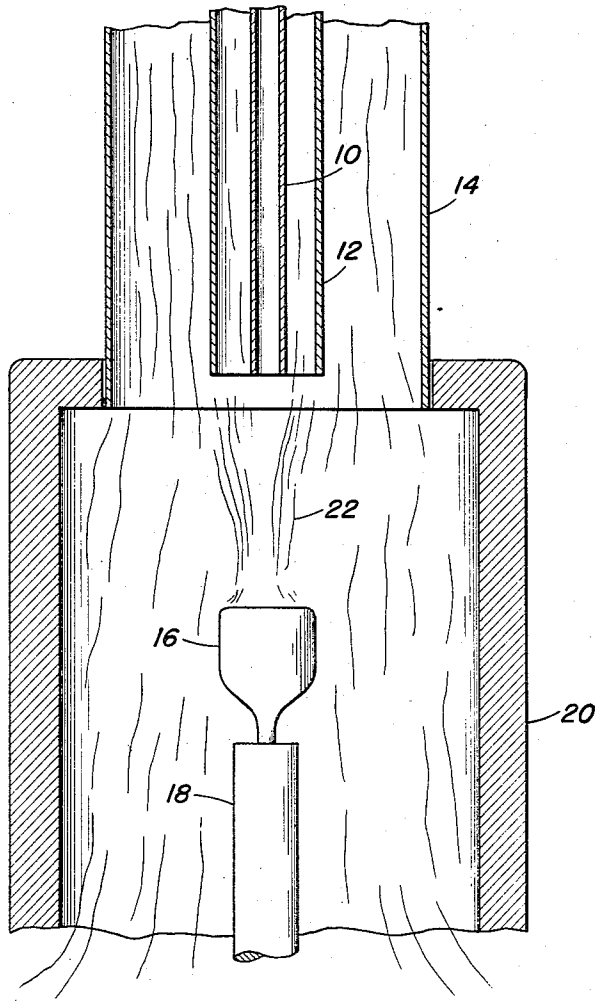
Sept. 2, 1958 A. LINZ, JR., ET AL 2,850,355

MONOCRYSTALLINE NICKEL TITANATE BOULE

Filed Nov. 5, 1953



INVENTORS
Arthur Linz, Jr.
Leon Merker

BY
Charles F. Kegebein
ATTORNEY

United States Patent Office

2,850,355

Patented Sept. 2, 1958

2,850,355

MONOCRYSTALLINE NICKEL TITANATE BOULE

Arthur Linz, Jr., and Leon Merker, New York, N. Y., assignors to National Lead Company, New York, N. Y., a corporation of New Jersey

Application November 5, 1953, Serial No. 390,396

1 Claim. (Cl. 23—51)

This invention relates to monocrystalline nickel titanate and to methods of making the same.

Nickel titanate powder material has been prepared by various methods but prior to this invention large single crystals of nickel titanate have not been prepared.

An object of this invention, therefore, is to provide monocrystalline nickel titanate as a new article of manufacture. Another object is to provide a method for producing monocrystalline nickel titanate. These and other objects will become apparent from the following more complete description of the invention.

Broadly this invention contemplates monocrystalline nickel titanate formed by crystallizing fused nickel titanate particles.

This invention also contemplates a method for the preparation of monocrystalline nickel titanate by fusing powdered nickel titanate in an oxyhydrogen flame, and crystallizing the molten material to form a monocrystalline mass of nickel titanate in the form of a boule.

This invention also contemplates a method for annealing the so-formed nickel titanate boule, which comprises heating said boule at temperature from about 650° C. to about 1500° C. to relieve the strains in the single crystal.

The term nickel titanate is intended to embrace both pure $NiTiO_3$ and $NiTiO_3$ which contains impurities or added coloring or modifying agents, either present or added, which are of a nature and in amount so as to not adversely affect the monocrystalline structure nor alter the desired physical characteristics of the nickel titanate material produced. In most cases the impurities are held to a minimum and ordinarily will not exceed a few tenths of a percent, and modifying or coloring agents are added in the amount necessary to produce the desired effect.

It has been found that the temperature of the flame should be maintained somewhat above the melting point of the nickel titanate feed material, but should not exceed a temperature where the molten material tends to flow over the edges of the pool at the top of the boule. The flame temperature may be maintained by adjusting the quantity and rates of flow of both the hydrogen and oxygen gases, but it is important that the flame be kept as constant and quiet as possible. The temperature range should be held between about 1620° C. and 1680° C.

The preferred apparatus used in the instant invention is similar in its general construction to that shown in application Serial No. 335,343 filed February 5, 1953, by Leon Merker, said application being assigned to the same assignee as the instant invention.

In the apparatus shown in the drawing, the burner comprises three substantially concentric tubes 10, 12, and 14. The powdered nickel titanate is introduced through the center tube 10 with a portion of the oxygen, and the remainder of the oxygen is introduced through the outer tube 14. The hydrogen is introduced through the intermediate tube 12. Tube 14, if desired, may be slightly longer than the tubes 10 and 12. The boule 16 is formed on a pedestal 18 of suitable refractory material, such as

firebrick or zirconia and, as the boule grows, the pedestal 18 is lowered so that the top of the boule always remains at about the same location in the flame.

