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Review

Recent progress in studies on the nano-sized particle layer in rock shear planes

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Abstract

Since the 1990s, an ultramicro-particle texture in nano- or micron-sized scale has been continually found in shear planes of various rocks, and recently further progress was made in generic physical mechanisms. In this article, the characteristics of the nano-sized particle layer in rock shear planes (including widespread distribution, layering texture, non-linear genetic mechanism, and multiple functions) on an ultra micro-scale were briefly introduced and more information was obtained by analyzing cases from home and abroad. Our findings suggest that (1) there is a paragenetic relationship between the development of shear frictional-viscous and the formation of nano-sized particles, and (2) in the shear movement, partitioning, segregating, and layering in rocks are initiated by the sliding motion of the nano-sized particle layer. Moreover, the plastic rheology of rocks is essentially the movement of ultra-micro-sized particles (nano-size and micro-size), and the nano-sized particle layer in rock shear planes is characterized by some particular physical and chemical effects.

Keywords: Shear plane; Nano-sized particle; Frictional-viscous; Plastic rheology; High field strength elements

1. Introduction

Nowadays, nanoscience is pervasive, touching almost every professional field from information sciences to geosciences. In fact, it has become a buzzword in our era [1]. With the use of a variety of high-resolution and high-efficiency electron microscopes [2], some of the so-called high quality nano-sized particles, which have the characteristics of extremely tiny ($\leqslant$100 nm) and homogeneous in size, consisted of polybasic materials, and possessing multiple functions [3], have been discovered and described since the middle of the 20th century. Examples include, (1) the nano-sized meteorite (5–40 nm cosmic dust) [4], (2) the natural gold particles with diameters of 7–10 nm in the Carlin Gold Deposite [5], and (3) the nano-sized metal particles such as Au, Ag, Sb, As, Zn, Fe, Cr, Sc, Cu, and Mo, as well as gold and other particles with diameters greater than 1000 nm, all captured from earth gas and eruptive volcanic materials [6]. Two fault structures related nano-phenomenon have been found: the rebind texture with a width of 20 nm in pseudo-tachylite [7] and particles with diameters less than 1000 nm in some fault gouge [8]. In addition, nano-sized particles were also discovered in mylonite at home [9]. However, reports on the abovementioned nano-sized materials are comparatively limited. Since the 1990s, we have found that, in several occasions, the nano-sized materials are distributed in thin layers [10–12].

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Incorporated with both physics and mechanics, recent genetic studies have brought forth new progress on this subject. We have identified four features of the nano-sized particle layer in rock shear planes, including widespread distribution, layering texture, non-linear genetic mechanism, and multiple functions. Next, we will briefly introduce each of them, separately.

2. Widespread distribution

2.1. Observational examples

In recent years, we have collected many oriental pocket-sized samples from three major rock types. These samples have many shear planes on different scales and of different kinds. Some of the shear planes were produced by pressure experiments. By synchronously applying both scanning electron microscope (SEM) (type LEO-1530 VP) and energy dispersive X ray (EDX, type OXFORD-INCA 300) onto the surface of these shear planes, we often found some nano- and micron-sized particles in high or para-high quality. We provide four examples below. Example 1, a cleavage plane within bedding slip (*ab* fabric plane) in Paleogene shale of the Shahejie formation was sampled from the H13D drilling bore in Jiyang depression, Shandong province; on the SEM images, we could see the 50–70 nm (diameter) particles in concentrated distribution, as well as the luder's line formed by the nano-sized lines on its surface (Fig. 1(a)). Example 2, a foliation plane (*ac*) in gneissic granitic mylonite of the Mesozoic metamorphic core complex was sampled from Wugongshan Mountain, Jiangxi province; on its surface the 60–80 nm particles were observed through SEM (Fig. 1(b)). Compared with others, the nano-sized particles in the above two samples are more homogeneous in shape and size, and have better roundness and sphericity. Example 3, this sample was taken from near the borderline of Sambagawa and Ryoke tectonic zones located at the Median Tectonic Line (MTL), Japan [13]; 70–90 nm particles were found on the foliation plane from Kashio mylonite of Jurassic system, forming concentrated mosaic textures (Fig. 1(c)). Example 4, Mesozoic middle-fine grain granites sampled from Tonggushan Mountain, Xingzi county, Jiangxi province were cut into long cylinder chucks ($17 \times 17 \times 40$ mm), then triaxial rock experimental machine (type CG 500) with piston type and HT/HP container was applied. Under axial pressure 1434 MPa, confining pressure 250 MPa, and temperature 600 °C, the specimen became mylonized when the pressure was sustained for 10 h. A surface was taken from its microfissure and analyzed under SEM; covered particles (40–60 nm) were observed that are similar to those from examples 1–3; and partial mosaic texture was also found (Fig.1(d)).

