Thermal conductivity of ZrO_2, $ZrSiO_4$, $(U,Zr)SiO_4$ and UO_2: Numerical approach

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Abstract: The thermal conductivity of the products of the interaction of molten core with concrete was derived using number theory. A formula has been found that describes the thermal conductivity of ZrO_2, $ZrSiO_4$, $(U,Zr)SiO_4$ and UO_2 over a wide temperature range. Formula is expressed in terms of the atomic numbers of elements, their valencies, the crystal structure of substances, and the thermal conductivities of individual chemical elements of the corium.

Keywords: fuel debris, corium, thermal conductivity, molten core, ZrO_2, $ZrSiO_4$, $(U,Zr)SiO_4$, UO_2.

1. Introduction

One of the basic components of the fuel debris and the molten core–concrete interaction products are ZrO_2, $ZrSiO_4$, $(U_x,Zr_{1-x})SiO_4$ and UO_2 [1-3]. Knowledge thermal properties of these substances are important in defueling processing. Existing recommendations of thermal conductivity estimations fit experimental data rather good in most cases [4] but very complicated and for each substance demand significant corrections. Using number theory it was attempt to obtain a formula expressing thermal conductivity through the combination of integers and rational numbers (atomic numbers and structure parameters) and thermal conductivity of pure elements included in the substance.

2. Theoretical statement

Let us consider some arbitrary substance with chemical formula $A_kB_lC_n...$ Number of elements in chemical formula should be two or more. We want express thermal conductivity λ of this substance through known values. It is clear that λ somehow depends from thermal conductivities of each separate element: $\lambda = f(\lambda_A, \lambda_B, \lambda_C, ...)$, where λ_A is the thermal conductivity of element A and so on. It is also clear that thermal conductivity of the substance depends from electronic structure of the substance which completely defined by the atomic numbers of elements and crystal structure of the substance: $\lambda = f(\lambda_A, \lambda_B, \lambda_C, ..., A, B, C, ..., h)$, where A is a atomic number of element A from the chemical formula $A_kB_lC_n...$ and so on, h is the integer or rational number characterizing the crystal group of a substance. It is also clear that valence of each element define physical characteristic of the substance, and taking into account that indexes in chemical formula have relation to valencies, we write that $\lambda = f(\lambda_A, \lambda_B, \lambda_C, ..., A, B, C,..., k, l, n,..., h)$. Thermal conductivities of elements

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λ_A, λ_B, λ_C,... define the dimension of searched λ, and all other values in formula will be integer numbers or rational. This is important moment because we know that periodic table of elements defines basic characteristic of each element through integers – position in row and column and atomic number. And crystal structure is defined through symmetry axes of certain order expressed through integer, number of the planes of symmetry and so on. Thus, we suggest that any physical value characterizing a substance also depends from these integers and rational numbers. Parameter h also in some form depends from lattice parameters: $h = h(a, b, c, \alpha, \beta, \gamma)$, though we assume that final value of h should be integer or rational number.

Application of number theory reveals that for thermal conductivity of substance $A_kB_lC_n$ best agreement with experiment gives next formula:

$$\frac{1}{\lambda} = \frac{10 \cdot 6 \cdot 4}{3 \cdot (k \cdot \lambda_A + l \cdot \lambda_B + n \cdot \lambda_C)} \cdot \left[\frac{1}{k \cdot A} + \frac{1}{l \cdot B} + \frac{h}{n \cdot C} \right], \qquad (1)$$

where parameter h connected with the most electronegative element, in our case with C. For substance consisting of two elements we have two summands in square brackets. Formula (1) was obtained for ZrO_2, $ZrSiO_4$, $(U_x,Zr_{1-x})SiO_4$ and UO_2.

3. Discussion

Thus for $(U_x,Zr_{1-x})SiO_4$, where $x = 0.016$ and 0.026, we have next formula:

$$\frac{1}{\lambda_{UZrSiO_4}} = \frac{10 \cdot 6 \cdot 4}{3 \cdot (x \cdot \lambda_U + (1-x) \cdot \lambda_{Zr} + \lambda_{Si} + 4 \cdot \lambda_O)} \cdot \left[\frac{1}{x \cdot U + (1-x) \cdot Zr} + \frac{1}{Si} + \frac{h}{4 \cdot O} \right], \qquad (2)$$

where we took into account that atoms of uranium replace atoms of zirconium, therefore their atomic numbers are included into the same denominator, and $U = 92$, $Zr = 40$, $Si = 14$, $O = 8$. In the Table 1 the result of use of (2) is shown.

