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Measurement of the Electrical Conductivity of Zircon at High Temperatures

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Abstract

Measurements of the electrical resistance of zircon ZrO_2+SiO_2 at the temperature interval from 1100 to 2500°C were made in the wolfram crucible placed in argon atmosphere. Electrical conductivity of zircon was estimated solving parameter identification problem for crucible-material-electrode system. Changes of activation energy are estimated in the phase transition area of the sample. Results of calculations are compared with literature data.

Introduction

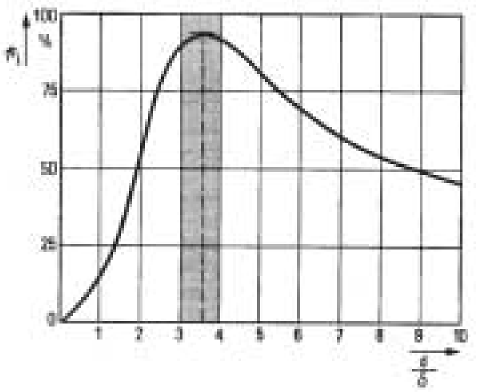

Fig. 1. Induction heating efficiency [9]

Cheap technologies for melting of ceramics, oxides and glasses, that ensure certain material quality and properties, must be developed for the mass-production of these high temperature melting materials. Induction melting in the cold crucible is a technology that is perspective for melting of oxides because the crucible material does not pollute the melt like using conventional methods, e.g. ceramic crucibles. Data about the electrical conductivity σ of the oxides at high temperatures (even higher than the melting temperature of material) are necessary for the design and construction of energy-effective induction furnaces.

Tab. 1. Conductivity and activation energy of oxides

Material	Temp., °C	Conduct., 1/(Ω·m)	Activat. en., 1/(Kcal·mol)	Melting temp.,°C
Al_2O_3	1875	0.005	42.5	2015
	2127	384		
	2424	769		
	2725		21.2	
47.25% Al_2O_3+ CaO	1500	35		
BeO	2611	1180	20	2550
Y_2O_3	2443	1843	13.7	2410
ScO	2509	1670	12	
TiO_2	660	3100	46	2325

The penetration depth $\delta = \frac{1}{\sqrt{\pi\sigma f\mu_0}}$ (σ is the electrical conductivity of the material, f is the working frequency of the generator and μ_0 is the magnetic constant) of the electromagnetic field affects efficiency of the heating. Heat losses grows up when temperature rises and it is very important to get optimal r_0/σ ratio (Fig. 1) [9] near the melting temperature. Measurement of electrical conductivity of oxides is very complex problem because of the high melting temperature (Tab.1) and therefore high chemical activity of the oxides.

Very often such physical properties as electrical or thermal conductivity are known only near the normal conditions. Data about electrical properties at high temperatures from reference books very often are rather old or contradictory. There are theories describing how these properties change when physical conditions are varied, but their results sometimes are unstable. It is very difficult to verify existing data under extreme conditions and to get new experimental data for further calculations. Aims of this work were:

1. Check of the ability to make qualitative measurements of the electrical resistance of zircon using an existing equipment at high temperatures (above 2400^0C) ;
2. Calculation of the electrical conductivity of zircon in order to get the temperature dependence;
3. Carrying out values of activation energy of the sample;
4. Comparison of the results with literature data.

1. Equipment

1.1. Characteristics of Zircon

Zircon $ZrSiO_4$ (Zr 51% and Si 14.5% of weight [6]) was chosen as material for our experiments. Powder of zirconium oxide ZrO_2 and powder of silicon oxide (SiO_2) were used as primary materials. Zirconium oxide has a melting temperature about 2700°C, but when it is mixed with silicon oxide, the melting temperature is lower.

Tab. 2. Interaction temperatures (K) of the selected high temperature materials [2].

	C	W	Mo	ThO_2	ZrO_2	MgO	BeO
BeO	2300	2000	1900	2100	1900	1800	---
MgO	1800	2000	1600	2200	2000	---	1800
ZrO_2	1600	1600	2200	2200	---	2000	1900
ThO_2	2000	2200	1900	---	2200	2200	2100

Zirconium oxide is stable in oxidized and moderate reduction atmospheres in contact with many metals and other oxides. When it is heated up to temperatures above 1000°C it has destructive expansion of volume [2].

The sample was made by pressing the powders together. The volume of the crucible was complete filled with the powder, but during the experiment the height of the sample becomes lower because of sintering and vaporization of materials. Zircon can be taken out from the crucible if it was not liquid during the heating process, but if it is heated above the melting temperature it sticks to the walls of the crucible and it could not be taken out without melting.

