July 25, 1967 C. KOOY 3,332,796

PREPARING NICKEL FERRITE SINGLE CRYSTALS ON A MONOCRYSTALLINE SUBSTRATE

Filed June 21, 1962 3 Sheets-Sheet 1

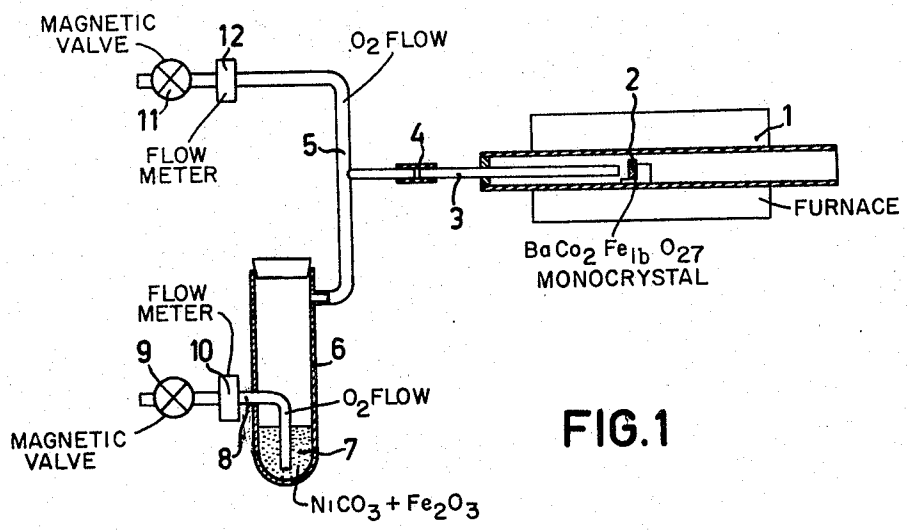


FIG.1

INVENTOR
GORNELIS KOOY
BY
Frank R. Trifari
AGENT

July 25, 1967 C. KOOY 3,332,796

PREPARING NICKEL FERRITE SINGLE CRYSTALS ON A MONOCRYSTALLINE SUBSTRATE

Filed June 21, 1962 3 Sheets-Sheet 2

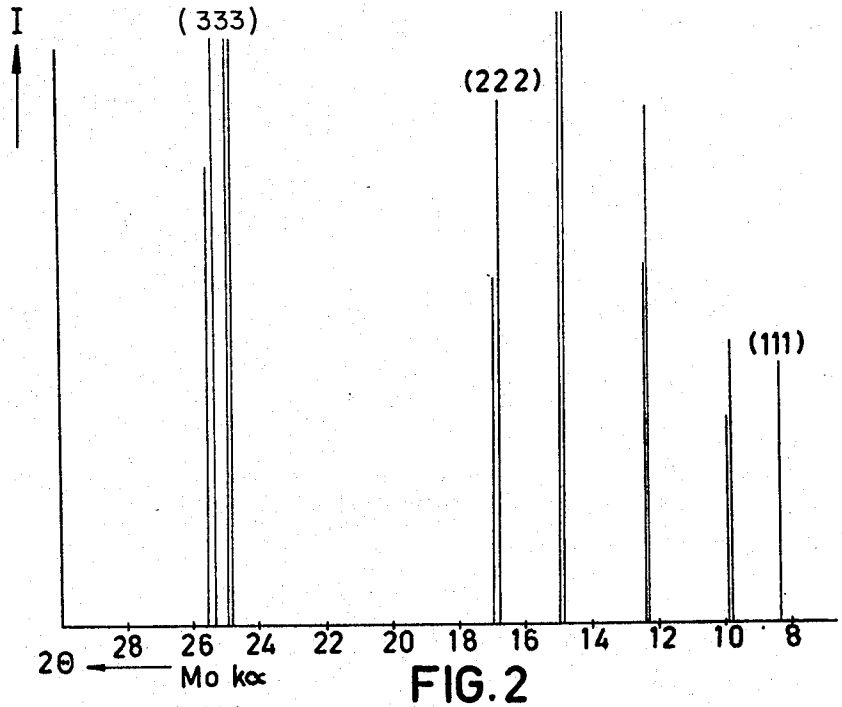


FIG. 2

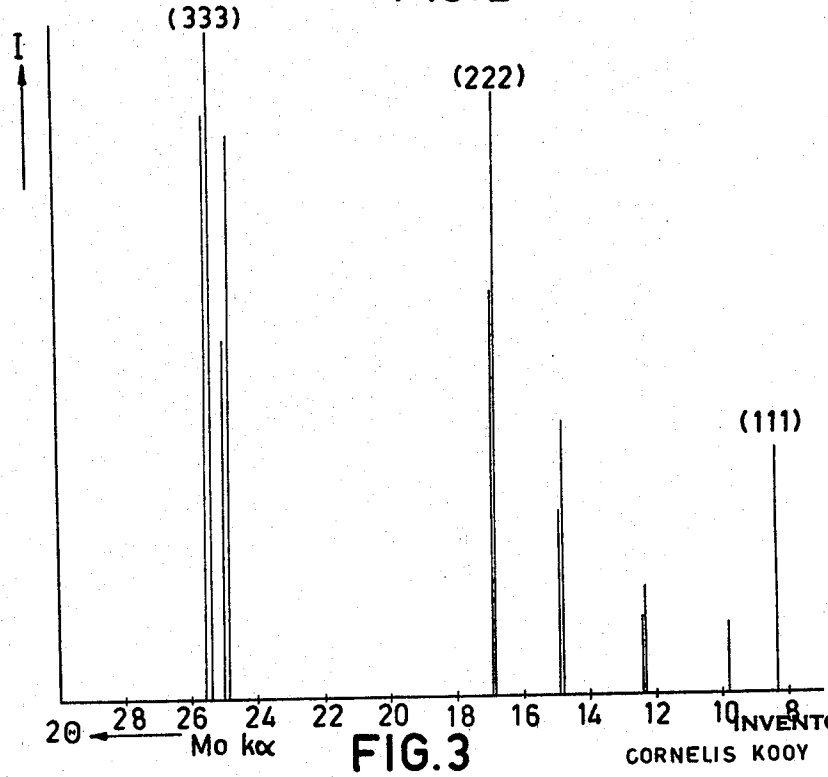


FIG. 3

INVENTOR
CORNELIS KOOY

BY Frank R. Trifari
AGENT

July 25, 1967 C. KOOY 3,332,796

PREPARING NICKEL FERRITE SINGLE CRYSTALS ON A MONOCRYSTALLINE SUBSTRATE

Filed June 21, 1962 3 Sheets-Sheet 3

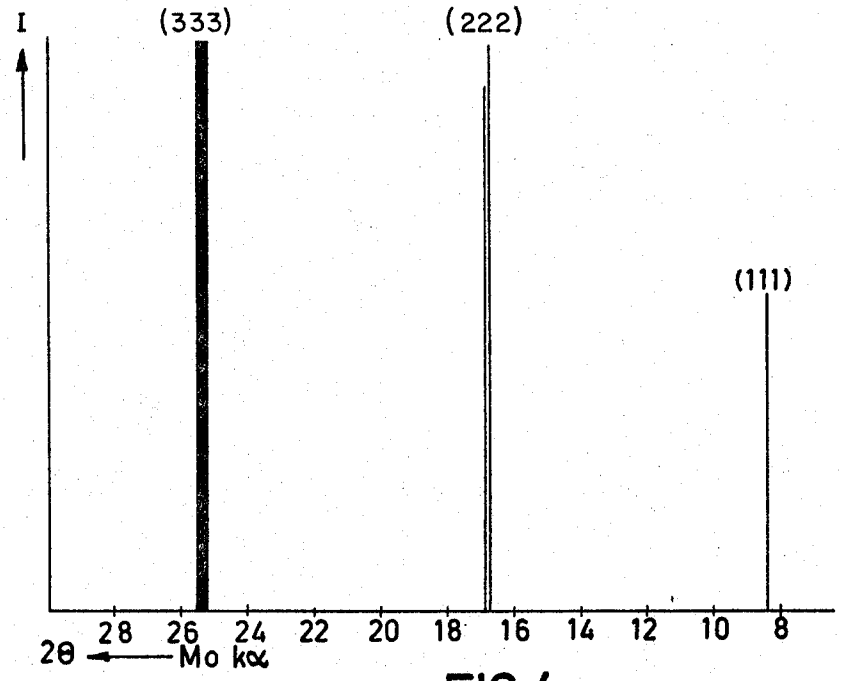


FIG.4

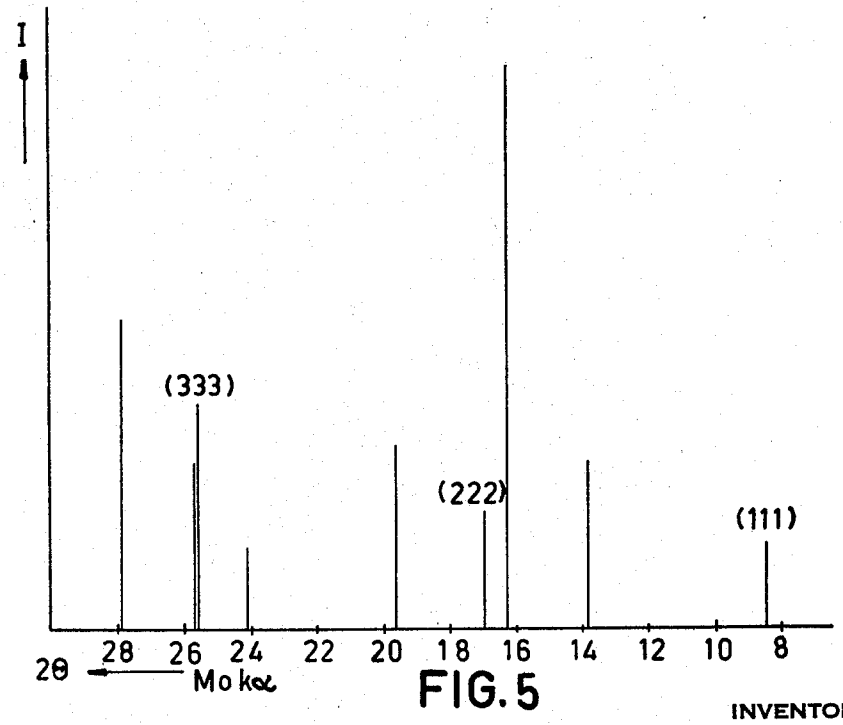


FIG.5

INVENTOR
CORNELIS KOOY
BY Frank R. Sinfair
AGENT

United States Patent Office 3,332,796 Patented July 25, 1967

3,332,796

PREPARING NICKEL FERRITE SINGLE CRYSTALS ON A MONOCRYSTALLINE SUBSTRATE