From Table 1 we see that crystal structure parameter h for $(U_{0.016}, Zr_{0.984})SiO_4$ decreasing with increase T and from around 600 K become fixed. We might assume that h will not be changed up to the probable structural transition at higher T. Thus, as T changes, there are variables in (2) represented only by the thermal conductivities of pure elements. For $(U_{0.026}, Zr_{0.974})SiO_4$ we see steady decrease of h with rise of T and probable fixing it at around 900 K.

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Table 1. Thermal conductivities of $(U_{0.016}, Zr_{0.984})SiO_4$ and $(U_{0.026}, Zr_{0.974})SiO_4$ calculated over formula (2) at different temperatures. λ_{exp} are the experimental values for $(U_x,Zr_{1-x})SiO_4$ taken in [2], red left column is for $(U_{0.016}, Zr_{0.984})SiO_4$ and right blue is for $(U_{0.026}, Zr_{0.974})SiO_4$. Thermal conductivities for pure elements taken in [5]. λ_{theory} are the values obtained from (2), red left column is for $(U_{0.016}, Zr_{0.984})SiO_4$ and right blue is for $(U_{0.026}, Zr_{0.974})SiO_4$. For h is the same coloring as for λ_{exp} and λ_{theory}.

T, °K	λ_{exp}, $W\cdot m^{-1}\cdot K^{-1}$		λ_U, $W\cdot m^{-1}\cdot K^{-1}$	λ_{Zr}, $W\cdot m^{-1}\cdot K^{-1}$	λ_{Si}, $W\cdot m^{-1}\cdot K^{-1}$	λ_O, $W\cdot m^{-1}\cdot K^{-1}$	h		λ_{theory}, $W\cdot m^{-1}\cdot K^{-1}$	
290	11.1	8.7	27.36	22.9	156.6	0.026	3	5	11.84	8.9
370	10.2	8.23	29	21.9	111	0.03	2	7/2	10.7	8.12
470	9.1	7.44	31.07	21.2	83	0.04	3/2	5/2	9.15	7.53
570	8.12	6.76	33.3	20.8	66.2	0.05	1	5/2	8.6	6.3
670	7.32	6.22	35.7	20.84	54.13	0.052	1	2	7.41	5.97
770	6.64	5.71	38.1	21.4	44.8	0.06	1	2	6.55	5.29
870	6.16	5.31	40.55	22.3	37.8	0.065	1	3/2	5.96	5.33
970	5.8	5.03	43.12	23.4	32.6	0.07	1	3/2	5.56	4.98
1070	5.6	4.7	45.6	24.54	28.9	0.076	1	3/2	5.3	4.76

We claim that for every T there is a rational number or an integer equal to h that is constant on some intervals of T. In last case, changing λ with T is defined by thermal conductivities of pure elements of substance expressed in (2). That is, we can write that $\lambda_{ABC}(T) = (\lambda_A(T), \lambda_B(T), \lambda_C(T), h(T))$.

For $ZrSiO_4$ we write formula (1) in the form:

$$\frac{1}{\lambda_{ZrSiO_4}} = \frac{10\cdot 6\cdot 4}{3\cdot(\lambda_{Zr}+\lambda_{Si}+4\cdot\lambda_O)}\cdot\left[\frac{1}{Zr}+\frac{1}{Si}+\frac{h}{4\cdot O}\right], \qquad (3)$$

where again atomic numbers are Zr = 40, Si = 14, O = 8. Since influence of λ_O is negligible as $4\cdot\lambda_O << \lambda_{Zr}, \lambda_{Si}$ in whole temperature range, we excluded it from calculations, results of which shown in Table 2.

From Table 2 we see that parameter h steadily decreases from room temperature and starting from around 600 K it is the constant. This is coincides with results for $(U_{0.016}, Zr_{0.984})SiO_4$. Probably h will be constant up to the structural phase transition of $ZrSiO_4$ close to 2000 K [1].

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Table 2. Thermal conductivities of $ZrSiO_4$ calculated over formula (3) at different temperatures. Thermal conductivities for pure elements taken in [5]. λ_{exp} are the experimental values for $ZrSiO_4$ taken in [1]. λ_{theory} are the values obtained from (3).

