The Properties of Pyroceramic Materials Syntheses by Concentrated Solar Energy

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Abstract: *The effect of the concentrated solar energy density on the microstructure and the properties of vitrocrystalline materials of pyroxene composition is studied. It is shown that the solar irradiation accelerates the processes of crystallization, formation of a perfect microstructure, and sintering of vitrocrystalline mate.*

It is well known that the preparation of materials with targeted properties by solid-phase synthesis is based on heating a substance or a mixture of components at a temperature below their melting points, 0.5 to 0.7 of r_{melt} [1]. In this case, the chemical reactions are determined by diffusion, viz., $10^{'6}$ to $10\sim^{12}$ cm^2/s, of the atoms of one of the components or the atoms of both components through a layer of solid reaction products. The low rates of the solid-phase reactions account for a longer duration of the synthesis process and difficulty in accomplishing the process, as a result of which the reaction product contains, as a rule, impurities of unreacted components, i.e., it is inho- mogeneous. Tn contrast to the solid-phase reactions, the melting techniques enable the preparation of high chemical purity materials with a perfect structure. Analysis [2] shows that the melts consist of clusters with ordered atoms, the arrangement of which is close to their arrangement in a crystal and a disordered intercluster zone. The grain pattern inherited by the liquid from the solid material can be transferred almost without any change to the new specimen of the solid material resulting from the following solidification. However, if a liquid with the inherited structure is, for example, overheated to transfer into the state of a simple structureless liquid, it will obviously lose all the retained structural features. Other impacts can alter the structure in the liquid state. For example, ultrasonic treatment and even ordinary stirring can reduces a grain of the liquid in size and an alternating magnetic field helps to "loosen" the boundaries of the grains and promote the flow along them, etc. [3].

Therefore, study of the structurization processes and the properties of the vitrocrystalline materials with a pyroxene structure synthesized from the molten state in a field of concentrated solar radiation of different densities is of interest. Pyroxene waste of the mining industry, viz., tungsten ores of the Ingichka deposit in the Province of Samarkand was used as the raw material for the synthesis of vitrocrystalline materials.

Tn Table 1, the average chemical composition of pyroceramic materials is presented.

Table1. *The average chemical compositions of pyroceramic materials Percentage per air-dry substance*

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	including		MgO	MnO	CaO	Na_2O	K_2O	P_2O_5	SO_2	LOI	H_2O	Mol
				Fe_2O_3	FeO										
36.1	0.07	5.11	11.23	2.06	8.16	3.30	0.85	40.2	1.32	0.9	0.04	0.8	9.4	0.5	8.7

It is known that the radiation equation of a heated body can be written in the form:

$$E = EE_0 - eC_o(77IO0)^4, \qquad (1)$$

where $C = EC_0$ is the radiation coefficient of a real body, $e = a/a_0$ is the material's emissivity factor, $C_0 = a_0 \times 10^{-8} = 5.67$ W/(m^2 K^4) is the blackbody coefficient, $ct_0 = 5.67$ W/(m^2 K^4) $\times 10^{-8}$ is the Stefan—Boltzmann constant, and T is the temperature (K) that allows the calculation of the temperature of a body that absorbs a certain amount of the energy according to the body's emissivity factor [4, 5].

Table 2 presents the flux density values that correspond to the melting temperatures of materials calculated according to Eq. (1). Tt should be noted that the calculation of the temperature did not

consider the reflection and the transmission of the target body and the convective heat loss. The actual flux density values to smelt oxide materials are rather high. For example, to smelt pyroxene materials, fluxes to 150 W/cm^2 are required. It is well known that the spectrum of the concentrated solar radiation when solar-panel mirror boosters are used covers the range from the near infrared: $X = 2$—3 |im and the quantum energy to 0.4—0.6 eV, to the near ultraviolet, $X = 0.3$—0.4 цтand the quantum energy to 3—4 eV. Consequently, if the band gap energy of an oxide material is above 4 eV, all solar energy penetrates the material bulk and the energy is absorbed owing to defects with energy levels within the band gap. A large contribution to absorption of the solar energy is made by spot defects, viz., impurities, vacancies, interstitial atoms, other structural defects, etc., and current carriers: the intrinsic concentration of current carriers can be very high, to 10^{20} cm^{-3} at temperatures of 1500—2500°C. The impurity precipitates and the phase inclusions also make their contribution to absorption of the solar energy.

