Sintering activation energy MoSi$_2$-WSi$_2$-Si$_3$N$_4$ ceramic

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Abstract. The activation energy of sintering process was calculated based on dilatometric studies of shrinkage processes (Mo,W)Si$_2$ + Si$_3$N$_4$ composite ceramic. (Mo,W)Si$_2$ powders was obtained by solid-phase solutions of 70 wt% MoSi$_2$ and 30 wt% WSi$_2$ by SHS in the ISMAN RAS. The concentration rate Si$_3$N$_4$ was from 1 to 15 wt.%. The sintering was carried out to 1850°C in Ar atmosphere the heating rate of 5, 10, 12 and 15°C/min by the way of dilatometer tests. Based on the differential kinetic analysis method (Friedman's method), the sintering process activation energy of (Mo,W)Si$_2$ + Si$_3$N$_4$ were calculated. The two-stage sintering process and the dependence of the activation energy on the Si$_3$N$_4$ content was shown. Average value of 370 kJ/mol for Q was obtained.

1. Introduction

MoSi$_2$ intermetallic compound is one of the candidate materials for high temperature applications because of its moderate density ($\rho = 6.23 \text{ g/cm}^3$), high melting point (2030 °C), excellent oxidation resistance at high temperatures ($\leq 1000$ °C) and low electrical resistivity ($\sigma = 21.6 \mu \Omega\text{cm}^2$) [1]. MoSi$_2$ has the highest oxidation resistance above 1000°C among all disilicides. The resistance to oxidation at high temperatures is due to the formation silicon oxide (SiO$_2$) coating on the surface, it prevents diffusion of oxygen.

MoSi$_2$-based materials are commonly used as a heating element for atmospheric high-temperature furnaces and protective coatings because of a unique properties: resistance to oxidation at high temperatures and electrical conductivity. The pure MoSi$_2$ has not been widely spread as a structural ceramic (for example, for the production of turbine blade) [2] due to brittleness at room temperature, creep at high temperatures, and low oxidation resistance at 500 to 800 °C. Molybdenum disilicide is subject to catastrophic oxidation ("pesting") in this temperature range [3] and is completely destroyed forming MoO$_3$ and SiO$_2$.

Since the discovery of molybdenum disilicide many different additives have been investigated to improve the properties of MoSi$_2$ (for example, WSi$_2$, TiB$_2$, ZrO$_2$, Cr$_2$Si$_3$, Y$_2$O$_3$, Mo$_5$Si$_3$, BN, NbB, Si$_3$N$_4$, etc.) [4,5,6 and 7]. The recent articles are devoted to the study of the silicon nitride (Si$_3$N$_4$) additive. Si$_3$N$_4$ ceramic samples have phenomenal strength, according to some data, their flexural strength are 1000-1200 MPa [8], Si$_3$N$_4$ ceramic has good resistance to oxidation up to 1500 °C [9]. The main drawback of this material, which prevents its use in its pure form, is the energy-consuming
process for obtaining dense ceramics, usually hot isostatic pressing (HIP) or hot pressing (HP) is used together with sintering additives to lower the firing temperature [3].

Since the earliest studies of sintering processes many models have been developed to relate the sintering rate to particle characteristics, density, atmosphere and sintering temperature. The kinetic parameters determination is necessary to predicting the thermal ageing process development: at what temperature and for how long can a given substance be used without impairing its properties. Computer data processing allows modeling and predicting even overlapping multi-stage processes. There are three main modifications of the iso-conversion method:

- differential (Friedman) [10];
- integral (Flynn-Ozawa-Wall) [11-12];
- improved integral, based on non-linear procedures (Vyazovkin) [13].

The determining kinetic parameters by Friedman method is based on the iso-conversion principle, that the reaction rate at a constant conversion degree \( \alpha \) is only a function of temperature. This method allows us to find the activation energy (E) (or the dependence of E on \( \alpha \)) without knowing the exact form of the dependence f(\( \alpha \)).

In previous work [14-15], it was shown that composites based on molybdenum disilicide with 30 and 50 wt% WSi_2 additive are characterised by a decrease in porosity and an increase in the flexural strength. The influence of tungsten disilicide in the MoSi_2 - WSi_2 system on the properties of ceramic samples Mo_xW_{1-x}Si_2, (where \( x \) varied from 1 to 0.3) was studied in detail in the paper [14]. It has been established that during solid-phase sintering of components mechanical mixtures at 1650-1800 °C for 30 minutes, complete interaction between disilicides of molybdenum and tungsten with formation a solid solution does not occur. Ceramic samples have greater strength and low porosity sintered from Mo_0.7W_0.3Si_2 powder (obtained by comminuting of cast sample and synthesised by SHS).

