Direct Observation of the Early Phase Formation Process of the NdCeFeB Phase via In-situ Annealing & Quenching STEM

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Supporting Information

S1 3D Modeling of FIB Sample

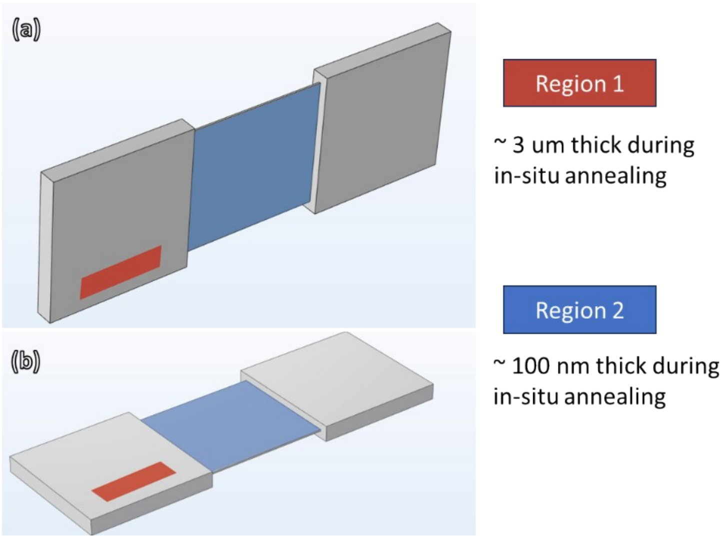

Figure S1. 3D modeling of FIB sample. (a) Vertical view; (b) Plan view

S2 Thermal condition of in-situ quenching experiment

(a)

Time (ms)	Temperature (℃)	Current (A)	Resistance (Ω)	Voltage (V)	Power (W)
1220304	700.0	0.002449	11553.52	28.2985	0.069313
1221305	599.9	0.002138	12780.77	27.3263	0.058426
1222304	500	0.001883	13908.73	26.1875	0.049306
1223304	399.9	0.001622	15136.39	24.5535	0.039829
1225305	199.9	0.000897	18478.52	16.5807	0.014878
1226304	99.9	0.000425	20600.36	8.74955	0.003716
1227104	25.0 (RT)	0.000100	22464.75	2.24780	0.000225

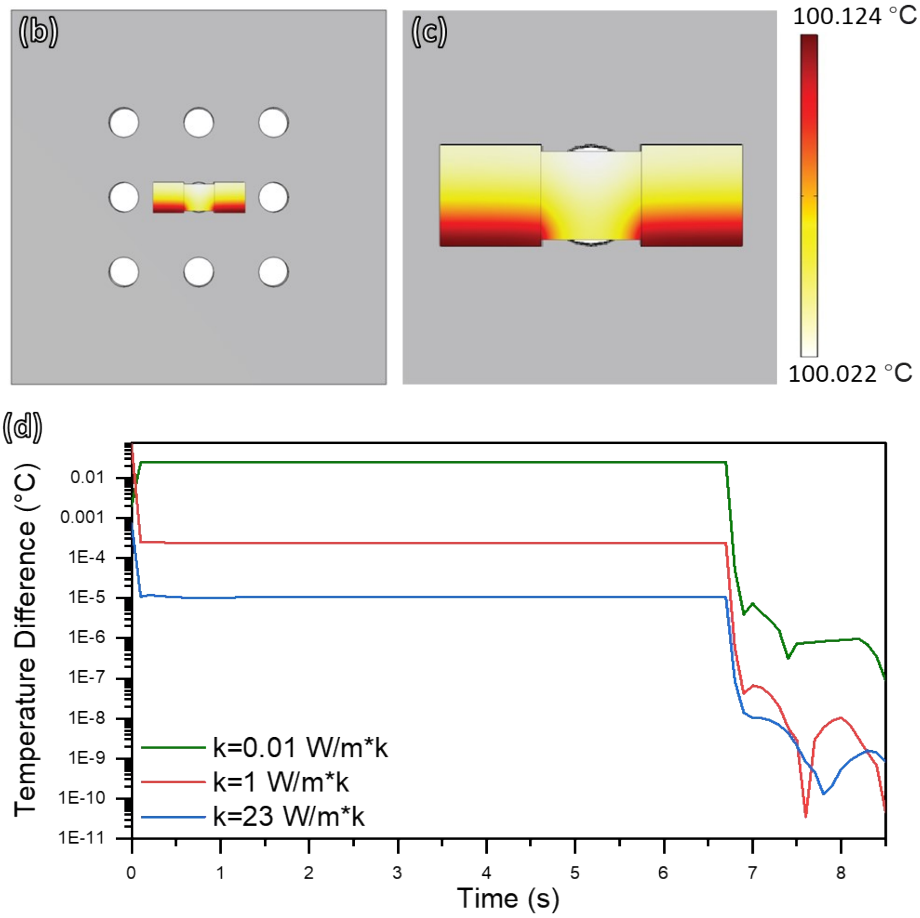

Figure S2. In-situ Heating Condition. (a) Raw data read from heating E-chips showing the quenching temperature; (b, c) 3D model showing the in-situ STEM experiment set up and even temperature distribution during cooling at t=6 s with k=0.01 W/m*k; (d) Temperature difference (ΔT) between region 1 (T_1) and region 2 (T_2) calculated by finite element analysis method, $\Delta T = T_2 - T_1$.

The in-situ TEM solution utilized in this study is provided by Protochips company. The system incorporates MEMS-based heating E-chips designed for precise thermal control and temperature measurement during in-situ TEM experiments. Each annealing chip is externally calibrated to ensure accurate temperature readings. This calibration process establishes a reliable relationship between circuit resistance and actual temperature at the targeted area.

During the in-situ experiment, the temperature is continuously monitored by measuring the electrical resistance of the heating circuit, as provided in Supporting Information S2 (a). The resistance changes with temperature in a predictable manner based on the material's temperature coefficient of resistance (TCR). These predictable changes allow the system to maintain precise temperature control. To be noticed, the heating resistor of the hearting chip is made by SiC film, which shows the reverse relationship between temperature and resistance due to the intrinsic behavior of semiconductors where thermal excitation generates additional charge carriers.

To evaluate the thermal condition of the sample during in-situ quenching STEM experiments, the finite element analysis method is introduced to calculate the temperature distribution based on the raw data read from the E-chip. The thermal finite element analysis was performed using COMSOL Multiphysics software. A 3D model including FIB lamella and E-Chip substrate is built based on the SEM/FIB images. The temperature field in the simulation domain can be described as:

$$\rho C_P \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) \tag{1}$$

where, ρ is the density, C_P is the specific heat capacity, T is the temperature, and k is the thermal conductivity. To simplify the problem, a uniform temperature is assumed for the FIB lamella during the quenching process with an initial temperature of 700 °C and a cooling rate of 100 °C/s. Therefore, a temperature boundary condition ($T = T_0$) is used for the FIB lamella and E-Chip interface. Due to the negligible radiation and convection heat transfer at the E-Chip surface, a no-flux boundary ($-n \cdot q = 0$) is used. Free triangular mesh with 540,000 cells was used for the simulation. A time-dependent solver with an interval time step of 0.1 s was used to solve the temperature field. The thermophysical properties of materials used in the simulation (k=23 w/m*k) are based on the data in the Network Database System [34].

The simulation result may not reveal the absolute actual thermal condition of the sample due to the complex interface thermal transfer mechanism and multiply phases system. Instead, it aims to analyze the temperature difference between Region 1 (mount area) and Region 2 (center area) during the in-situ quenching experiment. Low thermal conductivity settings (k = 1 w/m*k, k= 0.01 w/m*k) are considered to evaluate the poor thermal transfer situation caused by the interface thermal resistance. The result shows the temperature is evenly distributed among the whole FIB lamella with a 100 °C/s cooling rate. Even with the lowest thermal conductivity setting k= 0.01 w/m*k, the temperature difference between Region 1 and Region 2 is less than 0.03 °C, which is negligible in material engineering. Thus, based on the finite element simulation result, we consider the thermal condition between Region 1 and Region 2 to be the same during the in-situ quenching experiment, and the oxygen concentration is the major factor that domain the reaction mechanism of the Nd-Ce-Fe-B system.

S3 Oxygen Distribution along Cross Section View

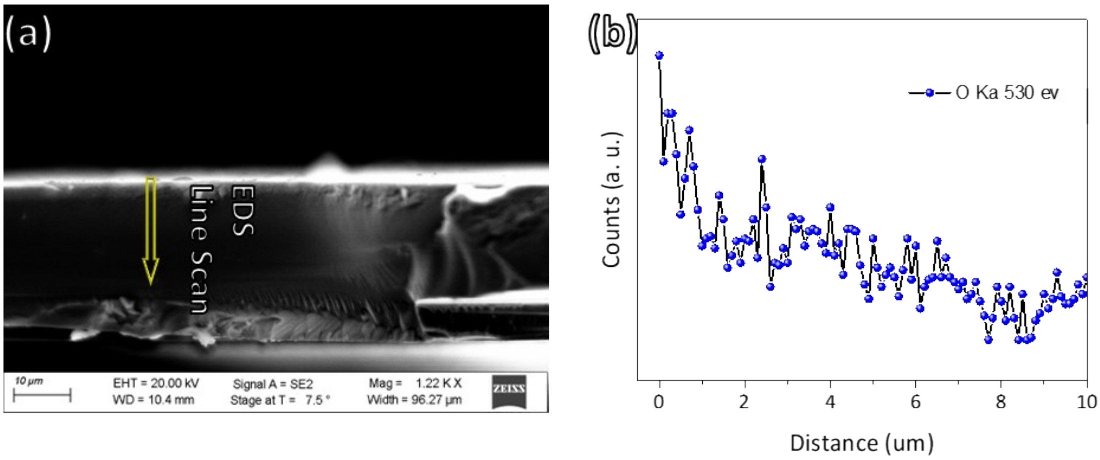

Figure S3. Oxygen distribution acquired from $(Nd_{0.75}Ce_{0.25})_2Fe_{14}B$ bulk sample. (a) SEM image showing cross-section view of bulk sample (b) EDS line scan from the surface to the bottom.

Reference

[34] Y. Yamashita, et al., Jpn. J. Appl. Phys. 50 (2011) 11RH03.