The four examples mentioned above help us in understanding the general conditions for the existence of nano-sized particles in rock shear planes. In fact, we have sampled extensively in Ningzhen Mountain, Jiangsu Province and Wugongshan Mountain, Jiangxi Province. In these systematically collected and determined specimens, nano-sized particles were often found in the shearing-slip planes including inverse and wrench fault planes, shear joint planes, fracture cleavages, flow cleavages, bedding gliding planes and the resulting shear-slip phyllite planes (formed in late period or postperiod), schistic planes, gneissic planes, and mylonitic planes of various foliation planes. Obviously, these planes are only different in development degrees. Micron-sized particles were also found in some slipping planes. However, we only focus on nano-sized particles in this paper. The nano-sized particles have heterogeneous development due to different conditions such as strong or weak deformation, rock strength, movement, mechanical characteristics and situated boundary. However, in general, they explicitly show some features of widespread distribution.

2.2. Developing stages

The nano-sized particles in rock shear planes are typically developed stably, with some formation and evolution patterns. The formation and evolution process can be roughly divided into four stages:

(1) Granularization stage: The granular nano-sized particles (usually tens of nano-meters in diameter) normally develop into particles with better roundness and sphericity. These smooth and evasive particles look like oyster pearls (Fig. 1(a) and (b)). Because the particles are caused by slipping and grinding, they are also called grinding grains [14].
(2) Converting stage: The alienation (or isomeric) particles become changing bodies, and they are closely aligned to each other, forming some mosaic textures (Fig. 1(c) and (d)).
(3) Reuniting stage: The individual grains concentrate into composed ones which are typically 200–400 nm in size. Composed grains are able to optimize their orientations (Fig. 1(c)), including preferred formal and crystallographic ones [15].
(4) Reproduction stage: Composed grains under shearing stresses undergo plastic volumetric deformation [15] and form different masses, and then new nano-sized particles can regenerate on the surface (Fig. 1(f)). In the spatial and temporal distribution, the nano-sized particles on rock shear planes have a life cycle including generation, development, and evolution (up to disappearance).

2.3. Shearing slip

According to Sander's fracture hypothesis, a slipping plane of rock shear fractures first develops along the crystal face [16]. Taking quartz, a pressure sensitive mineral, as an example, the crystal face slipping, which will result in nano-sized particles no matter in nature or in experiments, hap-