This work is aimed at dilatometric properties studying of Mo_0.7W_0.3Si_2 solid solution depending on the content of \( \alpha \)-Si_3N_4 reinforcing additive in Mo_0.7W_0.3Si_2 + Si_3N_4 composite. Conclusions are made about the sintering rate influence on the sintering start point displacement, relative shrinkage. The activation energy of the sintering process for Mo_0.7W_0.3Si_2 + Si_3N_4 (from 1 to 15 wt.%) are calculated.

2. Materials and methods of researches

The cast mixture 70 wt% MoSi_2 and 30 wt% WSi_2 (Mo_0.7W_0.3Si_2) [14], was obtained by the SHS method at the Institute of Structural Macrokinetics and problems of materials science of the Russian Academy of Sciences (ISMAN RAS) in Chernogolovka Russia and characterised by SEM, X-ray and granulometric analyzes. The dominant fraction in powder Mo_0.7W_0.3Si_2 is 10÷20 μm particles.

The Si_3N_4 powder was presented by well-crystallized silicon nitride whiskers, with an average length about 2 μm and a thickness up to 200 nm. The \( \alpha \)-Si_3N_4 content is not less than 95%, the specific surface area of the powder is 8.2 m^2/g. The impurities content are O_2 = 1.64 wt%, Fe = 0.023 wt%.

The powder was obtained by SHS method at the ISMAN RAS in Chernogolovka.

The Mo_0.7W_0.3Si_2 + \( \alpha \)-Si_3N_4 mixtures containing 1; 2.5; 5; 10 and 15 wt% (respectively 2.3, 5.6, 10.8, 20.3 and 28.8 vol%) of Si_3N_4 were prepared in a planetary mill (Pulverisette 5 from Fritsch GMBH, Germany).

The mixtures were formed in the cylinders about 6x10 mm at 200 MPa uniaxial pressing on a hydraulic press in a metal form at room temperature. The weight of each sample was about 1 g.

The microstructure and phase composition were examined on an electron microscope (Supra 50 VP (LEO, Germany) with an INCA Energy + Oxford microanalysis system with a prefix for local X-ray spectroscopy) and X-ray (Rigaku D/MAX 2500 with a rotating anode, Japan).

Dilatometric studies were carried out on a dilatometer (DIL 402C Netzsch, Germany), capable of recording up to 2000°C [16]. The sample was placed in a horizontal graphite holder equipped with a graphite pusher with a high-precision displacement transducer (measuring range 500-5000 μm). The thermocouple (tungsten-rhenium alloy) was in close proximity to the sample and accurately recorded its temperature, the second thermocouple (tungsten-rhenium alloy) is in the chamber with a heater. This chamber has an independent of the working chamber argon atmosphere. The flow of argon
introduced into the furnace was 70 ml/min, the heating rate was 5, 10, 12 and 15 °C/min, the heating was continued to 1850 °C, the isothermal section was 60 minutes, it was cooled to room temperature at a rate of 20 °C/min. The samples obtained after dilatometric studies density determined by archimedean method. Distilled water was used as a liquid.

Assuming isotropy in densification of all the specimens, the relative density of the sintered specimen \( \rho_s \) was calculated using the following equation

\[
\rho_s = \left[ \frac{1}{1 + dL/L_0 - \alpha(T - T_0)} \right]^3 \rho_g
\]

where \( dL/L_0 \) is instantaneous linear shrinkage obtained by the dilatometer test, \( L_0 \) is the initial length of the specimen, \( T \) is the measured temperature, \( T_0 \) is the room temperature, \( \rho_g \) is the green density, and \( \alpha \) is the coefficient of thermal expansion. From a practical point of view, \( \alpha \) is determined from the cooling steps of the dilatometer run \[17 \]. An average value \( \alpha \) as a function of temperature \( T \) by the following estimation equations was determined from the cooling steps of the dilatometer runs performed with the different heating rate adopted during our investigations \[17 \].

