

Dynamics of Incongruent Melting of ZrO_2 - SiO_2 in Inductor Crucible

V. Frishfelds, A. Jakovics, A. Muehlbauer, B. Nacke

Abstract

Numerical modelling of high frequency inductive heating of $ZrSiO_4$ with high processing temperature in inductor-crucible furnace is considered. Specifics of melting of this two-component mixture in comparison with ZrO_2 are discussed. Necessary initial heating of the load is performed by insertion of Mo ring. Melt flow is described using equations for incompressible fluid. Different regimes of voltage, current, and gas burner during a set of stages of induction process are studied. The shrinkage of porous material is included. Basing on the numerical studies, the characteristic power requirements and main heat losses are estimated.

Introduction

Melting of $ZrSiO_4$ is essentially different from melting of one-component oxide ZrO_2 [1] despite the properties in both cases are quite similar for purely solid and liquid cases. This occurs due to continuous incongruent melting. According to phase diagram in Fig. 1, SiO_2

part melts first at 1960 K and ZrO_2 continuously afterwards up to 2632 K. Between this range of temperatures there is yet another discrete phase transition point at 2523 K, where considerable part of ZrO_2 melts.

High frequency skull melting in inductor crucible furnace with skull layer as an insulator is used for heating. This works quite well for treatment of oxide materials with low heat and electrical conductivities at room temperature such as $ZrSiO_4$. Such furnace ensures high purity of final material. Major heat losses and, consequently, power requirements depend significantly on the properties of the layer [1]. The main operational problem is energy transfer to melt at low temperatures that requires special regime of pre-heating. Here the initial heating by Mo ring is considered which oxidises at high temperatures. The appropriate control of power is

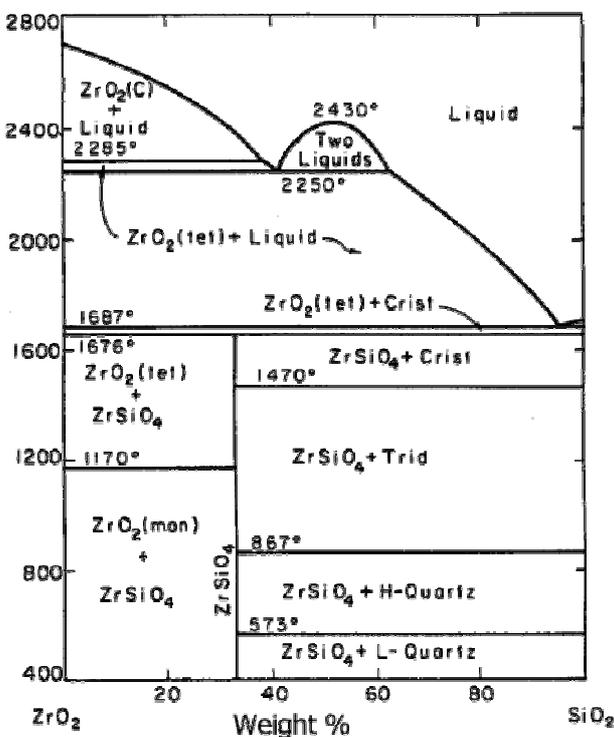


Fig. 1. Phase diagram of ZrO_2 - SiO_2 according to [2]

essentially required in all the cases ensuring the heating up to the processing temperatures.

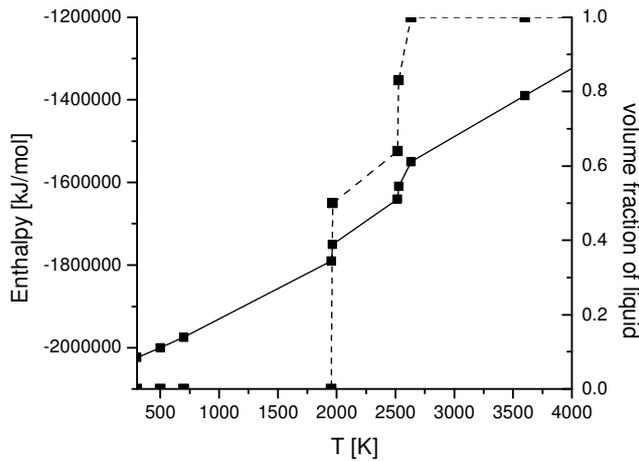


Fig. 2. Dependence of enthalpy (solid line) and liquid fraction (dotted line) on temperature for $ZrSiO_4$ mixture according to [4]

