Formation of graphite during high-velocity friction experiment under $H_2$ atmosphere

Kiyokazu OOHASHI$^{1,*}$, Raehee Han$^2$, Takehiro Hirose$^3$, Kentaro Omura$^4$, Tatsuo Matsuda$^4$, Toshihiko Shimamoto$^5$

$^1$Graduate School of Sci, Hiroshima Univ., $^2$KIGAM, Korea, $^3$KCC, JAMSTEC, $^4$NIED, $^5$China Earthquake Administration

Graphite-bearing brittle faults are often found within the non-carbonaceous host rocks such as granite or marble (e.g., Nojima fault; Arai et al., 2002). Precipitation of graphite from C-O-H fluid system is widely accepted under the high P/T conditions of lower crust. However, it is considered to be difficult to awaken graphite precipitation under the upper crustal conditions, and formation process along the shallow fault zone is still not understood. Meanwhile, in last several years, experimental studies clearly suggested that mineralogical transformation took place in a few tens of seconds during coseismic fault slip (e.g. Han et al., Oohashi et al., 2011). Thus, we conducted high-velocity friction experiment under the C-O-H atmospheric conditions to determine if graphite forms from non-carbonaceous host rocks during rapid sliding.

Experiments were conducted using rotary-shear, low- to high-velocity friction apparatus under $H_2$ gas atmosphere, and Carrara marble (99% calcite and very small amount of silicate) is used for the host rock. Rock to rock experiments (bare surfaces) were conducted at normal stress of 2.0 MPa and slip rate of 1.3 m/s under the $H_2$ purged atmosphere. After the friction experiment, we can observe patches of blackish material on the slip surface, whereas the slip surface deformed under the air/Ar atmosphere maintains original white color. According to laser Raman spectroscopic analysis, two broad peaks correspond to the fundamental peaks of the graphite (or carbonaceous material) at a wavenumber of $1350\pm1$ and $1590\pm1$ cm$^{-1}$ were detected from the patches of blackish material.

The Carrara marble used for the experiment is very pure and composed of 99% calcite, thus, it is unlikely that graphite appeared from carbonaceous material originally presents in the rock. Additionally, no visible color change was observed prior and after the HV friction experiment under the air and Ar atmospheres. Hence, the appearance of solid carbon is attributable to the atmospheric difference during the experiments. Possible explanation is formation of graphite via gas phase reaction of following chemical reaction: $2H_2+CO_2>\rightarrow C+2H_2O$. Salotti et al. (1971) conducted reaction experiment of calcite at the temperature of 500 degrees celcius, gas pressure of 13.8 MPa and duration of 6 hours under C-O-H atmosphere, and demonstrated formation of well-crystallized graphite on the surface of calcite. Although two of these conditions were not met in our high-velocity experiments with gas pressure of 0.1 MPa and duration of less than hundreds of seconds, temperature must have exceeded 500 degrees celcius since calcite decomposed into CaO and CO$_2$ (decomposition temperature of calcite: $>720$ degrees celcius). The reaction is temperature dependent so this is why the reaction accomplished at these experimental conditions. This result suggests that if rapid faulting occurs within the calcareous rocks (e.g., marble, limestone and rock rich in carbonate vein) under the reducing environment ($H_2$ or CH$_2$ atmosphere), graphite forms in response to frictional heating.

[References]
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Keywords: Nojima fault, Graphite, Carbonate minerals, High-velocity friction, Mechano-chemical reaction