The boule 16 and top of the pedestal 18 are surrounded by a chamber 20 of firebrick, or the like, and this chamber preferably surrounds the lower end of the outer tube 14. The gases are preferably fed at such rates that the flame fills and extends through the entire chamber 20 around the boule, and in this way the temperature and other conditions around the boule are kept substantially constant. It has been found that smaller flames may be unsteady due to currents within the chamber, and variations in the flame may cause damage to the boule.

In practice, the powdered nickel titanate is generally introduced periodically into the pipe 10 with a minor portion of the oxygen, and the major portion of the oxygen is introduced through pipe 14. In one burner the oxygen in the inner pipe 10, the oxygen in the outer pipe 14, and the hydrogen in the intermediate pipe 12 are introduced in the proportions 4:26:16 respectively.

A cone 22 forms within the flame below the pipes 10 and 12, and the pedestal 18 is preferably positioned so that the molten top of the boule 16 is at or near the point of the cone 22. In order to start such a single crystal to form it is desirable to first form a seed on the pedestal, and then gradually build up the amount of molten material on the seed to form the crystal. Such a procedure allows the crystal to build up upon itself, gradually increasing in diameter until a boule or carrot-shaped single crystal of nickel titanate is formed. The size of the orifices of the oxygen-hydrogen torch determines the size of the intensely heated zone which, in turn, determines the diameter of the carrot-shaped crystal produced.

It is preferred to employ nickel titanate in finely powdered form. The nickel titanate starting material should be substantially free from objectionable or incompatible impurities which detrimentally affect the crystal structure or the physical properties of the crystal. Starting material should be finely divided and fairly uniform in size. For most efficient results, the nickel titanate starting material should possess an open structure with units capable of being rapidly melted. A nickel titanate starting material having an ultimate unit particle size of less than 1 micron has proved especially satisfactory. Aggregates of these small particles greater than 100 mesh should also be avoided as they do not tend to melt completely. The feed material should be free-flowing in order to feed properly. A satisfactory nickel titanate feed material is more fully described and claimed in co-pending application Serial No. 381,114 filed by Leon Merker and entitled, "Preparation of Metal Titanate," now U. S. Patent No. 2,767,050 issued October 16, 1956, and assigned to the same assignee as the instant application.

Using an oxygen-hydrogen burner having concentric orifices, the center orifice carrying the oxygen gas and powdered nickel titanate feed material entrained in the oxygen, the intermediate orifice carrying the hydrogen gas, and the outer orifice carrying the rest of the oxygen gas, a single crystal boule of nickel titanate was prepared. The total gas flow of oxygen was 30 liters per minute, 4 liters through the center orifice, and 26 liters through the outer orifice, while the flow of hydrogen was 16 liters per minute through the intermediate orifice. The boule was then subsequently annealed at temperature between 650° C. and 1500° C. to remove the strains. The time of annealing varies upon the size of the boule and the temperature employed. However, it has been found that from 6 hours to 24 hours are satisfactory for producing relatively strain-free crystals, although longer times may be used if desired.

The single crystal of nickel titanate possesses useful electrical properties for resistors and the like. The single

crystal has a dielectric constant of 20 and has a power factor of 0.05% at room temperature over a frequency range of 100 cycles to 10 megacycles. The temperature coefficient of the dielectric constant is +220 parts per million per degree centigrade from −50° C. to 150° C.

When electron acceptor and donor type impurities are added to the feed material, the single crystal of nickel titanate becomes a semi-conductor, and if various types of impurities are added alternately to the feed material, and n and p type junction may be formed in the single crystal thus producing a rectifier.

While this invention has been described and illustrated by the example shown, it is not intended to be strictly limited thereto, and other modifications and variations may be employed within the scope of the following claims.

We claim:

Monocrystalline nickel titanate boule formed synthetically by introducing powdered nickel titanate into a of oxygen, surrounding said stream of oxygen with a stream of hydrogen and forming a flame having a central

oxygen cone, melting the powdered nickel titanate in said flame, forming the monocrystalline nickel titanate at a temperature from between 1620° C. and 1680° C., crystallizing the molten nickel titanate in the form of a boule adjacent the end of the oxygen cone, maintaining the flame about the boule and subsequently annealing said boule by heating at a temperature from about 650° C. to about 1500° C. from about 6 hours to about 24 hours to remove the strains therefrom.

References Cited in the file of this patent

UNITED STATES PATENTS

2,591,561	Lester et al.	Apr. 1, 1952
2,628,156	Merker et al.	Feb. 10, 1953
2,767,050	Merker	Oct. 16, 1956

FOREIGN PATENTS

662,782	France	Mar. 25, 1929
664,889	Great Britain	Jan. 16, 1952
686,490	Great Britain	Jan. 28, 1953

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,850,355 September 2, 1958

Arthur Linz, Jr., et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 19, before "of oxygen", first occurrence, insert -- stream --.

Signed and sealed this 23rd day of December 1958.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents