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THORIA DISPERSION STRENGTHENED NICKEL ALUMINIDE AND METHOD OF MAKING

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ABSTRACT OF THE DISCLOSURE

Nickel aluminide powder having submicron size particles of thorium dioxide (thoria) uniformly dispersed therein is prepared by reacting an aluminum halide compound in the vapor state with thoria dispersion strengthened nickel powder, the resulting nickel aluminide powder being particularly suitable for hot pressing into components requiring improved high temperature strength.

This invention relates to thoria strengthened materials which exhibit relatively high physical strength at elevated temperatures. More particularly, this invention relates to thoria dispersion strengthened nickel aluminide and to a method of making the same.

The intermetallic compound nickel aluminide, containing substantially equal atomic proportions of nickel and aluminum, has been found to be useful in fabricating articles which are to be subjected to corrosive, high temperature environments. The utility of nickel aluminide as the leading edge portion of gas turbine engine stator vanes for example, operating at 2200° F.–2500° F. was described in a copending application Ser. No. 636,325 filed May 5, 1967 assigned to the assignee of this application. However, as it is desired to further increase the operating temperatures of gas turbine engines and other machinery and devices which operate at elevated temperatures, materials are sought which will stand up and operate under even more severe conditions. It is known that the hot strength of some materials such as the iron group metals (iron, nickel and cobalt), may be substantially increased by uniformly dispersing therein submicron size particles of refractory oxides. These materials and a method of making them is described in Alexander, et al. U.S. 3,087,234. A specific material of the group disclosed in the above-identified patent is thoria dispersion strengthened nickel. This composition is basically pure nickel containing about 0.5 to 50% by volume fine particles of the refractory oxide, thorium dioxide (ThO_2), uniformly dispersed therein. The average dimension of the refractory oxide particles is in the range of 5 to 1000 millimicrons. Nickel so strengthened is useful at temperatures up to about 2000° F. While nickel aluminide has been operated in turbine engine components at temperatures of 2200° F.–2500° F., I have now increased the usefulness of nickel aluminide in a high temperature environment by means of dispersion strengthening. Heretofore, classical powder metallurgical processes of incorporating particles of a refractory oxide with powdered nickel aluminide to provide a dispersion strengthened intermetallic compound have been unsuccessful because the refractory oxide has congregated at the grain boundaries. This concentration of the refractory oxide phase at the grain boundary of the intermetallic compound phase does not improve the high temperature strength of the intermetallic compounds, but actually weakens it.

It is an object of this invention to provide a thoria dispersion strengthened nickel aluminide composition wherein submicron particles of thoria are uniformly dispersed throughout the nickel aluminide matrix.

It is another object of this invention to provide a method of preparing thoria dispersion strengthened nickel aluminide wherein submicron particles of thoria are uniformly dispersed throughout the nickel aluminide.

In accordance with my invention, these and other objects are accomplished by providing thoria dispersion strengthened nickel in particulate form and preferably in finely divided powder form. A method of preparing nickel having submicron particles of thoria uniformly dispersed therein is fully described in the above-identified patent. Particulate thoria dispersion strengthened nickel is reacted with an aluminum halide compound in the vapor state to convert substantially all the nickel to the intermetallic compound, nickel aluminide, having substantially equal atomic proportions of nickel and aluminum. The submicron particles of thoria are not affected by the reaction but remain uniformly dispersed throughout the reaction product nickel aluminide matrix. The thoria dispersion strengthened nickel aluminide powder is processed by known powder metallurgical techniques to form an article of predetermined shape. The formed article is sintered to produce a thoria dispersion strengthened nickel aluminide component suitable for use in a high temperature, corrosive environment, such as for example, a gas turbine engine.

Thoria dispersion nickel in particulate form such as powder, chips, or shavings may be used in the practice of this invention. This mateiral is characterized by the presence of submicron size thoria particles (5–1000 millimicrons in average particle dimension) uniformly dispersed throughout the nickel. Thoria dispersion strengthened nickel is isotropic in its physical characteristics. The nickel component is present essentially as a continuous phase. This fact is demonstrated by the relatively high electrical conductivity of the refractory oxide reinforced metal. The ultra fine particles of thorium dioxide are uniformly dispersed throughout the material and effectively increase the high temperature physical properties of the nickel. For purposes of the present invention, the nickel preferably contains 1–10% by volume of the thorium dioxide particles dispersed therein.