The characteristic shape of the furnace for melting of zirconium oxide and glass are as in [3]. The massive and water-cooled inductor acts also as the crucible. The typical values of frequency used for melting of oxides with poor conductivity are several hundreds of kHz. Axial-symmetric model of calculations has been made where the electromagnetic, heat and mass transfer processes have been examined.

1. Equations

In order to calculate the thermal and convection parts of inductive heating in the load, electromagnetic field must be known. The common way in axial symmetric case is to use vector potential $\mathbf{A}(t) = \mathbf{A}e^{i\omega t}$ with only one vector component, which in non-magnetic material gives following equation

$$\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial(rA)}{\partial r} \right) + \frac{\partial^2 A}{\partial z^2} = \mu_0 \sigma(T) \left(i\omega A + \frac{1}{r} \frac{\partial U}{\partial \varphi} \right), \quad (1)$$

where A is azimuthal component of complex vector potential \mathbf{A} ; U is the scalar potential the azimuthal gradient of which differs from zero only in the inductor. The conductivity of the oxide material rapidly increases with temperature, which requires frequent recalculation of electromagnetic field during heating of the load. The conductivity of the most of oxides and glasses increases exponentially with temperature like semiconductors

$$\sigma = \sigma_i \exp\left(-\frac{E_i}{2kT}\right) + \sigma_p \exp\left(-\frac{E_p}{kT}\right), \quad (2)$$

where $E_i > E_p$. The conductivity saturates close to melting temperature of the oxide. The conductivity depends very much on the impurities and microscopic modifications of the oxide material. Therefore, the exact knowledge of the properties of oxide material remains a serious difficulty. The used data of conductivity are shown in Fig. 3.

The available data of Mo ring conductivity are up to 900 K and shows that it is essentially temperature dependent (see Fig. 4). These data are well approximated by

$$\rho_{Mo} = AT \exp\left(-\frac{B}{kT}\right), \quad (3)$$

where A and B are constants.

The equation of thermal equilibrium including Joule heat sources and convective transport in axis symmetrical case is

$$\rho c_p \left(\frac{\partial T}{\partial t} + v_r \frac{\partial T}{\partial r} + v_z \frac{\partial T}{\partial z} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left(r \lambda(T) \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left(\lambda(T) \frac{\partial T}{\partial z} \right) + \frac{\sigma(T) |A|^2 \omega^2}{2}. \quad (4)$$

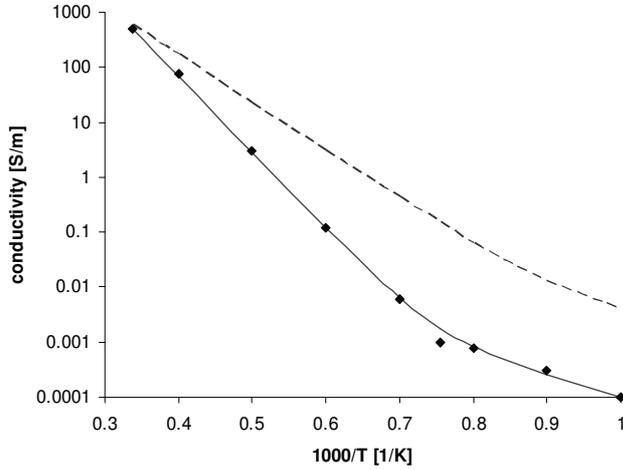


Fig. 3. Dependence of oxide conductivity on temperature. Dashed line – approximated conductivity of ZrO_2 [3]; rhombs – conductivity of zircon according to data in [6]; solid line – approximation of zircon conductivity by model equation (2)

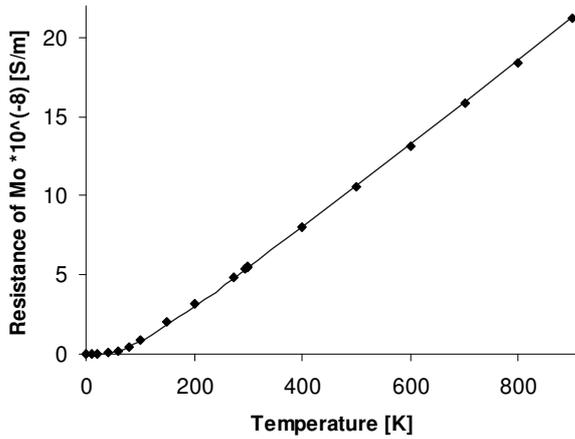


Fig. 4. (right) Resistance of Mo as a function of temperature: black rhombs – data in [5]; solid line – approximation of these data by model equation.

zircon increases by order of magnitude by this increase of temperature according to typical data of oxide conductivity.

In order to account for the convective transport in (4), the flow of the melt should be calculated which is created by the body forces. The current induced by magnetic induction

The thermal conductivity depends both on temperature and porosity. Radiation heat losses from the top of melt are included while the surface temperature can reach 2000 K yielding considerable amount of heat losses. Thermal insulation layer is added with metallic interfaces, i.e. inductor and metallic bottom, where thin skull layer with high heat resistance is present. That makes heat losses considerably lower. It is assumed that heat conductivity of this thin skull layer is 0.2 W/m/K and thickness is 1 mm. Thus, the resistance of the layer is $0.005 \text{ m}^2\text{K/W}$.

The burn-out, i.e., oxidation of Mo ring is a source of energy that should be considered, too, because it could rise the local temperature quit high. Unfortunately, there is lack of data about the oxidation energy in $ZrSiO_4$ environment at high temperatures. As a guess, let us assume that pure Mo burns in atmosphere, where the liberated energy is 36 kJ/mol [5]. This additional heat energy is liberated locally and we can assume that duration of burning is very small. Thus we can increase the local temperature in place of Mo ring by equation

$$\Delta T = \frac{q_b}{c_p}, \quad (4)$$

where q_b is burning enthalpy of Mo and c_p heat capacity. For the given system the temperature increases by about 361 K. That makes the start of melting of zircon much easier as conductivity of

leads to the appearance of Lorentz force in melt material. In addition to the Lorentz force, thermo-gravitational force is present especially for melt with relatively high linear expansion coefficient α . Thus the total resulting force density in Bouyoancy approach is

$$\vec{f} = \vec{j} \times (\nabla \times \vec{A}) - \bar{g} \rho_0 \alpha (T - T_0), \quad (5)$$

where g is the gravitational acceleration, ρ_0 – density at reference temperature of melt T_0 . Resulting force creates melt motion inside the crucible. The two velocity components and pressure follow from momentum equation

$$\rho \left(\frac{\partial \vec{v}}{\partial t} + (\vec{v} \nabla) \vec{v} \right) = \nabla(\mu(T) \nabla \vec{v}) - \nabla p + \vec{f} \quad (6)$$

and the continuity equation $\nabla \vec{v} = 0$. The boundary conditions of velocity are chosen in correspondence with physical model, i.e., non-slip boundary conditions along solid boundaries and gradient free boundary condition for tangential velocity on axis of symmetry and top of the melt.

2. Melting specifics of ZrSiO₄ mixture

In previous studies melting of ZrO₂-SiO₂ mixture is calculated in insoluble approximation. However, the temperature of the liquidus curve then is highly overestimated as the mixture of ZrO₂-SiO₂ is completely melted already at 2632 K. Moreover, ZrO₂-SiO₂ mixture below the temperature of eutectics forms ZrSiO₄ compound. Thus the properties of condensed material should be described assuming that it as ZrSiO₄. At the initial stage, the macroscopic properties can either be more similar to ZrO₂-SiO₂ mixture or ZrSiO₄ compound depending on the preparation of initial material. Thus, the properties of the load depend not only on the temperature and condition but also on preparation history of the material. Let us now describe the properties of material as of ZrSiO₄ as it more close to situation at continuous stage of melting.

