XRD results verified the thermodynamic calculations. However, TiC and ZrC phases calculated were not detected by XRD. This can be due to low amount of Ti, Zr and C in the pre-mixed TZM powder [12].

Table 1 shows the mass change values of specimens during oxidation tests for all composition and temperature. When mass loss of monolithic TZM and TZM-5B₄C specimens were compared at 1000 °C, there was an approximately 66.3% decrease in mass loss by addition of 5% B₄C. Yang et al. investigated the effect of La addition into TZM alloy on oxidation behavior. They evaluated the decrease in mass loss as an enhancement in oxidation resistance [13]. It is assumed that formation of Mo₂B by addition of B₄C into TZM alloy could provide a resistance to oxidation according to specific mass change results.

Table 1. Mass changes of the specimens after oxidation test at 600-1000 °C

<table>
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<tr>
<th>Holding Temperature (°C)</th>
<th>Specific Mass Change (mg/cm²)</th>
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<tbody>
<tr>
<td>600</td>
<td>0.065 0.054 0.048 0.039 0.020</td>
</tr>
<tr>
<td>800</td>
<td>0.043 0.038 0.033 0.028 0.020</td>
</tr>
<tr>
<td>1000</td>
<td>0.720 0.685 0.659 0.639 0.622</td>
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Fig. 5 shows the SEM images of the surface morphology of the samples oxidized at 600, 800 and 1000 °C. Oxide products were observed on the surface of the samples. However, surface morphology of the samples oxidized at 600 °C (Fig. 5(a)) was different from the ones oxidized at 800 and 1000 °C (Fig. 5(b-c)). Differences could derive from formation of the different oxide types of Mo on the surface. The oxides caused to a slight increase in mass was in type of MoOₓ (2<z<3) were occurred at 600 °C. However, mass loss was observed by formation of MoO₃ over this temperature. Lamellar type structure was shown on the surface at 800 and 1000 °C, indicating that this morphology belongs to MoO₃. Yang et al. also observed lamellar slices on oxidation tests of TZM and TZM-La [6]. The lamellae particles composed of volatile MoO₃ were more dense for monolithic TZM when compare to TZM-5B₄C. Formation of less MoO₃ on surface by
increasing amount of B₄C addition demonstrated the enhancement of oxidation resistance.

Figure 5. SEM images of the surface morphology of oxidized samples at 600 ºC (a), 800 ºC (b) and 1000 ºC (c)

4. Conclusion

Pre-mixed TZM powders with variable amount of B₄C between 0-5 %wt were sintered by spark plasma sintering method. Thermodynamic calculations showed that Mo₂B, Mo₂C, Mo (not pure) and TiC-ZrC complex carbides were possible phases which could be formed during sintering process at 1420 ºC. The density values decreased by an increase in the amount of B₄C. The sintering was performed at 1420 ºC under 40 MPa for 5 min. Vickers hardness was increased from 1.9 to 7.8 GPa by addition 5 wt% B₄C into TZM. Mass loss after the oxidation test at 1000 ºC for 60 min was decreased ~66% in the same amount of B₄C addition. Oxidation resistance of TZM was improved by formation Mo₂B.

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References