Chemistry

1964

SovietRxiv

Abstract

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Chemistry

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Synthetic Fibrous Fluorine-Magnesium Arfvedsonite

(Presented by Academician I. V. Tananaev, February 8, 1964)

The problem of obtaining artificial inorganic fibrous materials is of great scientific interest and is of considerable importance for practice, if one takes into account the need for such materials in certain branches of new technology.

Such materials in the form of silicates of the amphibole type can be obtained by synthesis from a melt or under hydrothermal conditions. Attempts to obtain artificial alkali amphiboles have been made repeatedly abroad ([1]-[6]) and in the Soviet Union ([7]).

We carried out work on the synthesis of needle-like fibrous varieties of alkali amphibole by crystallization from a mixture of oxides in the presence of certain low-melting salts.

Chemically pure reagents were used as the starting components of the experimental batches: amorphous SiO_2, Na_2CO_3, MgO, MgF_2, Fe_2O_3. The batch was prepared in accordance with the stoichiometry of fluorine-containing magnesium arfvedsonite, $Na_3Mg_4Fe'''Si_8O_{22}F_2$. Fluxes were additionally introduced into the batch in the form of sodium fluoride and chloride in an amount of 5-50%, and wood sawdust to loosen the batch during heating.

Table 1

Data of chemical analyses of synthetic and natural arfvedsonites*

Oxides, wt. %	Synthetic arfvedsonite, wt. %	Natural rezhikite, wt. %
SiO_2	55.35	56.56
Al_2O_3	0.45	0.90
Fe_2O_3	9.03	7.93
FeO	–	0.56
NiO	–	0.08
MnO	–	0.06
CaO	0.62	0.96
MgO	22.22	19.61

Oxides, wt. %	Synthetic arfvedsonite, wt. %	Natural rezhikite, wt. %
K_2O	–	0.69
Na_2O	9.42	10.54
F	3.44	0.02
Cl	1.17	–
H_2O+	–	2.12
Sum	101.70	100.01
F	1.44	0.01
O equiv. Cl	0.26	–
	100.00	100.00

* Chemical analyses were performed by T. M. Makarova and A. V. Bystrova.

The experiments were carried out in electric furnaces with silite heaters at temperatures of 800-1000°. Cooling at a specified rate was carried out with the aid of an electronic programmed unit. The experimental regime was: raising the temperature in the furnace for 2-3 hours, holding at the specified temperature for 12-15 hours, cooling at a rate of 1-5-10° per hour to a temperature of 700-600°, after which the furnace was switched off.

Syntheses were carried out in corundum or platinum crucibles with lids. For better thermal insulation and sealing (taking into account the presence of volatile components), the crucibles with the batch were placed in larger corundum crucibles and covered with electrocorundum. Under optimal experimental conditions (the ratio between the contents of the main components of the batch and the amount of fluxes, the holding temperature and the cooling rate), the initial batch crystallized almost entirely in the form of amphibole. The amphibole was represented by three morphological varieties: needle-like, fibrous, and fine-grained. In addition, sodium chloride and no more than 5% silica in the form of γ-tridymite were present in the synthetic product.

In the course of the work it was preliminarily established that the crystallization regions of needle-like and fibrous amphiboles are different: the temperature of obtion of the first lies within 950-1050°, of the second 800°. With the aid of a high-temperature chamber mounted on the microscope stage, the changes undergone by the charge during heating were observed. It was found that at 750-800° the amount of liquid phase in the charge is small, and the dissolution in it of solid particles—components—is limited. It may be assumed that the formation of fibrous amphibole under these conditions proceeds by solid-phase reactions with the active participation of the liquid and gas phases.

When amphibole synthesis is carried out at higher temperatures (950-1050°), almost complete dissolution of the main components of the charge in the melt

Fig. 1. Structure of the synthetic product. Thin section. 150×.

Figure 1: Fig. 1. Structure of the synthetic product. Thin section. 150×.

of low-melting salts occurs. Under these conditions the formation of amphibole may be regarded as crystallization from a solution in a melt. It has been experimentally established that the more slowly the melt is cooled, the longer the amphibole needles are, and the less flux is introduced into the charge (as a result of which a more supersaturated solution—melt—is obtained), the thicker the synthesized needles are.

Table 2

Optical properties of synthetic and natural arfvedsonites

	Synthetic arfvedsonite	Natural riebeckite
Refractive indices	1.630	1.640
N_g		
N_m	1.623	1.635
N_p	1.618	1.630
Birefringence	0.012	0.010
Extinction angle	$cN_m = 12$-$20°$	$cN_m = 0$-$5°$
Angle of opt. axes	−(35-45°)	not measured
Pleochroism	N_g −yellowN_m −pale yellowN_p −colorless	N_g −blueN_m −greenN_p −pale yellow

Despite some differences in the crystallization conditions, the synthetic products have the same structure. In external appearance they are a porous fine- or thin-grained mass of yellow color, consisting of intergrown star-shaped aggregates. Under the microscope it is seen that the central part of the aggregate has a fine-grained structure and has the appearance of a "lump," from which thin needles or fibers grow in different directions (Fig. 1). The synthetic product obtained at a temperature of 800° is covered on top with a dense brush of fibers 1-2 mm long, with a maximum of 4 mm.

