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Change in generally accepted regularity of phase transformations of quartzite

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Abstract. The subject of this research is phasic transformations of quartzites that are under temperature treatment to remove moisture. This technology is used in enterprises operating melting furnaces. The studies have shown that using a temperature regime consisting in heating to 800° C and holding for 2 hours, after cooling, quartzite changes its color and appears a shift in the angle of the interplanar distances of the crystal lattice by 6.6% in it. The use of a temperature treatment regime consisting in heating to 200° C and holding for 4 hours does not reveal such changes. With subsequent exposure to these samples of the temperature regime corresponding to the sintering process of the liner, the following is established. In a sample pretreated with a temperature of 800° C, at a temperature of 1550° C, a tridymite phase appears. In the sample of a 200° C pretreated with temperature, a phase of cristobalite appears without tridymite.

1. Introduction
Quartzite, based on silica, is widespread in the metallurgical industry, where it is used in the production of ferroalloys and as a raw material for acid refractory bricks – dinas. Quartzite also allows producing unshaped refractory materials for manufacture of linings for induction furnaces, iron smelting and steel-casting ladles. The active use of induction crucible furnaces for smelting synthetic pig iron from a metal scrap, consisting only of steel scrap, carburizing and ferroalloys, reduces sharply the resistance of the acid liner and causes a more careful study of the properties of quartzite on exposure to various temperatures. Because the melting temperature has risen to 1550-1600 °C, it is necessary to get a more thermally stable phase of quartzite – cristobalite after sintering in the lining. Traditional technology is used to obtain the tridymite phase, so the temperature regime for removing moisture in the original quartzite is 800-900 °C. Then, a lining is made from this quartzite, which, after sintering, guaranteed the appearance of the tridymite phase. This phase is the most stable at operating temperatures not higher than 1470 °C. The research objective is to determine the conditions under which the phase of cristobalite appears bypassing the tridymite phase in the lining after its sintering.
2. Materials and methods

Research was conducted on a BRUKER D8 ADVANCE X-ray diffractometer with Bragg-Brentano focusing. An HTK 16 high temperature chamber was used to carry out temperature experiments on a diffractometer. An X-ray tube with a copper anode was used; the diffraction spectrum was recorded with a high-speed position sensitive detector VÁNTEC-1. The survey was carried out at scanning angles $2\theta = 10^\circ - 90^\circ$ in steps of 0.007 [1].

In 1912, Fenner C.N. published in [2] the diagram of a single-component SiO$_2$ system (Figure 1). According to the diagram, it was believed that the changes occurring in quartzite when it is heated to 870 °C are insignificant and do not affect refractories manufacturing technology. This fact was noted in [3, 4], but Wettegren V. I. found distortions of the crystal lattice of the $\alpha$-phase of quartz under the influence of growth dislocations [5].

![Figure 1. A diagram of a single-component SiO$_2$ system constructed by K. Fenner](image)

On that base, at the first stage let us assign the task of studying the changes in the crystal lattice of quartzite under different temperature regimes to remove moisture. Two samples were prepared. The first sample was exposed to a temperature regime consisting in heating to 800 °C and holding for 2 hours (the diffractogram is shown in Fig. 2).
Figure 2. A diffractogram of quartzite: heated to 800 °C, held for 2 hours, removed after cooling to a temperature of 30 °C: ■ is quartzite; d is the interplanar distance, Å

After cooling, quartzite changed its color and the following changes occurred in its crystal lattice.

1. The average value of interplanar distance \(d_{av}\) at 25 °C was 1.89674 (Å) and at 800 °C – 1.9856 (Å); that is, it increased by 4.5%. In the interval of angle \(2\Theta = 20.419-59.859\), this value increased from 2.089 (Å) to 2.46992 (Å) (15.4%). With subsequent cooling to 30 °C, value \(d_{av}\) was 1.88221 (Å), and in the interval of angle \(2\Theta = 20.419-59.859\), this value was 2.28278 (Å). Thus, with heating, soaking and cooling, \(d_{av}\) decreased by 0.77%, and in the interval of angle \(2\Theta = 20.419-59.859\) this value increased by 8.5%.
2. The intensity decreased by 10.3%.
3. The angle of interplanar distances \(2\Theta\) shifted to the right by an average of 0.2% which could be interpreted as an error. But in the interval of angle \(2\Theta = 20.419-59.859\), the shift was 10.9% at 800 ° C, and with further cooling up to 30 °C, it was 6.6% relative to the original, which in the authors’ opinion led to a change in the color of the original quartzite.
4. Along with the change in the interplanar distance, the density of unit cell \(D_x\) changed. At 25 °C \(D_x = 2.643g / cm^3\), and at 800 °C \(D_x = 2.216g / cm^3\), the density decreased by 16.2%; with further cooling to 30 °C, it took the initial value.
5. The density of unit cell \(V\) was changed. At 25 °C \(V = 113.28 Å^3\), and at 800 °C \(V = 118.86 Å^3\). The density increased by 3.6%; with further cooling to 30 °C, it took the initial value.
6. Simultaneously with these changes, the size of the lattice was changed. At 25 °C, \(a = b = 4.921 Å, c = 5.400 Å\), and at 800 °C, \(a = b = 4.994 Å\) and \(c = 5.438 Å\). Sizes \(a\) and \(b\) increased by 1.86% and the size of \(c\) increased by 1.5% and with further cooling to 30 °C took the initial value.