Cornelis Kooy, Emmasingel, Eindhoven, Netherlands, assignor to North American Philips Company, Inc., New York, N.Y., a corporation of Delaware

Filed June 21, 1962, Ser. No. 204,238
Claims priority, application Netherlands, June 26, 1961, 266,376
3 Claims. (Cl. 117—21)

The invention relates to a method of manufacturing a single crystal body of a compound which is capable of being sintered.

It is known to manufacture single crystal bodies by melting the relative compound and, during cooling, taking such measures that the particles of the solidifying melt arrange in a particular manner with respect to each other. This may occur, for example, by inducing the crystallization in the melt with a "cold finger" which usually comprises a small seed crystal. It is also known to heat the powder of the compound in question in the flame of an oxyhydrogen blowpipe, the powder being taken along by the inner pipe of the blowpipe. The powder is caught on a refractory rod and solidifies to form a single crystal body. In these cases, the method is carried out at the melting temperature of the pure compound. Naturally, the gas atmosphere should be adapted to the equilibrium of the compound at this temperature. In connection with the high melting temperature, this is often hard to realize, as a result of which some compounds decompose entirely at the melting temperature.

Alternatively, methods are known which are carried out at a temperature lower than the melting temperature of the pure compound. The melt contains, in addition to the pure compound, one or more other compounds which are active as fluxes. This method may be used in those cases in which a suitable flux exists for the compound in question. In addition, special measures should be taken to influence the nucleation and to check uncontrolled nucleation.

The invention relates to a particular method which is also carried out below the melting temperature of the pure compound. It is based on the recognition of the fact that a controlled recrystallization takes place if a thin layer of powdered particles is applied on a monocrystalline substratum and sintered.