According to the state diagram (Fig. 2) [6] the temperature of about 2400°C must be reached to get a liquid phase of zircon. But the melting temperature of silicon oxide is less and the pressure of vapours is about one atmosphere at 2200°C (temperature of vaporisation is 1800°C). Because of this silicon intensively comes out and it changes the chemical composition of the sample so that can influence the final measurements.

1.2. Experimental Equipment

A crucible made of wolfram (W) which has a melting temperature 3410°C [2] was used for the melting process (Fig. 3). The height of the crucible was 80 mm, the diameter was 80 mm and the inner diameter was 64 mm.

The crucible was covered by a wolfram cap and molybdenum bars. For heating the sample a Chochralsky machinery was used. This device is a crucible induction furnace with vacuum chamber. The furnace supply generator works at 8 kHz frequency. The inductor (10 turns) is made of copper and water-cooled. The maximum voltage is about 100 V.

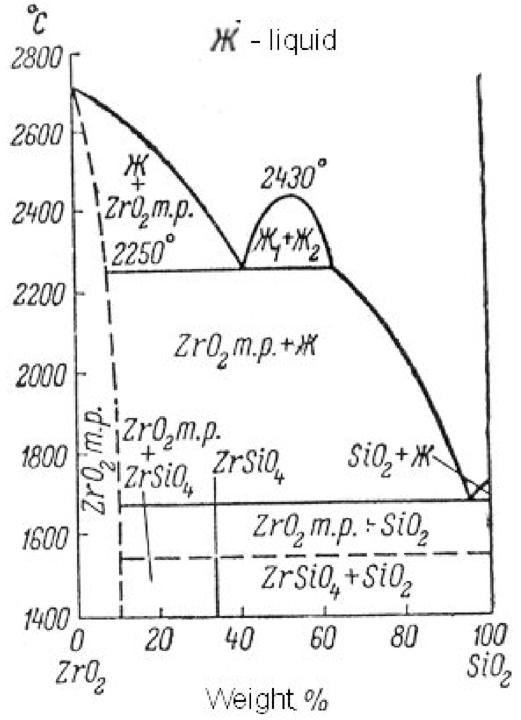

Fig. 2. State diagram of $ZrSiO_4$ [6]

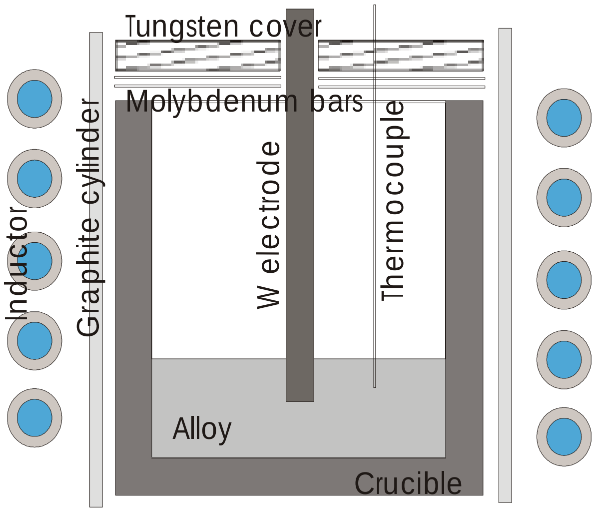

Fig. 3. Scheme of the crucible

Tab. 2. Characteristics of thermocouples [2]

	Max. working temp., °C	Ther. volt. at 1000°C, mV	Ther. volt. at 2000°C, mV
W-Re	2200	15.9	28.0
W-Mo	2400	-0.8	5.30
W-Ir	2200	14.25	38.88

The wolfram crucible with the sample was placed in the vacuum chamber. Isolation and the inductor are arranged around the crucible. The first layer of isolation was realized by the powder of magnesia (MgO). The second layer was a quartz cylinder. In the third experiment only a graphite cylinder was used. To reduce chemical reactions between sample, crucible, isolation and electrodes all experiments took place in argon atmosphere.

One electrode for the resistance measurements was attached to the moving twig, that is usually used for crystal holding, in the vacuum chamber. The second electrode was attached to the bottom of the crucible. Resistance measurements were made using alternating current at 1 kHz frequency by voltmeter-ammeter method. The voltage on the sample and on the precision resistor was controlled and finally the resistance value was calculated using the Ohm's law.