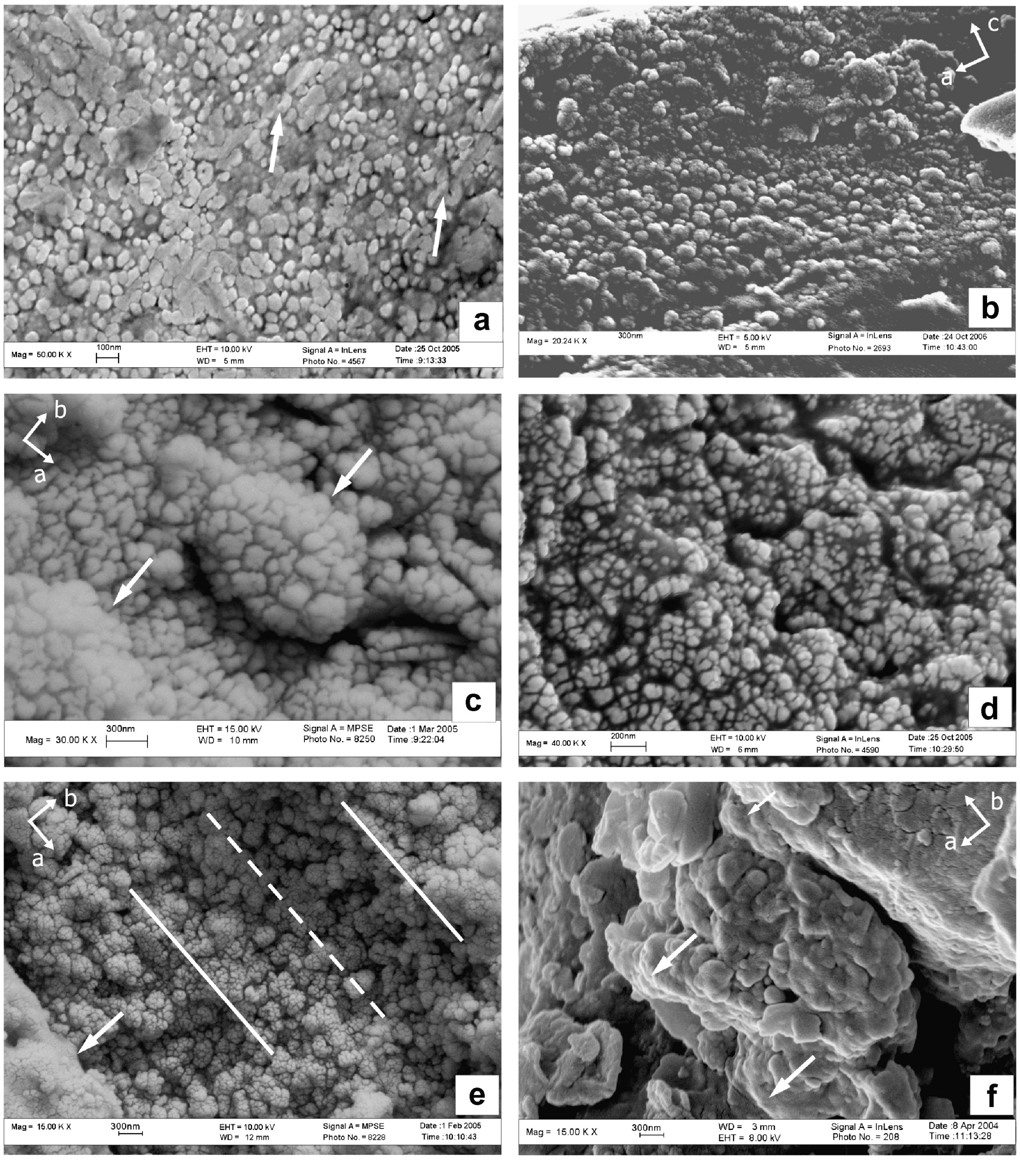

Fig. 1. SEM photos of the nano-sized particle layer in shear plane in different rocks, on different scales and for different kinds. (a) Nano-sized particles occurring in concentrated distribution and Luder's lines (arrows) formed by nano-sized lines in cleavage plane (ab fabric plane) of bedding slip in shale; (b) nano-sized particles closely arranged in foliation plane in gneissic grainitic mylonite; (c) nano-sized particles with alienation and mosaic texture, concentrating into composed grinding grains (arrows) (the direction of its long axis is parallel to the a axis in Kashio foliation, Japan); (d) nano-sized particles forming mosaic textures (ab) in micro-shear fissure plane in mylonition granite undergone test with high temperature and high pressure; (e) two-layer structure, both smooth plane (arrow) and rough plane, on the surface of dynamic thin shell in Mesozoic wrench normal fault, and rough plane forming composed grinding grains, slipping ridges (solid line direction) and slipping depressions (dashed line) paralleling to the a axis; (f) composed grinding grains in pancake shapes from dynamic thin shell of the inverse fault in sandstone, and front edge of plastic flow showing a tongue shape feature.

pens in the direction parallel to plane m $(10\bar{1}0)$ along $\langle a\rangle\langle c\rangle$ axes (perpendicular to each other) (Fig. 1(d)). In a mature shear zone, the initial shear plane is mainly induced by the slipping movement of the crystal face and usually is parallel to it [17]. Stress minerals (e.g., muscovite, calcite, hydrotale, and alkali-feldspar) mostly slide along the cleavage plane and twinning plane, and the formation of the nano-sized grinding grains is a relatively widespread phenomenon. Therefore, we conclude that there is a paragenesis relationship between the initial development of the rock shear movement and the formation of the nano-sized particles.