In the method according to the invention, a layer of at most 200 microns, preferably at most 20 microns, of a powder of the compound in question or of substances which form the compound in question on heating having a particle size of at most 5 microns, is provided on a single crystal body and heated to a temperature which lies in the recrystallization temperature range of the compound in question. The method is carried out below the melting temperature since the recrystallization temperature range lies below the melting temperature. The recrystallization temperature range lies between ½ and ⅔ of the absolute melting temperature. A temperature in this range is sometimes termed Tamman temperature. With this method, the particles of the powder recrystallize according to an ordered pattern as a result of the monocrystalline substrate on which it is provided. The thickness of the layer is at most 200 microns to prevent arbitrary recrystallization from taking place in part of the applied layer. Good results are obtained with a layer thickness of at most 20 microns. The particles of the powder are on the substrate in an arbitrary orientation. The ordered growth turns out to start from those particles of the powder which, as far as the crystal orientation is concerned, are rationally linked with those of the substrate. The particle size of the powder should be at most 5 microns for the powder to be reactive.

So the compound is not applied in an atomic or molecular form but in the form of small crystalline powdered particles. The powder may consist of particles of the compound in question. Then the method according to the invention substantially comes to a recrystallization with a controlled nucleation of the recrystallization nuclei. The powder may also consist of substances which form the compound in question on heating. In this case, both a reaction and an ordered crystallization take place. The powder is applied on a single crystal body. The composition of this body may be equal to that of the body to be manufactured but it may also have a different composition and even a crystal structure which differs from that of the single crystal body to be manufactured. In this latter case, a sufficiently large difference should exist between the interfacial surface energy with respect to the substrate with oriented and non-oriented particles of the powder so as to form recrystallized orientation nuclei. The powder layer may be provided on the substrate in various manners. It may be effected in the form of a suspension, after which the substrate with the suspension layer are heated. It is also possible to provide a thin powder layer immediately on a heated substrate by blowing the powder on it by means of a gas stream.

In this manner, thin monocrystalline layers are formed which can easily be separated from the substrate. To obtain single crystal bodies having a larger thickness, the method according to the invention is repeated several times.

Compounds, of which single crystal bodies can be manufactured by means of the method according to the invention are, for example, $BaTiO_3$ and $NiFe_2O_4$. Since it is very difficult to obtain a single crystal body of $NiFe_2O_4$ according to a known method, use is made according to the invention of a signal crystal body having a magnetoplumbite structure, for example a body of a composition $BaFe_{12}O_{19}$ or a single crystal body having a different hexagonal crystal structure, for example a body of a composition $BaCo_2Fe_{16}O_{27}$.

In order that the invention may readily be carried into effect, it will now be described, by way of example, with reference to the accompanying drawings and the ensuing examples.

FIG. 1 diagrammatically shows an apparatus which may be used in the method according to the invention.

FIGS. 2, 3 and 4 show intensities of an X-ray diffraction pattern of bodies manufactured according to the method according to the invention.

FIG. 5 shows the intensities of an X-ray diffraction pattern of a known body.

EXAMPLE I

A mixture of $NiCO_3$ and Fe_2O_3 in a ratio of 1:1 was ground for 16 hours in ethyl alcohol in a ball mill and then another 16 hours in a vibrating mill. After drying, a suspension in amyl acetate with approximately 0.25% nitrocellulose was made of the powder. Of this suspension a 20 micron thick layer was coated on the (0001) face of a single crystal body of $SrFe_{12}O_{19}$, which, after drying, yielded a homogeneously distributed layer of powder particles on the surface of the single crystal body. This was heated in oxygen for 15 minutes at 1250° C. Of this product an X-ray diffraction pattern was made which, in addition to the reflections of the basal plane of the $SrFe_{12}O_{19}$ single crystal, also showned the (111), (222), (333) and so on reflections of the spinel lattice of $NiFeO_4$. The method was repeated several times. After five times, the X-ray diffraction diagram invariably showed only the (111) reflections of spinel and those of the basal plane of $SrFe_{12}O_{19}$, from which it appears that the layer of $NiFe_2O_4$ formed is monocrystalline or that it has a very pro-

nounced orientation with the (111)-axis parallel to the hexagonal *c*-axis of the substrate crystal.

