Terent'ev A.V., Kunts A.F. Modifications of carbonate rocks under thermal and hydrothermal influences.

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The results of an experimental study of the re-crystallization processes in mineral aggregates of carbonate rocks at thermal and hydrothermal influence are shown. The major mechanisms of transformations are considered. Data on the experimental modeling of the re-crystallization of carbonate rocks in the wide range of temperatures and pressures, as well as data on variations of some physical properties of the transformed rocks (i.e. porosity, water absorption), are presented.

A role of carbonate rocks in the formation of hydrothermal and metasomatic stratified deposits is exclusive and is conditioned by both their composition and physico-chemical properties during the ore deposition. In nature, the zones of alteration of the host carbonate rocks are thoroughly developed around veins and metasomatic ore bodies. These zones are marked mostly by re-crystallization of carbonate mineral aggregates. Mechanism of such re-crystallization are not recognized so far. These problems are not solved by experiments as well.

In order to study the processes of re-crystallization of mineral aggregates in marble and dolomite, two experimental series have been carried out. They include a dry annealing and a hydrothermal treatment in autoclaves. The temperature interval was 100-400^{O}C with step 50^{O}C for the dry annealing, and 150-500^{O}C for the hydrothermal experiment.

In the first experimental series, structural modifications of the calcite aggregate were observed during the first days. The process of re-crystallization is observed during the thermal treating of marble without pressure at all temperatures. The increase of temperature intensifies the process. A coarsening of mineral aggregate occurs with the increase of temperature up to 300^{O}C. At temperatures 400 and 500^{O}C, due to the intensive process of re-crystallization, the mineral aggregate becomes more equally grained. The granulometric analysis shows that the content of calcite grains of size up to 0.096 mm decreases from 28 (in the starting sample) down to 4 % (at 350^{O}C) during the thermal treatment. By contrast, the content of grains of size above 0.384 mm increases from 2 (in the starting sample) up to 20 % (at 400^{O}C). Other regularities are observed in dolomite. An amount of grains of size up to 0.032 mm varies from 12 % (in the starting sample) down to zero (at 250^{O}C) toward the decrease and from 12 up to 20 % (at 350^{O}C) toward the increase. The most coarse grains of sizes from 0.128 to 0.16 mm, which are absent in the starting sample, appear only at 150, 250, and 300^{O}C.

At slight axial pressure, the processes are almost analogous to the thermal treatment without pressure. With the increase of the inhomogeneity of strain, the process of re-crystallization strengthens the granular inhomogeneity of the mineral aggregate. Thus, for development of the re-crystallization process (grain coarsening or re-crystallization), one of two factors, i.e. temperature or pressure, is necessary and sufficient. The maximal coarsening of grains is observed at the quasi-equal strain, whereas the degree of coarsening decreases with an increase of the dynamic loading. The decrease of the degree of re-crystallization of the mineral aggregates with the increase of temperature and pressure can be explained by the role of re-crystallization at deformation loading, when some large grains break into smaller grains instead of coarsening.

The character of the hydrothermal influence on the mineral aggregates of calcite and dolomite was investigated in the second experimental series. Both in marble and in dolomite, the structural modifications appear already at 150^{O}C. Similar to the dry annealing, an amount of calcite grains of the size up to 0.096 mm decreases from 28 (in the starting sample) to 4 % (at 350^{O}C). An amount of calcite grains of the size above 0.384 mm increases from 2 to 20 % (at 350^{O}C). An amount of dolomite grains of the size up to 0.032 mm abruptly decrease with temperature up to their complete disappearance. On the other hand, grains with the size above 0.128 mm, which were absent in the initial sample, appear at 150^{O}C and they are more common at 250^{O}C.

The experimental study of transformations in marble and dolomite in dependence on thermal and baric conditions and variations of acidity and alkalinity of hydrothermal solutions was carried out on the high-pressure apparatus UVD-3. An amount of calcite grains with area below 0.033 mm^2 decreases during the hydrothermal treatment, and, by contrast, an amount of grains with area 0.033-0.726 mm^2 increases, and grains with area above 0.726 mm^2 appear. Such changes in the distribution of grains by size allows conclusion that calcite aggregates are affected by the re-crystallization processes with grain coarsening. Histograms show a dissolution of smaller grains and a growth of larger grains after them. Similar regularity is observed for dolomite as well. In the experiments with solutions of pH 2.5 and 10 at different P-T conditions, the changes in the distribution of grains by sizes, reflecting the re-crystallization processes, were not found.