T, °K	λ_{exp}, $W \cdot m^{-1} \cdot K^{-1}$	λ_{Zr}, $W \cdot m^{-1} \cdot K^{-1}$	λ_{Si}, $W \cdot m^{-1} \cdot K^{-1}$	h	λ_{theory}, $W \cdot m^{-1} \cdot K^{-1}$
300	14.3	22.7	148	5/3	14.4
370	12.4	21.9	111	4/3	12.03
470	10.46	21.18	83	3/3	10.2
570	9.1	20.8	66.2	2/3	9.3
670	8.1	20.84	54.13	2/3	8
770	7.2	21.4	44.8	2/3	7.05
870	6.5	22.3	37.8	2/3	6.4
970	6.1	23.37	32.61	2/3	5.97
1070	5.7	24.54	28.9	2/3	5.67
1170	5.42	25.67	26.36	2/3	5.54

For UO_2 we write formula (1) in the form:

$$\frac{1}{\lambda_{UO_2}} = \frac{10 \cdot 6 \cdot 4}{3 \cdot (\lambda_U + 2 \cdot \lambda_O)} \cdot \left[\frac{1}{U} + \frac{h}{2 \cdot O} \right], \qquad (4)$$

where again atomic numbers are U = 92, O = 8. Since influence of λ_O is negligible as $2 \cdot \lambda_O << \lambda_U$ in whole temperature range, we excluded it from calculations, results of which shown in Table 3.

Table 3. Thermal conductivities of UO_2 calculated over formula (4) at different temperatures. Thermal conductivities of uranium taken in [5]. λ_{exp} are the experimental values for UO_2 taken in [3]. λ_{theory} are the values obtained from (4).

T, °K	λ_{exp}, $W \cdot m^{-1} \cdot K^{-1}$	λ_U, $W \cdot m^{-1} \cdot K^{-1}$	h	λ_{theory}, $W \cdot m^{-1} \cdot K^{-1}$
600	5.45±0.5	34	1	5.8
700	4.83±0.5	36.4	3/2	4.35
800	4.33±0.44	38.8	3/2	4.64
900	3.93±0.4	41.3	4/2	3.8
1000	3.6±0.36	43.9	5/2	3.28
1100	3.3±0.34	46.3	5/2	3.46
1200	3.1±0.34	49	6/2	3.09

From Table 3 we see that parameter h steadily increases from 600 K with rising of T. We see that at some intervals of T the parameter h is a constant.

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For ZrO_2 we write formula (1) in the form:

$$\frac{1}{\lambda_{ZrO_2}} = \frac{10 \cdot 6 \cdot 4}{3 \cdot (\lambda_{Zr} + 2 \cdot \lambda_O)} \cdot \left[\frac{1}{Zr} + \frac{h}{2 \cdot O} \right], \quad (5)$$

where atomic numbers are Zr = 40, O = 8. Since influence of λ_O is negligible as $2 \cdot \lambda_O << \lambda_{Zr}$ in whole temperature range, we excluded it from calculations, results of which shown in Table 4.

Table 4. Thermal conductivities of ZrO_2 calculated over formula (5) at different temperatures. Thermal conductivities of Zr taken in [5]. λ_{exp} are the experimental values for ZrO_2 taken in [3]. λ_{theory} are the values obtained from (5).

T, °K	λ_{exp}, $W \cdot m^{-1} \cdot K^{-1}$	λ_{Zr}, $W \cdot m^{-1} \cdot K^{-1}$	h	λ_{theory}, $W \cdot m^{-1} \cdot K^{-1}$
600	1.7±0.18	20.7	2	1.72
800	1.69±0.16	21.6	2	1.8
1000	1.66±0.16	23.7	3	1.4
1200	1.64±0.16	26	3	1.53
1400	1.62±0.16	27.9	3	1.64
1600	1.59±0.16	29.7	3	1.75

Parameter h for ZrO_2 increases with T as we see this for UO_2. Because of experimental errors we think that rise of h for ZrO_2 in some degree is smeared.

The form of formula (1) cannot be considered by parts as it is possible for formulas used as recommendation in λ calculations [4]. Last contain different terms representing phonon, electronic and thermal radiation contribution in the whole thermal conductivity. Formula (1) contains the thermal conductivities of all chemical elements of substance and their atomic numbers which with aid of structural parameter h define the thermodynamic processes.

4. Conclusion

We obtain formula describing thermal conductivities the basic components of corium with use of number theory. To further development of this approach we need to continue describing of thermodynamic properties of other fuel debris and for generalizations of results to continue describing of thermodynamic properties of different rock minerals in wide range of temperatures and pressures.

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