In order to describe the melting of two-component mixture, enthalpy function is now introduced into calculations. It has been given in report [4] and shown in Fig. 2. Looking on the dependence of enthalpy on temperature we can see that it very well corresponds to the phase diagram given in Fig. 1. Heat capacity C_v is obtained by differentiation of the enthalpy function

$$C_v = \frac{\partial H}{\partial T}. \quad (7)$$

Enthalpy function is slightly smoothed at phase transition points to escape from singularity.

Looking on to the dependence of enthalpy we see two major phase transition points, where the jump of enthalpy is significant. First occurs at the temperature of eutectics 1960 K, when the compound ZrSiO₄ splits into solid phase of ZrO₂ with small fraction of SiO₂ and liquid SiO₂ with small fraction of ZrO₂. Increasing the temperature up to 2523 K more and more ZrO₂ dissolve into liquid phase of SiO₂. At the temperature of 2523 K quite a big fraction of remaining solid ZrO₂ phase dissolves into the liquid SiO₂ phase and only small amount (20% of molar fraction) of solid ZrO₂ is remaining in the system. The system is completely melted at 2632 K.

In general the constitution of the mixture by components could vary. For example, SiO_2 fraction could be dominant at places with higher temperature but ZrO_2 at lower temperatures. For simplicity, let us neglect now this redistribution.

3. Simulations

We have noted in paper [1] that it is necessary to get the temperature distribution as homogeneous as possible during initial heating, in order to decrease the maximal voltage or current for continuing the heating process. In opposite case the load could cool down after the initial heating is finished, because the material has significant conductivity only at some small region. Therefore, it is necessary to use moderate initial heating of metal ring.

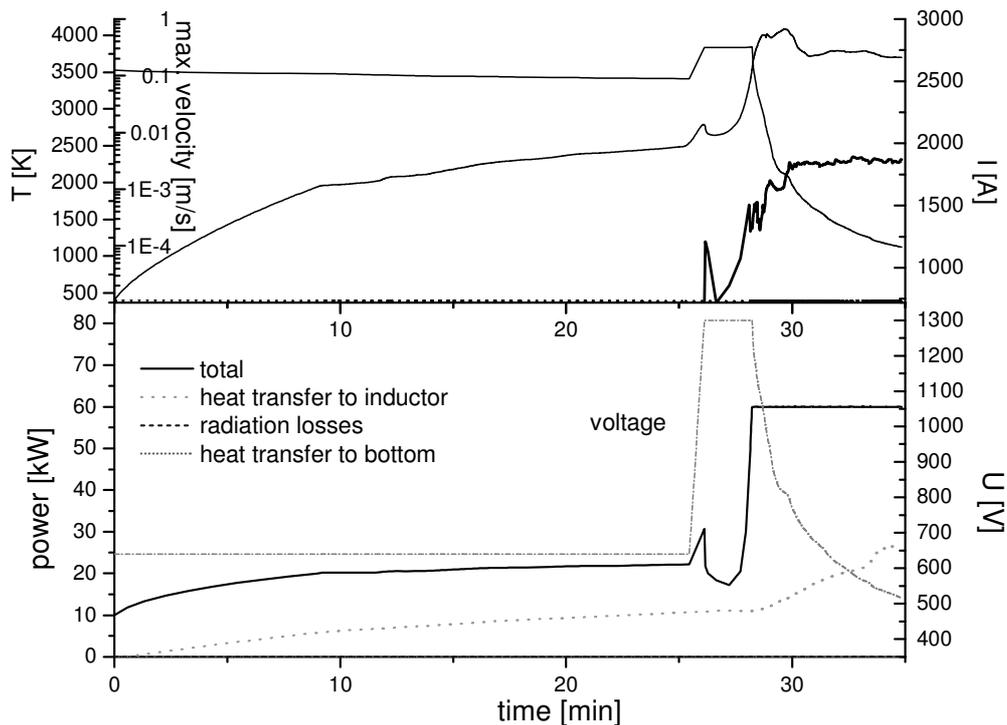


Fig. 5. Behaviour of power, temperature, voltage, current, maximal velocity with time during inductive melting. Initial voltage (amplitude) is 630 V and voltage just after destruction of Mo ring is 1210 V (amplitude). The temperature of destruction of Mo ring is set to 2500 K. Its height is 3 cm and placed 1 cm from the inductor.