3. Layering texture

The nano-sized particles, nano-sized line (Fig. 1(a)) and nano-sized layer (Fig. 1(b)) are formed by rock shearing friction, and the dynamic thin shell and dynamic thin film are constructed by the thin layer of ultra-micro particles. Together they form the nano-confinement layer. This nano-sized layer conveying loss capacity or slippage determines strength or weakness of the friction, as well as the transformation between strong frictional stick-slip sliding and weak frictional smooth-slip sliding [18]. Based on the surface tension law or Boltzman's law [19], the theory of ion surface energy [20] and the modern physical characteristics of body wear, the frictions can be subdivided into the kinetic friction and the static friction [21]. Kinetic friction is determined by different shaking rates of the slip systems, which has the characteristics of discontinuous displace, sudden disappearance of the strength, and brittle deformation. The kinetic friction can possess two-substrate sliding, forming a binary nano-layer system [22,23]. For example, the surface of the dynamic thin shell of wrench normal fault in Mesozoic granite, specimen sampled from the southern Tan-Lu fault zone, Anhui province, was determined by electron microscope. Both smooth plane and rough plane were found from upper and lower structures of the two layers. On the smooth plane, the alienated, nano-sized grinding grains show irregular shape and mosaic texture. In contrast, on the rough plane, individual particles (70–90 nm in diameter) of the grinding grain are slightly smaller than those on the smooth plane, and they form composed grinding grains and emerge in the substrate structure of two layers (200–300 nm in diameter) (Fig. 1(e)). Static friction which has a smaller value is controlled by the stick action of the slipping plane, and it is a quasi-static cumulative slip under para-static condition. Moreover, the static friction displays continuous finite displacements, and the distribution size of the ultramicro-particles is relatively homogenerous with a stronger penetration (Fig. 1(b)). It is called unitary nano-layer system (Fig. 1(b)) due to its ductile characteristics [24]. According to the above examples, the width of the binary nano-sized layer system of brittle deformation is relatively thin, from several millimeters to 10 cm. However, in example 5 (Fig. 1(e)), the width of the dynamic shell containing nano-sized layer is only 5 mm. The unitary nano-sized layer system of the ductile deformation has thinner individual layers but thicker in total. As to example 2 (Fig. 1(b)), the width of the mylonitic foliation containing nano-sized particle layer is only several to tens microns, but the width of mylonite zone of the ductile deformation can reach 24 km in total.

Shearing motion itself leads to partitioning, segregating and layering in rocks [25,26]. It is essentially a result from the interface opening caused by frictional actions [27], and by the actions of both tectonic metamorphic process and structural thermal behavior [28]. Strictly speaking, the initial stage starts with partitioning, segregating and layering of the nano-sized particles and nano-sized particle layers, with nano-sized particles and nano-sized particle layer, play a dominant role. The nano-sized particle layer with layering characteristics similar to those of ductile deformation layer can result in different ductile deformation structures under continuous stress.

4. Non-linear genetic mechanism

The nano-sized particles (nano-sized grinding grain) in rock shear planes are caused by wearing, friction, and grinding [11,12]. It is called a separating build way in physics, i.e., larger solid grains become finer particles and finally form the nano-sized particles through shattering [29]. In the other kind, which is named compounding build way, smaller particles are compounded into nano-sized particles through gas evaporation (or melting coagulation from liquid state) [29]. The latter type has yet to be discovered in rock shear planes. The rock's frictional process is a non-stable complex system restricted by multiple element actions of non-linear strong coupling [30]. The process of shattering and wearing is far from equilibrium, and its energy dissipation results in self-organization, self-feed back and self-catalysis function and forms an ordered structure (called dissipative structure) [31–33]. Obviously, the distributive layering of the nano-sized particles in the examples mentioned above in Fig. 1, all of which reflect a feature of the dissipative structure, is clearly illustrated in the *ac* fabric plane (Fig. 1(b)).

In 1995, a new concept about multiphase nano-composite coating of equal ion was proposed in material science [23]. This is also called nano-smearing films or nano-modulated films and their widths may reach 3–20 μm [34,35]. In fact, chemical composite plating (commonly 20 μm in width), which often leads to changes of physic, chemical and mechanic functions, had been applied in practice early [36], and the "tribo-glazing" in tribology is a good example. This tribo-glazing layer typically appears white when observed in metallography and therefore it is also called the "tribological white layers" [37]. From the theory mentioned above, it is quite clear that the formation of nano-sized layer on shear surface in rocks is actually coating, plating and smearing under frictional force action. This is so far the best explanation for its genetic mechanism. In ordinary conditions, the width of a single layer of the nano-sized coating in ductile shear plane, corresponding to the chemical plating of material, is mostly on a micron scale (Fig. 1(a)–(d)). The nano-sized coating of brittle shear plane with larger width of a single layer is suitable with the tribo-glazing of metallography. In particular, the nano-sized layer consisting of light color stress minerals (quartz, calcite) on a shallow structural level shows a white color layer (Fig. 1(e) and (f)).