With the reducing band gap of the material, an increasingly large part of the solar energy is absorbed in the thin near-surface layer of the material and in the case of the metallic conductivity the solar energy is absorbed only in the thin near-surface layer, generating giant temperature gradients in the material.

From Table 2 it can be seen that in substances with a very large band gap, such as aluminum oxide, silicon oxide, and calcium oxide, the absorption upon solar heating occurs owing to structural defects and impurity inclusions. In other substances, combined radiation absorption owing to interband transitions and absorption in the structural defects occurs. At the first stage, the materials were smelted in a solar furnace at a definite flux density. The melts were cooled by being poured into water at a rate of 10^{3}°C/s. The castings were subjected to electron-microscope and phase- structural analysis.

Figure 1 shows electron-microscope images of pyroceramic materials prepared from a melt depending on the density of the concentrated radiant flux.

Table2. *Flux density values that correspond to the melting points of the materials*

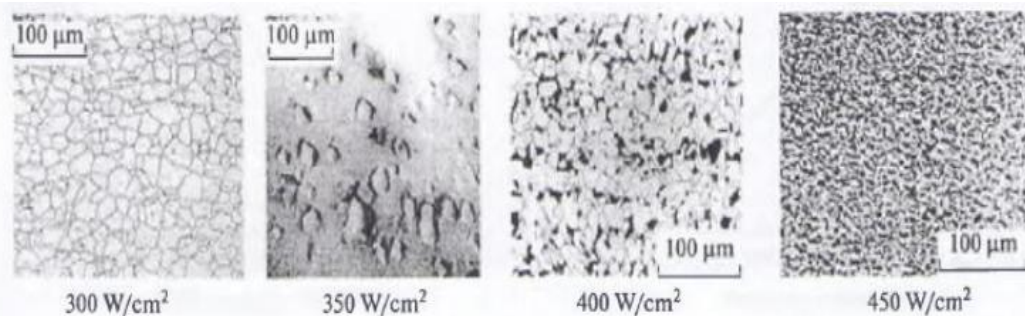| Oxides	T'mdt, °C	£$_g$,Ev	6	Q, W/cm^2
Fe$_2$0$_3$	1390	2.2	0.8	35
Si0$_2$	1550	5.7	0.73	45
Ti0$_2$	1870	3	0.78	93
Al$_2$O$_3$	2050	6.5	0.8	135
CaO	2614	7	0.93	366
MgO	2825		0.72	376
Pyroxenes	1390		0.8	35

Fig. 1. Electron microscopic photographs of pyroceramic specimens prepared from a melt under the impact of fluxes with different power values.

The microscope analysis showed that the smelted vitrocrystalline materials predominantly had a shagreen surface, with the homogeneity increasing with the increasing flux density. Occasional air inclusions were observed. The presence of pyroxene crystal nuclei of a white color and ore mineral inclusions of a black color should be pointed out. Such inclusions could be Fe$_2$0$_3$ (FeO) magnetite phases. It was established that the basaltic-rock-based glass materials change their color from dark brown to black with the flux energy increasing from 300 W/cm^2 to 450 W/cm^2 at a constant cooling rate, which was caused by transition of Fe^{3+} to Fe^{2+}, which, in turn, resulted in the prevalence of the crystallization of diopside—hedenbergite Ca(MgFe^{2+})Si$_2$0$_6$ over aug- ites (Ca,Na) (Mg,Fe^{2+}, Al,Fe^{3+},Ti) [(Si,Al)$_2$0$_6$] and was evidence of the enhanced quality of the target product [5] since hedenbergite, as an isostructural compound of diopsite, possesses better mechanical properties.

The micrograph analysis data are summarized in Table 3 and Fig. 2 presents the dependences of the pyroceramics grain size limit values on the flux density.

From Table 3 it can be seen that an increase in the dispersity of the material is observed with the flux energy increasing above 300 W/cm^2, i.e., the degree of overheating of the liquid. In the dependences of the grain size on the flux density, a nonmonotonic reduction in the grain sizes can be observed. Such a decrease, however, tends to saturation at flux density values of 400—450 W/cm^2.