The viscosity coefficient of ZrO_2 is very high below melting point and almost constant above melting point. Therefore, notable velocity is only in the molten region of ZrO_2 load. Its size increases but flow pattern significantly depend on linear expansion coefficient α and dynamic viscosity coefficient μ . The properties of molten ZrO_2 are poorly known. Hence, we can study only on the influence of these parameters [3]. The melting starts in place, where the temperature is the highest, i.e., where the ring is burned out. Next, the molten area moves either towards the centre if thermal expansion of the load is small or upward in opposite case. It must be noted that filtration of melt in porous material is neglected as the condensed part of melt could quickly fill the pores near the fluid front. If the melt moves to the centre, the resulting power decreases at constant voltage or current of inductor as the electromagnetic coupling becomes weaker. Afterwards, the area of molten region becomes wider until the stationary distribution at constant power is reached. The constant voltage regime is changed to

constant power regime at the moment when the total power of the inductor exceeds certain value.

Taking into account that the mixture of ZrO_2 - SiO_2 melts at 2632 K rather than 2953 K (melting temperature of pure ZrO_2) and the fact that Mo ring destroys continuously the melting of $ZrSiO_4$ should require not so high voltage as in previous estimations for ZrO_2 . However, the lower conductivity of zircon in comparison with ZrO_2 does not enable to decrease the required voltages and currents considerably. Example of development is shown in Fig. 5. The temperature of Mo destruction is set to 2500 K. But in this case the initial current is much lower: ~2600 A (amplitude) instead of ~3500 A. If the resistance of Mo ring at high temperatures is higher than approximated from (3) then these currents and voltages would be much lower. The same can be said about the conductivity of the zircon at high temperatures.

Conclusions

Basing on the axialsymmetric model of inductive heating in inductor crucible, the estimation of characteristic inductive heating parameters has been studied. The simulations showed high importance of the pre-heating regime of the load, and it should be performed with moderate power in heating by metal ring. It was noted that critical requirements of current and voltage depend significantly on how the Mo ring burns out. It however depends on a number of parameters which are not known quite well. Therefore, it is quite hard to obtain the same initial behaviour as in experiments. Moreover, component specific properties are significant at the initial stage. More easy is to simulate the stationary regime or periodic regime at high temperatures when Mo ring is not more present. Then the number of modelling parameters is lower, and the power, voltages and currents are quite close to experimental values.

References

- [1] Nacke, B., Frishfelds, V., Jakovics, A. (2003). Modelling of key factors in modelling of oxides in inductor crucible, Proceedings of the conference *Electromagnetic processing of materials*, Lion, France, 157 – 162.
- [2] N.A. Toropov, F.Ya. Galakhov (1956) Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk, p. 160.
- [3] Frishfelds, V., Jakovics, A., Nacke, B. (2004). Study of melting dynamics of oxides in inductor crucible. Proceedings of the conference *Heating by Electromagnetoc Sources*, Padua, Italy, 157-164.
- [4] Muehlbauer, A., Baake, E., Lessmann, H.-J. Untersuchung der Funktion einer Zirkon-Silikat-Schmelzanlage. Bericht. – Hannover, Institut für Elektrowärme, Oktober 1995, 40 S.
- [5] David R. Lide ed. Handbook of Chemistry and Physics. CRC Press 84th edition, 2003-2004.
- [6] Walter, F. Grundlagen der elektrischen Ofenheizung. Leipzig: Akademische Verlagsgesellschaft Geest & Portig, 1950

Authors

Dr.-Phys. Frishfelds, Vilnis
Prof., Dr.-Phys. Jakovics, Andris
LMMETP laboratory,
University of Latvia,
Zellu 8, LV-1002 Riga, Latvia

Prof., Dr.-Eng. Muehlbauer, Alfred
Prof., Dr.-Eng. Nacke, Bernd
Institute for Electrothermal Processes
University of Hanover
Wilhelm Busch Str. 4
D-30167 Hannover, Germany