Young and Cutler \[17 \] have derived the sintering-rate equations that are applicable to quantitative analysis for shrinkage data measured under constant rates of heating (CRH) and estimated the activation energy to induce diffusion at the initial sintering stage. Wang and Raj \[22, 23 \] have derived the sintering-rate equation used for estimation of the activation energy at intermediate sintering stage by CRH technique. Matsui et al. \[24, 25 \] derived two sintering equations for constant heating rate as follows.

\[
\frac{dL}{L_0} = \frac{K\gamma\Omega D_0 R}{k_b} \exp \left( \frac{nQ}{RT^{2-n}} \right) \exp \left( -\frac{nQ}{RT} \right)
\]

where \( T \) is absolute temperature, \( C \) the heating rate, \( d\rho/dT \) the densification rate, \( Q \) the activation energy, \( R \) the universal constant of gases, \( f(\rho) \) the function of density, \( K \) the numerical constant, \( \gamma \) the surface energy, \( \Omega \) the atomic volume, \( D_0 \) the frequency factor, \( k_b \) the Boltzmann’s constant, \( a \) the particle radius, \( dL = L_0 - L \) the change in length of the compacts, \( L_0 \) the initial length of the compacts, and the parameters \( n \) and \( p \) the order depending on the diffusion mechanism. Eqs. (2) and (3) is applicable to the fractional shrinkages of <4%, which fulfill the initial or early stage sintering condition.

Using CRH experiments, the analysis method that is able to determine the diffusion mechanism at the initial sintering step is derived as follows: in Eq. (2), using the slope \( S_1 \) of the Arrhenius-type plot of \( \ln[TC \frac{d\rho}{dT}] \) against \( \frac{1}{T} \) at same density, the activation energy is expressed as:

\[
Q = -RS_1
\]

In equation (3), using the slope \( S_2 \) of the Arrhenius-type plot of \( \ln[T \frac{d(dL/L_0)}{dT}] \) against \( \frac{1}{T} \), the apparent activation energy is expressed as:

\[
nQ = -RS_2
\]

Equations (3)–(6) were used to determine the values of activation energy. Combining equations (4) and (5) we have:

\[
n = \frac{nQ}{Q} = \frac{S_2}{S_1}
\]
3. Results and discussion
In this paper cast Mo$_{0.7}$W$_{0.3}$Si$_2$ solid solution dilatometric studies were carried out depending on the α-Si$_3$N$_4$ reinforcing additive content in the composite. The dilatometry was carried out at rate of 5, 10, 12 and 15 °C/min to 1800 °C. Figures 1 and 2 highlight the change of the shrinkage Mo$_{0.7}$W$_{0.3}$Si$_2$ with Si$_3$N$_4$ additive (from 1 to 15 wt.%).

![Figure 1](image1.png)

**Figure 1.** The curve of the continuous shrinkage of Mo$_{0.7}$W$_{0.3}$Si$_2$ and Mo$_{0.7}$W$_{0.3}$Si$_2$ + 1; 2.5 and 5 wt.% Si$_3$N$_4$, heating rate 10 °C/min

![Figure 2](image2.png)

**Figure 2.** The curve of the continuous shrinkage of Mo$_{0.7}$W$_{0.3}$Si$_2$ and Mo$_{0.7}$W$_{0.3}$Si$_2$ + 5; 10 и 15 wt.% Si$_3$N$_4$, heating rate 10 °C/min

The figure below shows the change of the shrinkage and shrinkage rate of Mo$_{0.7}$W$_{0.3}$Si$_2$ + 1 and 15 wt.% Si$_3$N$_4$ compact during non-isothermal sintering at three different heating rates of 5, 10 and 15 °C/min, respectively (figure 3). In the previous work [14-15] it was shown that Si$_3$N$_4$ additive concentration increase led to shift the composite sintering beginning point from 1150 °C to 1697 °C and the composite shrinkage changed from 6.75% to 20.21% (respectively, at 1 and 15 wt.% Si$_3$N$_4$). The comparative data of the sintering response is summarised in Table 1.
Figure 3. Effect of heating rate on the shrinkage and shrinkage range of (A) Mo<sub>0.7</sub>W<sub>0.3</sub>Si<sub>2</sub> + 1 wt.% Si<sub>3</sub>N<sub>4</sub> and (B) Mo<sub>0.7</sub>W<sub>0.3</sub>Si<sub>2</sub> + 15 wt.% Si<sub>3</sub>N<sub>4</sub> compact as a function of temperature

