Supplementary Material

Current rate flash sintering of nickel at ambient temperature in < 1 minute

by

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Calorimetry: Measurement of endothermic enthalpy for estimate of defect generation

Brief Summary

Current rate flash experiments with ceramics have consistently shown that the energy lost to radiation and stored as specific heat falls short of the input electrical energy. The difference is attributed to the endothermic generation of point defects, e.g. Frenkel pairs. Here we apply the same methodology to current rate sintering experiments with nickel, estimating the defects to be approximately 0.3% mol fraction.

The Analysis

The objective is to measure the difference between the input electrical energy, and the energy lost to black body radiation, to convection and energy stored as specific heat[1,2]. This difference is expressed by the following equation:

$$\Delta H^*(t) = \int_0^t \left(W(t) - W^*(t) \right) dt \tag{1}$$

Here, $W(t)$ is the electrical work expended (in Watts, or J s^{-1}) into the sample, and $W^*(t)$, also in Watts is the energy lost to radiation, convection and specific heat. Note that the energy deficit, $\Delta H^*(t)$ in expressed in Joules.

The (rate of) energy loss is equal to the sum of three terms: black body radiation, convection loss and the energy stored as specific heat. All are a function of the temperature. Each of them, respectively, are written as follows:

$$W^*(t) = W^*_{BBR}(t) + W^*_{conv}(t) + W^*_{spht}(t) \tag{2}$$

They are given by the following expressions:

$$W^*_{BBR}(t) = \epsilon_m S\sigma(T_K^4 - 298^4), \tag{3}$$

$$W^*_{conv}(t) = hS(T_K - 298) \tag{4}$$

$$W^*_{spht}(t) = mC_p \frac{dT_K}{dt} \tag{5}$$

Here, S is the surface area of the specimen, ϵ_m is the emissivity of nickel (equals to 0.12[3]), σ is the Stefan-Boltzmann's constant (5.6704×10−8 W/m^{-2} K^{-4}). 298 K is the ambient temperature (since the experiment was carried out without the furnace). The mass of the specimen was 0.000326 kg. .The specific heat of nickel, C_p is 133 J kg^{-1} K^{-1}, and T_K is the specimen temperature measured with the pyrometer, in Kelvin.

Equations (3), (4) and (5) are integrated with respect to time to obtain the energy loss in units of J.

The next step is to express ΔH^* in Eq. (2) as a molar quantity, which is done by first by calculating the number of moles of nickel, N_W, in the specimen, obtained by dividing the physical volume of the specimen by the molar volume of Ni:

$$N_W = \frac{V_{specimen}}{V_{molar}} \tag{6}$$

Therefore, the enthalpy in Eq. (1) as a molar quantity (in units of J mol^{-1} is given by

$$\Delta H^*_{mol} = \frac{\Delta H^*}{N_W} \tag{7}$$

The mole fraction of defects, x_F, is obtained by dividing Eq. (7) by the energy of formation of the defects, E_F, in units of J mol^{-1}.

$$x_F = \frac{1}{N_W}\frac{\Delta H^*}{E_F} \tag{8}$$

The parameter for calculating x_F are given in Table I:

Parameters	Symbol	Values	Units
Stefan-Boltzmann Constant	σ	5.67×10^{-8}	$W\ m^{-2}\ K^{-4}$
Emissivity	ϵ_m	0.12	
Specimen Volume	$V_{specimen}$	52.1	mm^3
Surface Area	S	173.6	mm^2
Molar Volume	V_{molar}	0.66	$cm^3\ mol^{-1}$
Initial Temperature (T_F)	T_F	298	K
Specimen mass	m	0.0004	kg
Specific Heat	C_p	445	$J\ kg^{-1}\ K^{-1}$
Formation energy	E_F	5.48	eV
		523	$kJ\ mol^{-1}$
Heat transfer coefficient	h	7*	$W\ m^{-2}\ K^{-1}$

Table I. The parameters used to estimate the energy deficit in Eq. (1).

*The heat transfer coefficient was estimated by comparing convective losses according to Eq. (4) with the BBR losses from Eq. (3), using the criterion that BBR losses dominate at temperatures above ~600 ºC (mild red optical emission). The usual value for h, for convective losses in air is in the 5 to 100 $W\ m^{-2}\ K^{-1}$. However, Ar used in the current experiment has a much lower heat capacity than nitrogen, and therefore h may be lower for the present experiments. A good fit to the transition was obtained for $h = 7\ W\ m^{-2} s^{-1}$, as shown in Fig. S1. (The literature values for h for Ni[4] range from 5 to 10 $W\ m^{-2} s^{-1}$).

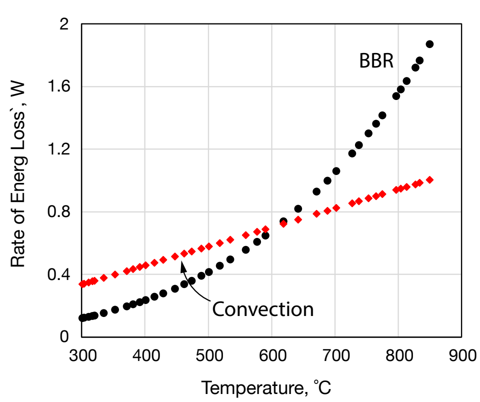

Figure S1: A plot for the BBR loss and the convective loss assuming $h = 7\ W\ m^{-2} s^{-1}$, The raw data and the values for the parameters derived from the above equations are given in Table II.