The second sample of quartzite was subjected to a temperature treatment regime consisting in heating to 200 °C and holding for 4 hours. Figure 3 shows the diffractogram.
Figure 3. Diffractogram of quartzite: heated to 200 °C, held for 4 hours, removed after cooling to a temperature of 30 °C: ■ is quartzite; d is the interplanar distance, Å

After cooling, quartzite obtained minor changes that did not affect the properties of quartzite:

1. The average value of the interplanar distance $d_{av}$ at 25°C was 1.8541 (Å), and at 200 °C – 1.9253 (Å); that is, it increased by 3.8%. In the interval of angle $2\Theta = 20.419$-59.859, this value decreased from 2.215 (Å) to 2.111 (Å) - by 4.7%, and at the subsequent cooling to 30 °C $d_{av}$, it was 1.85243 (Å), and in the interval of angle $2\Theta = 20.419$-59.859, this value was 2.215 (Å). Thus, with heating, soaking and cooling, $d_{av}$ decreased by 0.1% (one could say that it did not change), and in the interval of angle $2\Theta = 20.419$-59.859, this value was equal to the initial value.

2. The shift of the angle of interplanar distances $2\Theta$ with heating to 200 °C and the exposure left to 2.94%, and with further cooling to 30 °C returned to the initial value.

Thus, the authors have established irreversible changes in the crystal lattice of quartzite, when exposed to a temperature regime consisting in heating to 800 °C, holding for 2 hours and then cooling. For this reason, the next stage of the study was the effect on these samples of the temperature regimes corresponding to the sintering of the liner. Figure 4 shows a diffractogram of quartzite, from which moisture removal was carried out at 800 °C.
As a result, it was found that at a temperature of 1550 °C, a tridymite monoclinic (rhombic) phase appears with lattice dimensions: \( a = 18.50400 \text{ Å} \), \( b = 5.00640 \text{ Å} \), \( c = 23.84500 \text{ Å} \), \( V = 2125.08 \text{ Å}^3 \), and the phase was quartzite hexagonal with cell dimensions \( a = b = 4.965 \text{ Å} \) and \( c = 5.424 \text{ Å} \), \( V = 116.79 \text{ Å}^3 \), \( D_x = 2.25 \text{ g/cm}^3 \).

Figure 5 shows the diffractogram of quartzite, from which moisture removal was carried out at 200 °C.
It is established that at a temperature of 1470 °C, there was a phase - cristobalite cubic with cell dimensions $a = b = c = 7.12000 \text{Å}$, $V = 360.94 \text{Å}^3$, and phase - quartzite hexagonal with cell sizes $a = b = 4.965$ and $c = 5.424 \text{Å}$, $V = 116.79 \text{Å}^3$, $D_x = 2.211 \text{g/cm}^3$, and phase - quartzite hexagonal with cell sizes $a = b = 4.965$ and $c = 5.424 \text{Å}$, $V = 116.79 \text{Å}^3$, $D_x = 2.595 \text{g/cm}^3$. Thus, the authors have received a phase - cristobalite cubic, bypassing the phase - tridymite monoclinic. The possibility of such transformation was noted in work [6].

3. Conclusion

It has been established that the drying of quartzite at a temperature of 200° C makes it possible to obtain the phase of cristobalite, bypassing the tridymite phase; after that, the lining of the induction crucible furnace on its basis is made on this basis and the cro-tobalite phase is carried out. In the future, the share of cristobalite content will increase by 30% with each melting cycle. Studies of the heat capacity and thermophysical properties of these quartzites showed the following advantages of quartzite, pretreated at 200° C in comparison with quartzite pretreated at 800° C:

1. The heat capacity from the cycle to the melting cycle varies smoothly and by a value greater by 100%.
2. The volume thermal deformation is lower by 40%.
3. The coefficient of linear expansion is less than 12 times.

All this allows us to conclude that the use of established changes in the crystal lattice of quartzite makes it possible to create a lining for an induction crucible furnace that has high resistance in smelting synthetic pig iron at a metal scrap that requires melting at temperatures above 1500° C.

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