EXAMPLE II

By means of the apparatus diagrammatically shown in FIGURE 1, small portions of a powdered mixture of $NiCO_3$ and Fe_2O_3 in a ratio of 1:1 where applied on the (0001) face of a single crystal body of $BaCo_2Fe_{16}O_{27}$, which was at a temperature of 1325° C. The tube furnace **1** contains the said single crystal body **2**. On the one side, the aluminum oxide tube **3** extends in the furnace so that it nearly touches the single crystal body **2**. By means of a connecting limb **4** the tube **3** is connected to the glass tube **5** having two branches. The glass container **6** containing the powder mixture **7** of $NiCO_3$ and Fe_2O_3 is provided in the one branch. The tube **8** which comprises a magnetic shutter **9** and a flow meter **10** extends in the vessel **6** in the powder mixture **7**. The other branch of the tube **5** comprises a magnetic shutter **11** and a flow meter **12**. A stream of oxygen was blown through the tube **8** at a rate of from 5 to 10 liters/min. which caused eddies in the container **6**, as a result of which the powder was more or less fluidized and the smallest particles were conducted into the tube **5** over such a distance that they were blown on the single crystal body **2** at a rate of from 10 to 15 liters/min. by a stream of oxygen supplied to the other branch of the tube **5**. The furnace temperature was 1325° C. By controlling the magnetic shutters, powder was blown on the single crystal body for 2 seconds every 10 minutes. 0.2 to 0.4 mg. of the powder mixture were applied to the surface of the single crystal body which had an area of 0.5 x 0.5 cm.^{2}. This method was repeated many times. The results are shown in FIGURES 2, 3 and 4 which are X-ray diffraction patterns after 14, 68 and 106 operations respectively. In the figures the intensity I of the reflections of a MoKα radiation is plotted in an arbitrary unit as a function of a deflection angle 2θ. From the increase of the ratio of the intensities of the (111) spinel reflection and the basal reflections of $BaCo_2Fe_{16}O_{27}$ it may be concluded that an ordered spinel layer is formed on the single crystal substrate. The orientation follows from the absence of all reflections other than those of the (111) plane. In FIGURE 4, the peak of the (333) line falls outside the plane of the drawing. For comparison, FIGURE 5 shows the reflections of a body constituting of $NiFe_2O_4$, in which the particles are arbitrarily present. Single crystal bodies obtained in this manner and having thicknesses of from 100 to 300 microns could be detached from the substrate.

The same result was obtained in a method in which the mixture of $NiCO_3$ and Fe_2O_3 was replaced by a powder of $NiFe_2O_4$, which was obtained by heating the powder mixture of $NiCO_3$ and Fe_2O_3 at 1000° C. and grinding the reaction product in alcohol in a ball mill for 16 hours and in a vibrating mill for 8 hours and then drying it.

What is claimed is:

1. A method of manufacturing a single crystal body of $NiFe_2O_4$ comprising the steps of applying a layer of powder $NiFe_2O_4$ not exeeding 200μ in thickness and composed of particles not exceeding 5μ in diameter on a monocrystalline substrate of $BaFe_{12}O_{19}$, and heating said layer to a temperature between ½ and ⅔ the absolute melting temperature of $NiFe_2O_4$ to thereby recrystallize the particles into a monocrystalline layer.

2. A method of manufacturing a single crystal body of $NiFe_2O_4$ comprising the steps, applying a layer of $NiFe_2O_4$ powder not exceeding 200μ in thickness and composed of particles not exceeding 5μ in thickness on a monocrystalline substrate of $BaCo_2Fe_{16}O_{27}$, and heating said layer to a temperature between ½ and ⅔ the absolute melting temperature of $NiFe_2O_4$ to thereby recrystallize the the particles into a monocrystalline body.

3. A method of manufacturing a single crystal body of $NiFe_2O_4$ comprising the steps, applying a layer of $NiFe_2O_4$ powder not exceeding 200μ in thickness and composed of particles each having a diameter not exceeding 5μ on a monocrystalline substrate of $SrFe_{12}O_{19}$, and heating said layer to a temperature between ½ and ⅔ the absolute melting temperature of $NiFe_2O_4$ to thereby recrystallize the particles into a monocrystalline body.

References Cited

UNITED STATES PATENTS

2,832,705	4/1958	Seidl	117—168 X
3,037,180	5/1962	Linz	252—62.3 X
3,047,429	7/1962	Stoller	117—215
3,093,517	6/1963	Lyons	252—62.3 X
3,100,158	8/1963	Lemaire	117—215
3,108,072	10/1963	Gutsche	252—62.3 X
3,109,749	11/1963	Di Ricco	117—215

NORMAN YUDKOFF, *Primary Examiner.*

MAURICE A. BRINDISI, *Examiner.*

H. T. CARTER, S. J. EMERY, *Assistant Examiners.*