The properties of the material obtained are comparable with similar characteristics used in conventional tool manufacture. However, cryochemical technology enables dense material to be produced at lower sintering temperatures. By varying the production conditions, materials can be formed which have the required overall properties.

LITERATURE CITED


THE SYNTHESIS OF FERROVANADIUM GARNETS

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UDC 546.65.72; 541.123.16

Complex oxides with the structure of ferrite garnet are widely used in modern technology. A promising class of compounds of this type is calcium—vanadium ferrogarnets. The favorable combination of electromagnetic and optical properties makes it possible to use calcium—vanadium ferrogarnets in electronics, microwave, computer, and superhigh frequency technology and magnetooptics. For a second selection of the optimum production conditions for production and quality control of the ferrite parts obtained it is necessary to know the physicochemical processes occurring in synthesis of calcium—vanadium ferrogarnets, which are distinguished by a number of features and at present have been insufficiently studied.

Earlier [1] we established that addition of rare-earth element oxides to the reaction mixture for production of calcium—vanadium ferrogarnets significantly eases synthesis of the single-phase products and stabilizes the structure of the garnet. In addition it was determined that depending upon the composition M_{3-2x}Ca_{2x}Fe_{5-x}V_xO_12 (M=Y, Gd) ferrogarnet is synthesized in interaction of the compounds actually existing in the reaction mixture in heat treatment:

3Ca_{2x}M_{1-2x}Fe_{1-x}V_xO_3 + Fe_3O_3 = Ca_{6x}M_{3-6x}Fe_{5-3x}V_xO_12 (I)*

or

MVO_4 + 2CaFe_2O_4 = Ca_2MF_{e}VO_12 (II).

Figure 1 shows the phases participating in the reaction and which coexist with calcium—vanadium ferrogarnet phase. The lines not lying in the plane of the CaO—V_2O_5—Fe_2O_3 triangle and also the line connecting CaFe_4O_7 with Ca_3V_2O_8 (the first is stable in a limited temperature range [2]) are designated by broken lines. For simplicity a portion of the lines has been omitted. Based on this, the choice of systems (I) and (II), in which the interaction of the components with formation of ferrogarnets was studied, is obvious.

Ferrogarnet with a composition of Ca_{4}Fe_{3.5}V_{1.5}O_{12} coexists in the reaction mixture [1] with Ca_3V_2O_8, CaFe_2O_4, Fe_2O_3, and CaFe_4O_7 phases (Fig. 1) and therefore to simulate the garnet-formation process the pairs of reactants Ca_3V_2O_8—CaFe_2O_4 (III), Ca_3V_2O_8—Fe_2O_3 (IV), and Ca_3V_2O_8—CaFe_4O_7 (V) were selected. Although the compound Ca_4V_2O_9 was not detected in the CaO—Fe_2O_3—V_2O_5 reaction mixtures, the Ca_4V_2O_9—Fe_2O_3 system (VI) is of interest since it is the only combination among those named in which obtaining a ratio of the elements stoichiometric for Ca_{9}Fe_{3.5}V_{1.5}O_{12} is possible: 3Ca_4V_2O_9 + 7Fe_2O_3 = 4Ca_3Fe_{3.5}V_{1.5}O_{12}.

*In parentheses is the number of the system (pair) of reactants.
In this work the garnet-forming processes were simulated by isothermal anneals in air of previously synthesized, sintered, and ground-in to one another tablets of the reactants by the free surface method [3]. CaFe$_2$O$_4$ was synthesized at 1050°C, GdVO$_4$, Ca$_4$V$_2$O$_9$, and YVO$_2$ at 1260°C, and the perovskites M$_{1-x}$Ca$_x$Fe$_{1-x}$V$_x$O$_3$ (x = 0.16) at 1150°C. The tablets of Fe$_2$O$_3$, MVO$_4$, Ca$_4$V$_2$O$_9$, and the perovskites were sintered at 1300-1320°C and of CaFe$_3$O$_5$ at 1180°C. The original reactants were certified as single-phase by x-ray diffraction (DRON-2 in FeK$_\alpha$- and CuK$_\alpha$-radiations) and metallographic (MIM-8) analyses. The density of the ceramic reached 96-100% according to x-ray analysis and the average grain size was 3-7 μm. The pressure on a pile of tablets to provide contact during annealing was about 0.1 MPa. The reaction zones were investigated by local x-ray-spectral analysis (JEOL JXA-5 microanalyzer). The conditions of determination of the metallic components of the oxide systems are shown in Table 1.

In studying the model systems (III) and (IV) the formation of garnet was not detected. Calcium—vanadium ferrogarnet phase was observed in interaction of the CaFe$_4$O$_7$—Ca$_3$V$_2$O$_8$ pair of reactants. The concentration profile of the distribution of the components in the reaction zone presented in Fig. 2a is quite complex. To the layer of garnet formed in contact with calcium orthovanadate Ca$_3$V$_2$O$_8$ there adjoins a layer of Ca$_n$V$_2$O$_{n+5}$ (n > 3), next there is an extended layer of calcium orthoferrite CaFe$_2$O$_4$, and then the main portion of the original tablet of CaFe$_4$O$_7$. The occurrence of Ca$_n$V$_2$O$_{n+5}$ (n > 3) phase may be explained by the fact that in interaction in system (V) the ratio of the metallic components does not correspond to the stoichiometric necessary for synthesis of Ca$_3$Fe$_{3.5}$V$_{1.5}$O$_{12}$. The original reactants are binary stoichiometric compounds and solid solutions do not form during interaction of them. Under these conditions the formation of calcium—vanadium ferrogarnet phase is possible with precipitation of an additional layer of Ca$_n$V$_2$O$_{n+5}$. Formation in the reaction zone of layers of products of different chemical composition differing in structure type and significantly differing in molar volume complicates synthesis of calcium—vanadium ferrogarnet and also may cause cracking and shearing of the layers occurring as the result of high mechanical stresses. According to the data of local x-ray spectral analysis interaction in system (VI) does not lead directly to formation of garnet. In this case a complex sandwich of several phases which in principle repeats the picture characteristic of system (V) is formed: Ca$_4$V$_2$O$_9$—Ca$_3$V$_2$O$_8$—Ca$_3$Fe$_{3.5}$V$_{1.5}$O$_{12}$—Ca$_n$V$_2$O$_{n+5}$—CaFe$_2$O$_4$—CaFe$_4$O$_7$—Fe$_2$O$_3$. The results obtained may be explained based on the ratio of the values of the standard Gibbs energy of the original reactants and of the reaction products with use, for example, of the data of [4]. Direct Ca$_4$V$_2$O$_9$—Fe$_2$O$_3$ interaction with formation of garnet is thermodynamically significantly less favorable than synthesis of calcium—vanadium ferrogarnet from Ca$_3$V$_2$O$_8$ and CaFe$_3$O$_7$ with formation of byproducts.