We did not use pyrometer for temperature measurements because of the problems as follow:

1. The melting point of SiO_2 is about 1800°C and if the temperature is higher then the vaporisation of SiO_2 becomes very serious problem. The windows for the temperature control was covered by some settlements after the experiment. So, it was not clear, how it changes characteristics of the pyrometer.

2. The pyrometer measured the temperature of the crucible, not of the melt and we could not control probable errors when interpolating values.

3. We had not mechanism to calibrate pyrometer at temperatures higher than 2000°C.

Therefore two thermocouples were used for temperature measuring. They were placed in the hot zone without any thermal protection. The first was W-Re and another one was W-Mo (Tab. 2).

Characteristic of W-Re thermocouple shows that the measuring interval is up to 2400°C, but working without thermocouple protection in the hot zone limited this range down to 2000°C. W-Mo thermocouple was controlled using W-Re thermocouple and vice-versa.

The other electrode placed in the crucible was made of iridium wire. It was intended to indicate about the temperature of melting point of iridium (2447°C). It was connected to a tester which indicated the resistance of this wire.

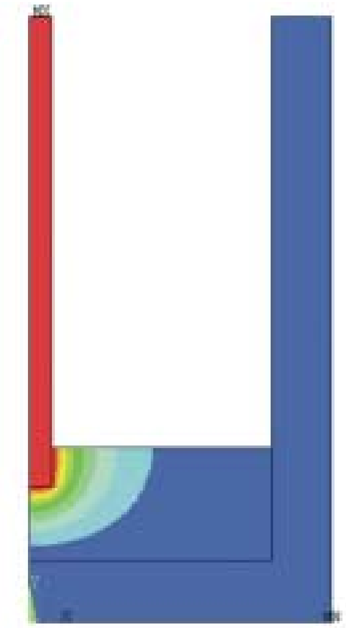

Fig. 4. Electrical potential distribution in the sample calculated by ANSYS

2. Mathematical Model and Calculations

There is a problem to calculate electrical conductivity after the experimental data measured. This problem usually is called problem of parameter identification. In our case electrical conductivity depends on the measured resistance, on the distance between the electrode and the crucible and on the height of the material in the crucible:

$\sigma = \sigma(R, h, h_{sample})$.

Last two parameters can change during the experiment and are known not so precisely. So the model must give opportunity to vary all these parameters and get the conductivity σ as a function of the measured resistance. For example, height of the sample changes because of sintering and vaporisation. These parameters are determinative for the error of the calculations.

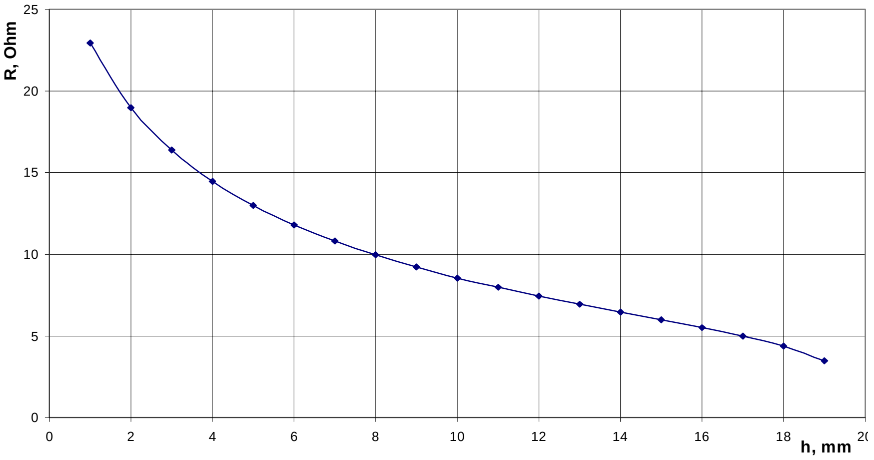

Fig. 5. Dependence of measured resistance on the distance from the bottom of the crucible

Mathematical model based on the field equations was made for the conductivity calculations. A model consists of three regions: wolfram electrode, zircon sample and wolfram crucible. Each region has its own electrical conductivity. Potential equation for each region is expressed as (in the case of stationary current):

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \varphi}{\partial r}\right)+\frac{1}{r^2}\frac{\partial^2 \varphi}{\partial \varphi^2}+\frac{\partial^2 \varphi}{\partial z^2}=0 \tag{1}$$

There are additional conditions:

1. The electric-potential is equal on the inner border between the regions;
2. There is a constant potential difference between the top of the electrode and the bottom of the crucible;
3. The condition that the current does not flow through the walls is expressed by equation:

$$grad_n \varphi = 0 \tag{2}$$

Sample and crucible with electrode were divided into elements (mashed) and for each element values of electrical field, potential and current were calculated (Fig. 4). The voltage at the sample is known and this gives the opportunity to calculate the resistance of the sample using the Ohm's law.