Time	Pyrometer Temp	Watts	BBR	BBR	Convection	Convec	Spec Heat	Total IN	Total LOSS	Deficit	Deficit/mol	Frenkels
sec	˚C		W	total J	W	total J	total J	J	J	J	J/mol	mol %
26	411	1.53	0.25	0.25	0.47	8.69	2.13	11	11	0	1	0.00
27	427	1.68	0.27	0.27	0.49	9.18	2.84	13	12	1	7	0.00
28	443	1.87	0.30	0.30	0.51	9.69	2.84	15	13	2	24	0.00
29	459	2.07	0.33	0.33	0.53	10.21	2.84	17	13	3	43	0.00
30	471	2.27	0.35	0.35	0.54	10.76	2.13	19	13	6	74	0.01
31	486	2.46	0.38	0.38	0.56	11.32	2.66	22	14	7	91	0.02
32	499	2.77	0.41	0.41	0.58	11.89	2.31	24	15	10	123	0.02
33	514	3.02	0.44	0.44	0.59	12.49	2.66	27	16	12	148	0.03
34	532	3.19	0.49	0.49	0.62	13.10	3.20	31	17	14	174	0.03
35	554	3.34	0.54	0.54	0.64	13.75	3.91	34	18	16	198	0.04
36	576	3.58	0.60	0.60	0.67	14.41	3.91	37	19	19	234	0.04
37	592	3.89	0.65	0.65	0.69	15.10	2.84	41	19	23	288	0.05
38	618	4.16	0.74	0.74	0.72	15.82	4.62	45	21	24	308	0.06
39	637	4.45	0.80	0.80	0.74	16.57	3.37	50	21	29	369	0.07
40	668	4.77	0.92	0.92	0.78	17.35	5.50	55	24	31	391	0.07
41	689	5.10	1.00	1.00	0.81	18.16	3.73	60	23	37	467	0.09
42	704	5.40	1.07	1.07	0.83	18.98	2.66	65	23	42	538	0.10
43	728	5.60	1.18	1.18	0.85	19.84	4.26	71	25	46	576	0.11
44	739	5.75	1.23	1.23	0.87	20.70	1.95	77	24	53	666	0.13
45	757	5.92	1.32	1.32	0.89	21.59	3.20	82	26	56	713	0.13
46	765	6.22	1.36	1.36	0.90	22.49	1.42	89	25	63	802	0.15
47	775	6.54	1.42	1.42	0.91	23.40	1.78	95	27	69	868	0.16
48	797	6.99	1.54	1.54	0.94	24.34	3.91	102	30	72	916	0.17
49	802	7.36	1.57	1.57	0.94	25.29	0.89	110	28	82	1036	0.20
50	815	7.82	1.65	1.65	0.96	26.25	2.31	117	30	87	1103	0.21
51	828	8.25	1.73	1.73	0.98	27.22	2.31	126	31	94	1194	0.23
52	833	8.78	1.76	1.76	0.98	28.20	0.89	134	31	104	1311	0.25
53	848	8.95	1.86	1.86	1.00	29.20	2.66	143	34	110	1388	0.26

Table II: Data from experiments and the calculation for the parameters expressed in Eqns (1) thru (8).

(a)

(a)

(a)

The data for the energy deficit and the estimated concentration corresponding to the endothermic energy deficit are plotted in Fig. 2.

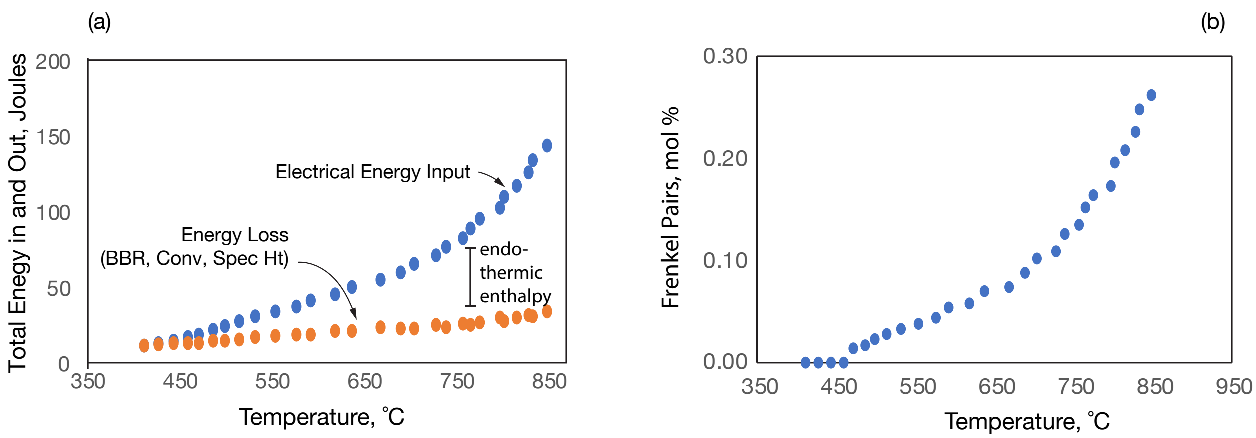

Figure S2: (a) Plots of the energy deficit, and (b) the corresponding concentration (in units of mol %) calculated from the endothermic enthalpy divided by the energy of formation of Frenkel pairs.

The slight step in the Frenkels in Fig. 2(b) most likely arises at the onset of flash. Note the very high values for the mol% of Frenkels generated from the endothermic nature of the flash experiments. It reaches up to 0.26 % or a mole fraction of $2.6*10^{-3}$. These numbers are many orders of magnitude higher that the value expected from thermal equilibrium given by exp(-523000/(RT)) where T = 1173 K, which gives $5*10^{-24}$. Clearly the formation of defects under flash is a new, far-from-equilibrium paradigm.

References

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