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GROWTH OF FERROUS-FREE COBALT FERRITE SINGLE CRYSTALS

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This invention relates to a method of growing single crystals of cobalt ferrite that are ferrous-free, do not contain appreciable quantity of other impurities, and exhibit superior electrical qualities.

Growing ferrite crystals from melts presents many problems. The material has a melting temperature in excess of 1550° C. requiring special high temperature furnaces and crucibles capable of withstanding the elevated temperatures. Additionally, the material gives up some of its oxygen at these temperatures requiring an oxygen pressure throughout the melting procedure.

Earliest efforts provided crystals that were not ferrous free. Later methods provided ferrous free crystals; but, involved ball milling of the ingredients prior to the melting operation, which procedure contaminated the crystal with other impurities. A later method involved the insertion of a cold finger of platinum into the melt which induced nucleation and the ultimate growth of a crystal. This method does not have as great a measure of assurance that a single crystal will be grown with successive operations, nor will the dimensions conform to predictable design requirements. Crystals produced by the present invention have resistivities two orders of magnitude higher than those produced by other techniques. Furthermore, in the megacycle region, crystals so produced have acoustic Q's of one order of magnitude higher than those produced by other techniques.

Therefore, an object of this invention is to provide a method of growing cobalt ferrite single crystals that are ferrous free.

Another object of this invention is to provide a method of producing covalt ferrite crystals that are pure and physically uniform.

Another object of this invention is to provide a method of producing cobalt ferrite single crystals having a high degree of repeatability.

Further objects and advantages of our invention will be understood from the following detailed specification.

The required materials are cobalt pyridinate and sodium ferrite. The cobalt pyridinate

$$(Co_3Fe_6(CH_3CO_2)_{17}O_3OH \cdot 12C_5H_5N)$$

was first decomposed thermally in an appropriate furnace. The sodium ferrite was formed by fusing sodium carbonate with an equimolar mixture of ferrite oxide.

The cobalt ferrite produced above does not melt at 1600° C. and 1650 p.s.i.g. oxygen pressure. The addition of sodium ferrite lowers this melting point. What is more, sodium ferrite has liquid miscibility with cobalt ferrite at elevated temperature but does not enter into solid solution. The required oxygen pressure may also be reduced owing to the addition of sodium ferrite.

Nineteen parts by weight of the decomposed cobalt pyridinate together with one part by weight of sodium ferrite are placed in a platinum crucible having a wall thickness on the order of two tenths of a millimeter.

The crucible is then placed in a suitable furnace. An R-F induction heated furnace having a sufficient wall thickness to withstand the high pressure and elevated temperature can be used effectively. The vessel's upper cap should be water cooled to avoid excessive heating.

Such a furnace is described in detail in a paper published by A. Ferretti, D. G. Wickham, and A. Wold in The Review of Scientific Instruments, vol. 32, No. 5, 566–568, May 1961 and entitled, "Induction Heated Pressure Vessel for Growing Oxide Single Crystals."

The sample is heated to about 1600° C. under an oxygen pressure of 1650 p.s.i.g., and maintained at that temperature and pressure for two hours. The power input is reduced such that the material is allowed to cool at the rate of approximately 6° C. per hour for sixteen hours; that is, until a temperature of 1490° C. is reached. The power input is further reduced such that the rate of cooling is permitted to increase to approximately 10° C. per hour for a period of ten hours or until the temperature is reduced an additional 100° C.

When the temperature is reduced to 1350° C., the rate of cooling is increased and the pressure is reduced simultaneously. The power is further reduced at this point such that the cooling rate is increased to approximately 40° C. per hour for the next nine hours. The pressure is reduced slowly over this same period to 0 p.s.i.g. When the material cools to 1000° C. the power is turned completely off and the material is permitted to cool to room temperature. The sodium ferrite is the last to solidify thereby floating on the other material and ultimately forming at the top of the ingot. The section containing the sodium ferrite is then cut off from the rest of the ingot by means of a diamond cutting wheel.

Using the oxygen pressure indicated above necessarily involves the use of heavy equipment. The wall thickness of the furnace must be substantial and sealing arrangements carefully constructed. However, the operating pressure can be reduced considerably without serious consequences under certain conditions. Furthermore, the operating temperature can be reduced. By increasing the proportional amount of sodium ferrite in the original charge the melting point is lowered, which in turn permits a reduction in operation oxygen pressure. The requirements indicated are conservative and other less stringent requirements will give satisfactory results.

The above method can be varied somewhat by using zoning techniques. Here, a boat of the material is passed through a furnace where only a small quantity of the material is exposed to a high temperature at one time. The material melts as it passes through the high temperature zone and cools forming a crystal as it passes out of that zone. The sodium ferrite solidifying last as it does thereby progressively flows against the motion of the boat ultimately forming at an extreme end of the boat. The portion containing the sodium ferrite can then be cut off.

Expanding the method still further use of a crucible can be eliminated. If the material is compacted into a rod and the rod is drawn through a hot zone of a furnace in a fashion similar to the above described method; but in a vertical mode, surface tension of the compacted material will keep the rod whole provided the temperature is not raised beyond the point where the material will flow out. As the rod moves down the sodium ferrite will progress upward increasing the sodium ferrite content of the mixture as it progresses. As a consequence, the temperature of the hot zone must be programmed such that it is continuously lowered in proportion to the richness of the mixture in sodium ferrite. This action will prevent the material from reaching a temperature where the surface tension will be unable to contain the rod.

While we have described our invention in connection with specific steps, it is to be clearly understood that this description is only made by way of example and not as a limitation on the scope of our invention as set forth in the objects thereof and in the accompanying claims.

We claim:

1. A method of making ferrous-free cobalt ferrite single

crystals comprising the steps of: decomposing cobalt pyridinate; fusing an equimolar mixture of sodium carbonate and ferric oxide in an appropriate furnace; combining one part by weight of said decomposed cobalt pyridinate with nineteen parts by weight of said fused sodium carbonate and ferric oxide in a platinum crucible; heating said combination in an oxygen atmosphere maintained at 165 p.s.i.g. to a temperature of about 1600° C.; holding said temperature for a period of about two hours permitting all extraneous nuclei to dissolve; cooling said heated combination at a rate of about 6° C. per hour for sixteen hours, than 10° C. per hour for the next ten hours, and finally 40° C. per hour until room temperature is achieved; and removing said oxygen atmosphere.

2. A method of producing ferrous-free cobalt ferrite single crystals according to claim 1 wherein the oxygen pressure is reduced gradually to atmospheric pressure coincident with said 40° C. cooling rate.

References Cited

Kunnmann et al.: Journal of Applied Physics, Supplement to vol. 33, No. 3, March 1962, pp. 1364–1365.

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