The purpose of the second experimental stage was the preparation of sintered pyroceramics by the ceramic method. The material that was smelted in a solar furnace at different flux density values was ground, molded, annealed in an electric furnace at definite temperatures, and slowly cooled afterwards. Analysis of the sintering kinetics in the electric furnace at 1000, 1050, 1100, and 1150°C showed that the properties such as the density and the water absorption, changed depending on the treatment temperature (see Figs. 3 and 4). With the increasing sintering temperature, the apparent density increased and the water absorption decreased.

To determine the bending strength by compacting at a unit pressure of 70 MPa, specimens in the form of bars with dimensions of 6 x 6 x 40 mm^3 were prepared from the ground powder of the smelted materials, annealed in a silicon carbide furnace at a temperature of 1150°C and then held at the maximum temperature for 1 hour.

Below, the dependences of the apparent density, the water absorption, and the bending strength of the vitrocrystalline specimens on the concentrated luminous flux density are presented in Table 4 and Figs. 5 and 6 and on the exposure time at the optimal concentrated luminous flux density of450 W/cm^2 in Fig. 7.

Table3. *Microstructural features of pyroceramic materials depending on the concentrated radiant flux power*

Flux density (W/cm^2)	Microstructure
300	Crystallites in the form of polyhedrons of various shapes; along with areas where individual crystallites can be seen, also areas with close-packed crystallites with particle sizes from 100 to 750 nm are observed; a certain orientation takes place.
350	Crystallites of various shapes in the form of degraded and deformed polyhedral crystals from 70 to 500 nm in size.
400	Close-packed oriented crystallites of oblong shape with particle sizes from 66 to 170 nm.
450	Close-packed crystallites in the form of polyhedrons of various shapes with particle sizes from 40 to 130 nm.

Table4. *The controlled parameters of sintered pyroceramic materials depending on the concentrated radiant flux density*

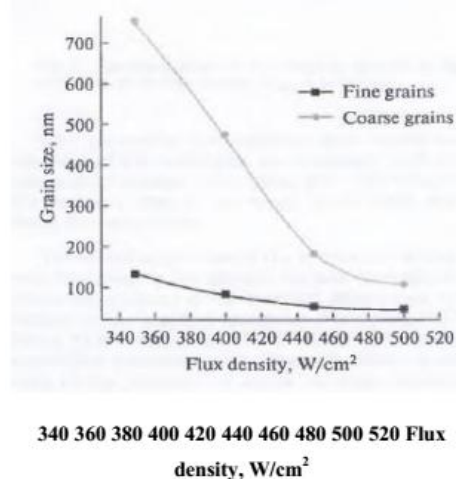| Parameters	Concentrated radiant flux density (W/cm^2)			
	300	350	400	450
Water absorption, %	0.05	0.04	0.03	0.02
Bending strength (MPa)	125	135	145	156

Fig2. *The dependences of the pyroceramic grain size limits on the flux density*
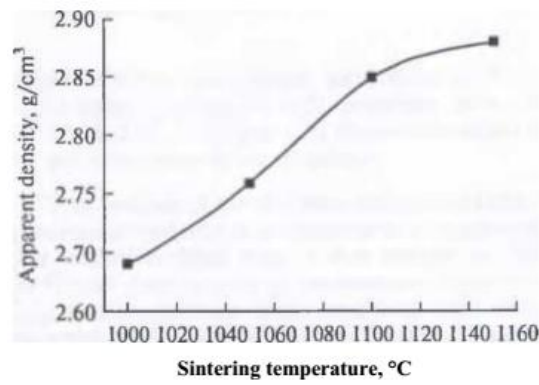
Fig3. *The dependences of the apparent density of the specimens on the sintering temperature*
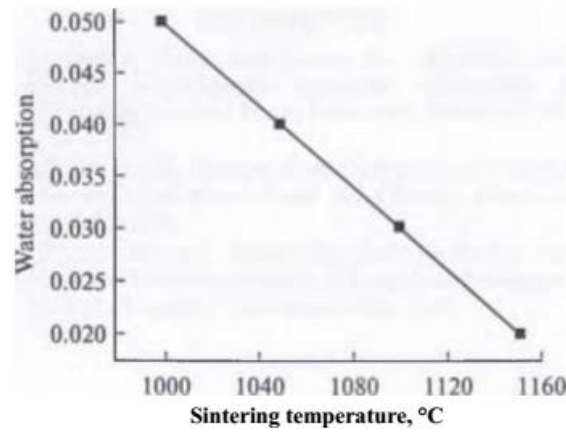