Fig. 1. Structure of the synthetic product.
Thin section. 150 ×.

The synthetic amphibole was diagnosed by chemical, optical, and X-ray methods of investigation. For comparison, the characteristics of natural fibrous magnesioarfvedsonite, known in the literature under the name riebeckite ([8]), are given.

Only the acicular and fibrous varieties were taken for chemical analysis. The analytical data are given in Table 1. Recalculation of them to the crystal-chemical formula of amphibole $X_{2-3}Y_5Z_8O_{22}(OH)_2$ gave the following results: the synthetic amphibole has the formula

$(\mathrm{Na}_{2,56}\mathrm{Ca}_{0,09}\mathrm{Mg}_{0,44})_{3,09}(\mathrm{Mg}_{4,21}\mathrm{Fe}^{\cdots}_{0,79})_{5,0}(\mathrm{Si}_{7,76}\mathrm{Al}_{0,07}\mathrm{Fe}^{\cdots}_{0,17})_{8,0}\mathrm{O}_{22}(\mathrm{O}_{0,19}\mathrm{F}_{1,53}\mathrm{Cl}_{0,28})_{2,0}$,

natural riebeckite

$(\mathrm{Na}_{2,84}\mathrm{K}_{0,12}\mathrm{Ca}_{0,15})_{3,11}(\mathrm{Mg}_{4,07}\mathrm{Ni}_{0,01}\mathrm{Mn}^{\bullet\bullet}_{0,01}\mathrm{Fe}^{\bullet\bullet}_{0,06}\mathrm{Fe}^{\cdots}_{0,82}\mathrm{Al}_{0,03})_{5,0}(\mathrm{Si}_{7,88}\mathrm{Al}_{0,12})_{8,0}\mathrm{O}_{22}(\mathrm{O}_{0,01}\mathrm{OH}_{1,98}\mathrm{F}_{0,01})_{2,0}$.

It is thus evident that the synthetic amphibole corresponds to the formula of an alkali amphibole in which the OH group is replaced by fluorine and chlorine. In composition it is close to riebeckite and differs from it only by a slight predominance of magnesium, which even enters the cation group X in the amphibole formula. A special feature of synthetic arfvedsonite is the partial replacement of silicon in the silicate-oxygen ribbons by trivalent iron. Ernst (9) noted an analogous fact for artificial hydroxyl-bearing arfvedsonite.

The optical properties of the amphiboles under consideration are given in Table 2, from the data of which it is evident that the refractive indices of artificial arfvedsonite are somewhat lower in comparison with riebeckite. This can apparently be explained by the fact that in the artificial amphibole, instead of the OH group, fluorine and chlorine are present, which lower the mineral' s light refraction. Dispersion of the axes of the indicatrix is characteristic of both amphiboles.

Table 3

Interplanar spacings of the most intense lines of amphiboles

Synthetic hydroxyl-bearing arfvedsonite (9), *I*	Synthetic hydroxyl-bearing arfvedsonite (9), *d*	Synthetic fluor-richterite (10), *I*	Synthetic fluor-richterite (10), *d*	Synthetic fluor-richterite (11), *I*	Synthetic fluor-richterite (11), *d*	Synthetic fluor-magnesian arfvedsonite, *I*	Synthetic fluor-magnesian arfvedsonite, *d*	Riebeckite, *I*	Riebeckite, *d*
6	3.108	10	3.099	9	3.087	10	3.095	5	3.135
5	2.729	9	2.711	10	2.705	10	2.687	10	2.706
2	2.606	3	2.581	8	2.589	2	2.568	2	2.572
4	2.533	3	2.505	8	2.517	2	2.510	6	2.517
1	2.178	3	2.163	8	2.180	5	2.150	4	2.162
		2	1.623	6	1.657	5	1.644	3	1.655
		2	1.415	7	1.421	8	1.418	5	1.431
		1	1.282	7	1.284	2	1.279	3	1.282

X-ray studies confirm that the synthetic mineral belongs to the amphibole group. The samples were recorded on an ionization apparatus with a copper anode.

For comparison, Table 3 gives the values of the interplanar spacings of the most intense lines of a series of artificial amphiboles. All of them show good agreement of values, which is evidence of the identity of their structures.

Thus, at temperatures of 800–1000° from a mixture of oxides taken in a stoichiometric ratio, with additions of fluxes in the form of chlorides and fluorides, a fluorine- and chlorine-bearing magnesian arfvedsonite with the general formula $Na_{2\ 5}Mg_{4\ 5}Fe^{+3}Si_8O_{22}(F,\ Cl)_2$ was synthesized. The amphibole was obtained in the form of needles and fibers up to 4 mm long. In chemical composition, optical properties, and structure the artificial amphibole is identical to natural hydroxyl-bearing magnesioarfvedsonite.

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Received
6 II 1964

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