Table 1. Dilatometry data for Mo<sub>0.7</sub>W<sub>0.3</sub>Si<sub>2</sub> + 1;5;10 and 15 wt.% Si<sub>3</sub>N<sub>4</sub> powder compact sintered at different heating rates (5,10 and 15 °C/min).

| Heating rate (°C min<sup>-1</sup>) | Mo<sub>0.7</sub>W<sub>0.3</sub>Si<sub>2</sub> + 1 wt.% Si<sub>3</sub>N<sub>4</sub> | Mo<sub>0.7</sub>W<sub>0.3</sub>Si<sub>2</sub> + 5 wt.% Si<sub>3</sub>N<sub>4</sub> | Mo<sub>0.7</sub>W<sub>0.3</sub>Si<sub>2</sub> + 10 wt.% Si<sub>3</sub>N<sub>4</sub> | Mo<sub>0.7</sub>W<sub>0.3</sub>Si<sub>2</sub> + 15 wt.% Si<sub>3</sub>N<sub>4</sub> |
|----------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 5                               | 1234 1282 1297 1531 1561 1675 1662 1721 |
| 10                              | 1240 1284 1322 1560 1614 1729 1723 1766 |
| 15                              | 1261 1299 1360 1588 1629 1750 1749 1772 |

Increasing the heating rate increased the temperatures at which sintering starts (arbitrary set to 0.5% shrinkage, T<sub>Onset</sub>) and proceeds. For example, T<sub>Onset</sub> 1234 and 1261 °C for Mo<sub>0.7</sub>W<sub>0.3</sub>Si<sub>2</sub> + 1 wt.% Si<sub>3</sub>N<sub>4</sub> when heating rates increased from 5 to 15 °C/min. It is a usual behaviour for this systems [17]. For the same reason, the shrinkage rate curves of specimens shifted to higher temperature, as the heating rate increased. The maximum shrinkage rate was found to be dependent on heating rate, i.e. the higher the heating rate, the higher is the instantaneous shrinkage rate whatever is the temperature.
Figure 4. Arrhenius type plots for estimate of activation energies of sintering Mo0.7W0.3Si2+1 wt.% Si3N4

Figure 5. Plot of ln[Td(dL/L0)/dt] against 1/T of Mo0.7W0.3Si2 + 1 wt.% Si3N4 at different heating rates (5; 10; 12 and 15 °C/min)

The activation energy (Q) and the apparent activation energy (nQ) of diffusion, and order on diffusion mechanism (n) can be appraised by applying Eqs. (2), (3) and (6) to the results in figure 3. Eq. (2) is applied in the following way. For each heating rate (dT/dt)=c, both T and (dT/dt) at the same relative density were determined, and their values were plotted as ln[Tc(dρ/dT)] against 1/T (figure 4). The Q at each relative density was determined from the slope of the straight line and as summarised in Table 2. On the other hand, Eq. (3) is applied in the following way. In the fractional shrinkage range of <4%, the nQ was determined from the slope of the straight line in the plot of ln[Td(dL/L0)/dt] against 1/T (figure 4). The proper plots at different heating rate are shown in figure 5. As summarised in Table 2.

The activation energy for each concentration of the composites was calculated. It was shown that activation energy decreased to when the concentration of Si3N4 increase. Average value of 370 kJ/mol for Q was obtained. All values of the activation energy are given in Table 2. The average value of 440 kJ/mol for nQ was obtained.
Table 2. Activation energy, apparent activation energy, and order on diffusion mechanism at the initial sintering stage of Mo0.7W0.3Si2 + 1; 2.5; 5; 10 and 15 wt.% Si3N4

|          | 1 wt.% Si3N4 | 2.5 wt.% Si3N4 | 5 wt.% Si3N4 | 10 wt.% Si3N4 | 15 wt.% Si3N4 |
|----------|--------------|----------------|--------------|---------------|--------------|
| Q, kJ/mol| 396±51       | 402±54         | 389±36       | 344±23        | 319±36       |
| nQ, kJ/mol| 550±88       | 540±64         | 400±64       | 373±83        | 349±76       |

4. Conclusion
Sintering in Ar atmosphere of Mo0.7W0.3Si2 + 1; 2.5; 5; 10 and 15 wt.% Si3N4 powder has been investigated by the way of dilatometer tests. Using the constant rates of heating technique and applying the analytical method, the activation energy value as Q = 370 kJ mol. The activation energy decrease when the concentration of Si3N4 increase in the composite.

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