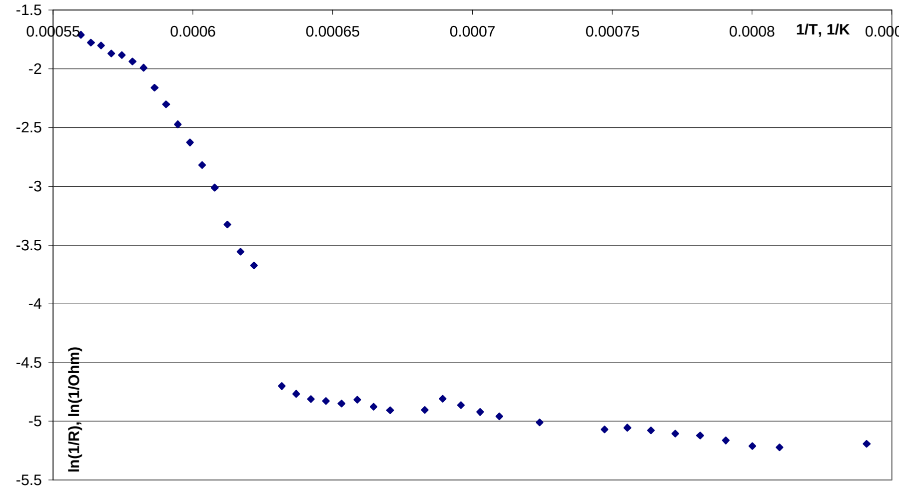

Fig. 6. Dependence of ln(1/R) on the temperature

This model helps to determine how the electrical conductivity depends on such parameters as measured resistance, distance between the electrode and the bottom of the crucible (Fig. 5) and the height of the material in the crucible. Two parameters can be set constant and then the electrical conductivity dependence on the third parameter can be calculated. While changing the electrical properties of the material (zircon area) we get the dependence of the electrical conductivity on the measured resistance. The model illustrates that $\sigma = const / R$. This is in accordance with theory and $const = 28.8$ $(\Omega{*}\mathrm{m})^{-1}$ in our case.

The value of measured resistance has limit of about 0.1 Ω) where this model can not be used because of large indeterminations.

3. Results

Experimental data are shown on the chart (Fig. 6) and the melted sample is shown on picture (Fig. 7).

The dependence of the electric conductivity on the temperature can be approximately expressed as :

$$\sigma = A \cdot e^{-\frac{E_a}{kT}} \tag{3}$$

where A is a constant, E_a is the activation energy, k is the Boltzmann constant. So the logarithm of the electric conductivity is proportional to $1/T$. There are two linear regions on the chart, that shows this dependence (Fig. 6), and cross point temperature between these regions approximately is equal to phase transition temperature. On the system state diagram (Fig. 2) is shown that SiO_2 has the phase transition at 1750°C, which can influence the values of the resistance.

The value of the electrical conductivity at 2500°C estimated with the ANSYS modelling, is $\sigma = 70$ *1/(Ω·m)*.

Fig. 7. Our samples after different experiments.

For the calculation we used the following data: resistance of the sample was 0.4 Ω, distance between electrode and the bottom of the crucible was 10 mm and the level of the material in the crucible was 15 mm. A second value which resulted from the analytical calculations is $\sigma = 65$ *1/(Ω·m)*.

Conclusions

1. It was shown that such experiments can be made using standard experimental and measuring equipment.

2. The experiment carried out that the electrical conductivity depends on the temperature as

$$\sigma \sim e^{-\frac{E_a}{kT}}.$$

Tab. 3. Values of activation energy

Temperature, °C	Activation energy E_a, kcal/mol	Activation energy E_a, eV
1100÷1700	5.5±0.6	0.24±0.03
1700÷2400	52±5	2.2±0.2

3. The dependence of the electrical conductivity of zircon ($ZrSiO_4$) on the temperature was carried out. The conductivity at a temperature of 2500°C was determined as $\sigma = 70$ 1/(Ω·m). This value is in accordance with data from other sources.

4. Values of the activation energy were determined for two temperature intervals (different phase states (Tab. 3)).

5. The experimental equipment and the mathematical model can be used to analyse systems like this and to calculate the influence of different factors on the measurements.

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