The rock's shear plane (zone) is just a plastic deformation domain (zone), with the slipping action dominating plastic rheology [38]. This frictional-viscous transition zone [39] actually carries on through a process involving multiple ductile-viscous (ductile deformation) or multiple brittle-viscous (brittle deformation) actions, and it has also improved diffusible creep and flow to follow subgrain rotation and recrystallization of grain boundary [40]. Thus, in finite width the frictional-viscous transition can promote a non-linear and heterogeneous rheological field with ductile detachment effect [41,42]. This ideal explanation for the frictional viscosity and creep rheology has been improved based upon microscopic observations. Through observation of the phenomenon on the shear planes with electron microscope, we may affirm that the plastic flow is essentially the motion of grinding grains in nanometer scales (including micron scales), due to that the nano-sized particle layer, which possesses larger activity and less resistance [36], corresponds to shear frictional plane. For example, composed grinding grains with pancake shape can be observed by electron microscope identification from the dynamic thin shell in the samples collected from an inverse fault in quartz sandstone of Wutong formation (D_{3w}) of the upper Devonian series, in Mufushan Mountain, Nanjing. In general, the plastic flow appears in tongue shape parallel to the *a* axis (Fig. 1(f)).

5. Multiple functions

Because of its heavier density and larger surface area, the nano-sized particle layer can induce activation and catalysis. Therefore, the physical and chemical reactions are multiple and novel [23]. The nano-sized particle layer in rock shear planes commonly has physical geological actions and chemical geological actions.

5.1. Physical geological actions

Earlier functional experiments had not achieved any advances under the condition of >15 Mpa pressure [12], including experiments with the friction force of rolling slip being only 1/20 of the non-rolling slip in nano-sized particle layer, and the breakthrough experiments containing the nano-sized particle texture of slipping lamellae of the whole sample (both dry and wet specimen). Recently, to study the change pattern of the falling tendency of nano-sized pore in diagenesis process and texture pore of minerals [43,44], we analyzed the surface area of foliated mudstone of the Permian system (using the instrument of model ASAP 2010M+C). The result of specimen analysis indicated that the numbers of the surface area of foliated mudstone with the nano-sized particle layer (SEM determining, type HITACH, X-650) are 3.2300 m^2/g and 4.2470 m^2/g. Due to a higher compaction degree and heavy density in rock, it can provide superior sealing efficiency to oil–gas reservoir. Thus, it is difficult to break through the whole specimen of slipping lamellae with nano-sized texture mentioned above.

5.2. Chemical geological actions

The studies on geochemical geological actions in rock shear planes have migrated from body faces and static attitude to surface faces and kinetic attitude, which are related to both surface chemistry and friction chemistry [45]. In the frictional process in rock shear planes, there are bigger change of entropy, higher rate of chemical reaction, and higher chemical properties of the catalysis, activation, and intensification. The wearing material itself produced by the frictional action in solid can give rise to catalysis which is called self-catalytic action [46]. Thus up to now, most studies on rock shearing mainly belong to an anchimetamorphism [47], which can generate high field strength elements (HFSE) such as Ti, Nb and Ta [48]. For example, the grinding grains on micron scale in shear slipping zone in mudstone of middle Carborniferous series, northern Shanxi Province, contain Ti 32.368% (average value),[1] and the nano-sized grinding grains in slipping zone in Mesozoic granite, Cajon Pass area, California, USA, contain Nb 85.374% and Ta 1.230%.[2] They both may be tens of times higher than those in margin zones.

6. Conclusion

We believe that the nano-sized particle layer holds rich information. However, studies on it are still at an early stage. We hope our new findings could provide a new discussion platform for constructive debates that would lead to a shared vision and understanding within Structural Geology and other related fields. In theory, the nano-sized particle layer developed in rock shear planes can be used to interpret the mechanism of shearing, layering and rheological actions, and their tripartite movements in harmonizing actions between each other. In view of the macroscopic law of geological structure which is only similar to microscopic regularity in essence, genetic discussion of the nano-sized particle layer will provide a theoretical platform for research. In experiments, on the basis of launching tests with both physical and chemical actions about the nano-sized particle layer, we have discussed the nano-sized microscopic dynamics acceleration actions of the catalysis, activization and intensification through composition comparison of the nano-sized particle layer (including major element, trace element, rare earth element and isotope) and the country rock [49,50]. In practice, weathering fractural granite commonly contains richer high field strength elements Nb and Ta in the southern China [11], and auriferous veinule and disseminated ores are usually distributed along mylonitic foliations in the northern China [51]. Synthetical analyses incorporated with the nano-sized particle layer and its activated way will help to search for some new regularities. In addition, through exploration for the seismotectonic fault with broad scope, seismo-geologists of Japan had found that the initial seismotectonic fault is very thin with only several centimeters in slipping zone [52,53].[3] We believe that observing the nano-sized particle texture (layer) and its rheological characteristics to frictional-viscous shear zone will lead us to attain new information and knowledge.

[1] EDS analysis assisted by the Testing Center, Changqing Petroleum Exploration and Development Institute, General Corporation of Petroleum and National Gas, China.

[2] EDS analysis assisted by Civil Engineering Department of California University (Berkeleg), USA.

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