We also investigated the changes of the open porosity and the water absorption, which are the most important features of the hydrothermal and metasomatic processes. The obtained data show that an increase of the water absorption and the open porosity with temperature occurs at all pH values. Pressure significantly influences on these parameters. As pressure increases up to 500-1000 atm., the water absorption increases by factor of 1.5-3 at the same temperatures. It suggests that the effect of the thermal de-consolidation actively operates under the influence of temperature and pressure. It is known that an increase of de-consolidation results in an increase of the rock electrical conductivity and the permeability, a volume weight and a solidity of rocks decrease, the velocity of elastic waves decreases as well [1]. Concerning to the problems of metasomatism, the most important consequence of the thermal de-consolidation is the significant increase of permeability, related to the opening of the interconnected net-work of micro-cracks along the grain boundaries [4].

The character and the degree of the above properties is mostly determined by grain size in a rock. From this point of view, the re-crystallization with coarsening could be considered as a process assisting to the intensive de-consolidation. It can not be excluded that the structural modifications of the mineral aggregate can proceed under influence of the thermo-elastic strains, which appear in it under temperature and pressure and caused by differences in the thermal expansion of separate grains. In this case, the re-crystallization can be a result of the de-consolidation.

The grain boundaries play an important role in the processes of modification in mineral aggregates. Configuration of the grain boundaries changes. Such properties as the mechanical firmness, elastic properties, plasticity, permeability also change. An ability of the grain boundaries to migrate explains the re-crystallization of mineral aggregates. The basic factors, which influence the migration ability of the grain boundaries, are the surface energy of the boundaries and strains under some internal and external factors. There is a hypothesis describing a structure of the grain boundaries, which is based on their dislocation model. The grain boundaries with low angles of relative disorientation of the lattices , as well as disorientation of the lattices of separate blocks in crystals, are the most suitable for application in the dislocation model, since in this case the suitable dislocation model can be scrupulously chosen. However, the intergrain boundary is an impediment for dislocations, which, being concentrated at the boundary, increase strains and distortions of the grain lattice in the boundary region. They could cause a plastic turn of separate blocks or groups of blocks. The low-angle boundary between the block and "old" grain transforms into the large-angle boundary, while the large-angle boundary between the block and new grain transforms into the low-angle boundary. The block (or their group) becomes "captured" by new grain, while the intergrain boundary displaces toward the "old" grain. A possibility of such mechanism is an abrupt character of migration of the grain boundaries commonly observed in metals [2, 3], as well as a principal possibility of the micro-block growth of crystals [8]. Apparently, such mechanism is responsible for the junction of grains and separate blocks during the heating of mineral aggregates of marble and dolomite, and the processes of re-crystallization with coarsening proceed mostly by this principle. An increase of temperature from 100 to 400^{O}C results in a decrease of an amount of grains of least sizes (more strained), whereas an amount of large grains (less strained) increases. At very high loading, the disorientation of the blocks in the initial grain could occur. The boundaries between blocks could transform into the intergrain boundaries, and the grain splits into smaller grains. Thus, the process of re-crystallization with fining of grains proceeds.

In the hydrothermal experiments, the simultaneous action of temperature and pressure amplifies the outer strains and, apparently, imparts a directed character to the re-crystallization processes. A notable monotonous growth of larger grains is observed. In the hydrothermal and metasomatic mineral formation, the thermal influence causes a re-crystallization of the initial rocks with the formation of the re-crystallization zones on a metasomatic front. According to the Korzhinskii's theory [5], a number of zones in the metasomatic column exceeds the number of minerals by one. Therefore, in the simplest case, an influence of a fluid, which does not carry components for new minerals, on the monomineral aggregate results in the formation of at least two zones: the zone of partial dissolution and the zone of re-crystallization. Dissolution and precipitation of a material do not occur in the second zone, since the fluid reaches saturation in the first zone. The re-crystallization of the mineral aggregate proceeds namely due to the thermal fluid effect. The re-crystallization zones at the metasomatic front are always observed both in nature and in the metasomatic columns form the experiments on modeling of the hydrothermal mineralization in carbonate rocks [6, 7]. Since a refinement of mineral grains from impurities and the formation and widening of the intergrain space occurs during the re-crystallization, the process somehow prepares the mineral aggregate (and a rock as a whole) to the subsequent metasomatism. This is a basic role of the re-crystallization of mineral aggregates during the hydrothermal mineral formation.

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