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Nanograin formation and reaction-induced fracturing due to decarbonation: Implications for the microstructures of fault mirrors

A. Pluymakers, A. Røyne *

Physics of Geological Processes, Department of Physics, University of Oslo, Postboks 1048, 0316 Oslo, Norway

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ABSTRACT

Principal slip zones often contain highly reflective surfaces referred to as fault mirrors, shown to consist of a nanogranular coating. There is currently no consensus on how the nanograins form, or why they survive weathering on a geological time-scale. To simplify the complex system of a natural fault zone, where slip and heat generation are inherently coupled, we investigated the effect of elevated temperatures on carbonate rock surfaces, as well as their resistance to water exposure. This allows us to isolate the role of the decarbonation process in the formation of nanograins. We used cleaved crystals of Iceland spar calcite, manually polished dolomite protolith, as well as natural dolomite fault mirror surfaces. The samples were heated to 200–800 °C in a ∼5 h heating cycle, followed by slow cooling (∼12 h) to room temperature. Subsequently, we imaged the samples using scanning electron microscopy and atomic force microscopy. Nanograin formation on all sample surfaces was pervasive at and above 600 °C. The Foiana fault mirror samples were initially coated with aligned naturally-formed nanograins, but display a non-directional nanogranular coating after heating. The nanograins that were formed by heating rapidly recrystallized to bladed hydroxides upon exposure to deionized water, whereas the nanograins on unheated fault mirror samples remained unchanged in water. This shows that the nanograins formed by heating alone are different from those formed in fault zones, and calls for a better characterization of nanograins and their formation mechanisms. Furthermore, we find a characteristic star-shaped crack pattern associated with reacted regions of the carbonate surfaces. The existence of this pattern implies that the mechanical stresses set up by the decarbonation reaction can be sufficiently large to drive fracturing in these systems. We propose that this mechanism may contribute to grain size reduction in fault zones.

1. Introduction

Natural fault zones typically consist of a damage zone and a fault core that occasionally contains a thin, localized principal slip zone that accommodates the main deformation (Faulkner et al., 2010; Smith et al., 2011). Such a principal slip zone often contains a highly reflective surface referred to as a fault mirror (Fondriest et al., 2013; Siman-Tov et al., 2013). The nanoscale resolution provided by state-of-the-art imaging techniques has shown that the mirror-like optical properties of these surfaces stem from sub-micrometric roughness, typically less than 100 nm, created by a compact or sintered layer of particles of nanometric size (Fondriest et al., 2013; Goldberg et al., 2016; Han et al., 2010; Siman-Tov et al., 2015; Smith et al., 2012; Verberne et al., 2014). This is similar to the surface structures found on shiny wear surfaces in metals (Adachi and Kato, 2000).

Fault mirrors have been found in natural fault zones of different lithologies, and have been produced experimentally for carbonate (e.g. Fondriest et al., 2013; Siman-Tov et al., 2015) and silicate rocks (Kuo et al., 2016; Toy et al., 2017). In this study we focus on carbonate rocks, since a larger body of literature is available concerning the formation of mirror-like slip surfaces in these lithologies. Carbonate rocks are known to host earthquakes of M5 and higher, for example in the Italian Apennines (Mirabella et al., 2008) or in the Longmenshan Fault Zone in China (i.e. the 2008 Mw 7.9 Wenchuan earthquake, Chen et al., 2013). Several carbonate outcrops with fault mirror samples have been shown to have a nanogranular coating (Collettini et al., 2013; Fondriest et al., 2015, combined with this study; Goldberg et al., 2016; Siman-Tov et al., 2013), with occasional signs of decarbonation (such as vesicles and poorly crystalline and/or amorphous phases). Decarbonation is inferred to occur during seismic slip of carbonate-rich faults, caused by the heat produced during the fast

* Corresponding author.
E-mail addresses: a.m.h.pluymakers@fys.uio.no (A. Pluymakers), anja.royne@fys.uio.no (A. Røyne).

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sliding (Collettini et al., 2013). High velocity (>1 m/s) friction experiments on calcite and dolomite also suggest decarbonation as a potential mechanism responsible for frictional weakening and nanograin formation (De Paola et al., 2011; Fondriest et al., 2013; Han et al., 2010).

A number of experimental studies have looked specifically into the formation and microstructure of carbonate fault mirror surfaces. These experiments were performed either on relatively pure calcite rocks and gouges or on dolomite rocks and gouges. Experiments have been performed over a range of sliding velocities. Complete fault mirrors are only found in fast (≥1 m/s) friction experiments (Fondriest et al., 2013; Green et al., 2015; Han et al., 2010; Siman-Tov et al., 2015; Smith et al., 2012; Spagnuolo et al., 2015). Both fault mirror coverage and roughness have been shown to correlate with sliding rate, and it has been proposed that fault mirror surfaces can be used as markers for seismic slip in carbonate rocks (Fondriest et al., 2013; Siman-Tov et al., 2013). However, shiny patches covered with nanoparticles are also found in low velocity experiments on calcite. For example, Tisato et al. (2012) found a smooth sliding surface covered with sub-micrometric and platy particles at slow sliding velocities, whereas fast sliding led to nanometric and nearly spherical particles. Slow sliding, aseismic experiments on calcite gouge have also produced surfaces with nanofibers composed of aligned, ∼100 nm diameter nanospheres (Verberne et al., 2014). Despite these being low velocity experiments, it is hypothesized that high temperatures can be generated locally by high strain rates due to localization. A short summary of the publication history of mirror fault surfaces can be found in Rowe and Griffith (2015).