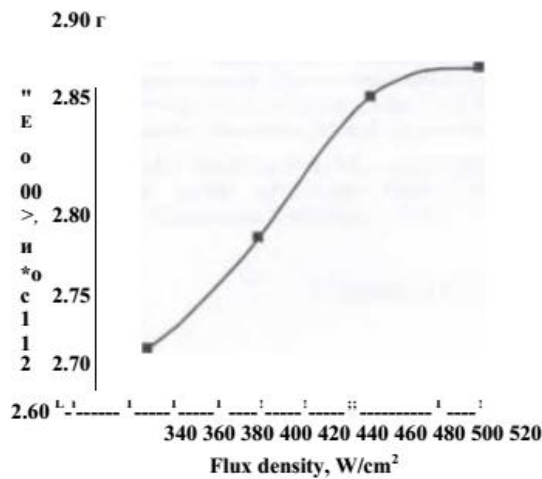**Fig4.** *The dependence of the water absorption of the specimens on the sintering temperature*

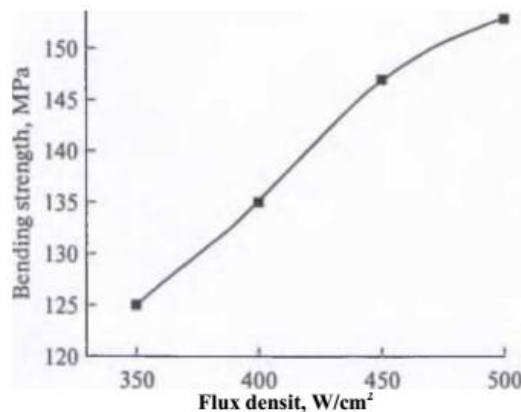**Fig5.** *The dependence of the apparent density of the specimens on the flux density = 1150°C)*

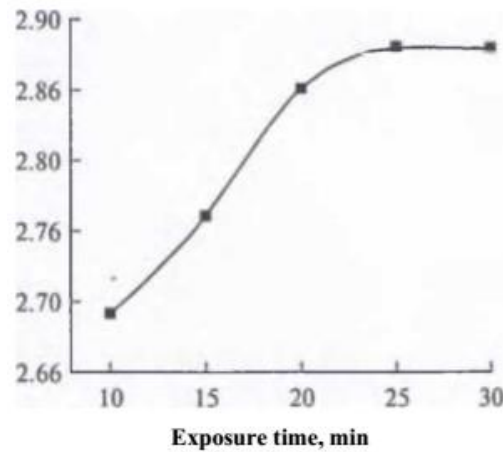**Fig6.** *The dependence of the bending strength of the specimens on the flux density (T_{mn} = 1150°C).*

Fig7. *The dependence of the apparent density of the specimens on the exposure time at a flux density of 350 W/cm^2 (T_{mn} = 1150°C).*

With increasing concentrated solar radiation the mechanical characteristics are enhanced with a tendency to saturation in the range 400—450 W/cm^2 and the exposure time in the range 25—30 min, respectively, for every curve.

The sintering process of the specimens during the heat treatment in the electric furnace depends on the phase composition of the material determined by the density of the incident luminous flux during the synthesis. At low densities to 350 W/cm^2, low values of the controlled parameters are observed, which is attributed to the presence of augite. At high densities to 450 W/cm^2, the properties and the structure of the material drastically change, which is caused by crys tallization of the basic phase, solid diopside—heden- bergite-based $Ca(Mg,Fe)Si_2O_8$ solutions *(d = 2.99, 3.24, 2.96, 2.57, 2.52, and 1.62 A)* and formation of a fine-grained pyroceramic structure.

Thus, analysis of the obtained data showed that if a pyroceramic material is synthesized in a concentrated solar radiation field with a flux density of 350— 450 W/cm^2 from a melt at temperatures higher than T'mclea homogeneous microstructural state with a fine-grained structure is achieved that provides high values of a material's mechanical properties, which enables it to be used for the manufacture of thread guides for thread-spinning looms and silk-winding machines.

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