Another intriguing feature of natural fault mirror surfaces is that they have survived weathering whilst being exposed in outcrops over decades. Manually polished carbonate surfaces, on the other hand, do not stay shiny, as commonly observed in weathering studies of tombstones. Surface retreat over 100 yr is measurable for a wide variety of locations, except at a few extremely dry localities (Meierding, 1993). On the nanoscale in atomic force microscopy (AFM) dissolution studies, manually polished calcite (Levenson and Emmanuel, 2013) and dolomite (Saldi et al., 2017) have been found to dissolve faster than cleaved or fluid-equilibrated grain surfaces. This is attributed to high curvature, highly reactive features on polished surfaces. Goldberg et al. (2016), also using AFM, found that a carbonate fault mirror coating dissolved at a much slower rate than a manually polished rock from the same location.

The chemical composition of the fault mirror coating might provide indications of both the formation mechanism and the origin of the weathering resistance of these surfaces. However, precise chemical analysis of these nanoscale features is a challenge. In experiments with calcite gouge or limestone, detailed studies have found that the nanoparticles in the reflective principle slip zone are composed of calcite (Siman-Tov et al., 2015; Spagnuolo et al., 2015; Tisato et al., 2012; Verberne et al., 2014). Experiments on dolostone have shown the presence of Mg-oxide and Mg-calcite (Fondriest et al., 2013), and traces of Si, Al and Fe have been found in natural fault mirrors of dolostone (Goldberg et al., 2016). It was suggested that these non-native elements were mobilized in fluids flowing along the fault, and incorporated into the slip surface during its formation. An alternative possibility would be contamination from one of the faulted layers, as often happens during clay smearing.

There is currently no clear consensus on how the nanogranular coating on natural fault mirrors forms. Proposed mechanisms can be grouped into two main categories: heat-controlled or slip-controlled. In the heat-controlled scenario, frictional heating gives rise to decarbonation of calcite and dolomite and the subsequent formation of oxide nanoparticles (De Paola et al., 2011; Green et al., 2015; Han et al., 2010; Smith et al., 2012). Slip is required to generate heat, but slip in itself is not required to generate nanoparticles. On the other hand, in the slip-controlled scenario, nanograins are formed mechanically through the generation and subsequent pile-up of dislocations (Fondriest et al., 2013; Siman-Tov et al., 2015; Spagnuolo et al., 2015; Verberne et al., 2014).

In this study, we set out to simplify the complexity of a natural fault zone, and isolate the effect of heat (and thus the role of decarbonation) alone. To this end, we compare the morphology and reactivity in water of naturally formed fault mirrors and manually polished dolomite surfaces heated to different temperatures. For comparison purposes we treat cleaved calcite crystals in the same manner.

2. Methods

2.1. Sample description

The dolomite samples were obtained from the Foiana Fault Zone in the Italian Apennines (described by Fondriest et al., 2015) that cuts through Triassic dolostones of the Mendola Formation. We used both fault mirror samples and dolostone protolith. X-ray powder diffraction analysis shows that the bulk rock is 100% dolomite (Fondriest et al., 2015), but there is no analysis available that determines the chemical composition of the mirror surface itself. The fault mirror samples display a natural smooth polish, interpreted to be associated with deformation and former seismicity in the area. We manually polished cm-sized samples of the undeformed host rock using regular carbide paper (stepwise, up to #4000 grit) and water, and finished to be visually mirror-smooth using a diamond suspension with 1 μm particles. These were cut into smaller blocks of roughly 1 × 1 × 0.5 cm. Before heating, samples were imaged with a scanning electron microscope (SEM) and an atomic force microscope (AFM). The SEM images show that before heating, the manually polished protolith samples (Fig. 2a, b) are smooth, with local polishing artefacts and occasional faint outlines of larger grains. The surface has pits up to 2 μm diameter, interpreted to be remnants of porosity or plucked out grains. The AFM indicates a smooth surface, without any nanoparticles coating the micron-sized grains. The fault mirror (Fig. 3a) is smooth under the SEM, with outlines of grains up to 40 μm and pits up to 5 μm diameter. The AFM images (Fig. 3b) show nanoparticles between 5 and 50 nm, often aligned to resemble nanofibers (terminology cf. Verberne et al., 2014). Calcite samples were cleaved from a single crystal of Iceland spar calcite of optical quality.

2.2. Experimental procedure

Samples were heated in a Naber N100/G chamber kiln to the target temperature using the following thermal cycle: 230 min ramp up to 100 °C below the target temperature, T_t, and then with a fixed ramp to T_t where it stays for 90 min, followed by slow cooling overnight. Samples were taken out of the oven when the temperature was between room temperature and 200 °C. The oven calibration was checked with an external K-type thermocouple and found to be within 10 °C of the set temperature. All samples and heating temperatures are listed in Table 1. After the thermal cycle, samples were imaged with an atomic force microscope (AFM) and/or secondary electron microscope (SEM). The maximum temperature for samples imaged with AFM is 600 °C, and 700 °C for SEM. For higher temperatures the samples lost cohesion, and could not be imaged any more. We used a Hitachi SU5000 Schottky field-emission scanning electron microscope (FESEM) at an accelerating