The nickel particles containing the dispersed thoria (preferably —100 standard screen powder) is placed in one compartment of a porcelain crucible. A mixture of ammonium fluoride and aluminum metal powder is placed in another chamber of the same crucible. The chambers are separated by a porous refractory filter and the crucible is covered to prevent the escape of vapors which are generated in the reaction which will be described. The crucible is heated in a suitable furnace to about 1900° F.–2050° F. for about one hour. Under these conditions the aluminum reacts with the nickel in the thorium dispersed strengthened nickel powder by a process commonly referred to as "pack diffusion." While the exact reactions which take place during the pack diffusion process are not known in detail, it is believed that, in general, the phenomenon may be explained in the following manner. As the temperature of the crucible and its contents approaches 2000° F. The ammonium fluoride dissociates into ammonia and hydrogen fluoride. The hydrogen fluoride vapor is trapped within the crucible and reacts with aluminum powder to form an aluminum fluoride compound and hydrogen. The aluminum fluoride compound in the vapor state permeates the porous refractory filter and enters that compartment of the porcelain crucible in which the nickel powder is located. The aluminum fluoride compound reacts with the nickel to form nickel aluminide. Although none of the aluminum powder actually contacts the nickel directly, nickel aluminide is formed as a consequence of the intermediate aluminum halide compound. At the high temperature, the nickel aluminide which is formed on the

surface of the nickel particles diffuses into the metal phase and the reaction is able to proceed until such time as substantially all of the nickel has been converted to nickel aluminide. It is preferred that the reaction be controlled as determined by experiment so that substantially equal atomic proportions of nickel and aluminum are obtained in the final product.

Material produced in accordance with the above-described process has been analyzed by X-ray diffraction techniques and found to contain substantially all nickel aluminide with small amounts of Ni_3Al also present. The particles of thoria are substantially unaffected by the reaction and are found uniformly dispersed throughout the nickel aluminide at the conclusion of the reaction. However, because of the addition of aluminum atoms to the metal phase, the original volume concentration of thoria is reduced to approximately half of its original value. Accordingly, the preferred concentration by volume of thoria in the final product is about 0.5–5% in accordance with the process as described. Other pack components can be employed in the process. For example, ammonium chloride may be used in combination with aluminum, instead of, or in combination with, ammonium fluoride. I have also found that ammonium fluoride, magnesium fluoride and aluminum metal powder may be employed as the pack material. The important thing is to incorporate suitable halide-containing materials which will react with the aluminum powder to generate an aluminum halide compound in vapor form. The aluminum halide permeates the chamber of the reaction vessel and reacts with the nickel powder to form nickel aluminide.

The thoria dispersion strengthened nickel aluminide produced in accordance with this method is in particulate form. If it is not already in powder form, the nickel aluminide is comminuted to powder suitable for powder metallurgical processing. The powder is vacuum hot pressed (about 1×10^{-4} torr) in a graphite susceptor die into an article of desired predetermined configuration. The compact is pressure sintered in the dies at about 2850° F. for 15 minutes under 6000 p.s.i. uniaxial pressure. These conditions have been found suitable for the practice of the invention. Obviously, the stated pressures and temperatures may be varied slightly by one skilled in the art to accomplish the desired result.

Thoria dispersion strengthened nickel aluminide components exhibit excellent corrosion resistance and high

strength properties when subjected to environments such as the high temperature zone of a gas turbine engine.

While my invention has been defined in terms of certain specific embodiments, it would be appreciated that other forms may readily be adopted by those skilled in the art and therefore it is to be considered limited only by the following claims.

I claim:

1. A method of making thoria dispersion strengthened nickel aluminide comprising the steps of placing particles of thoria dispersion strengthened nickel in close together but spaced apart relationship with a mixture comprised of aluminum particles and an ammonium halide salt taken from the group consisting of ammonium fluoride and ammonium chloride; and heating said nickel particles and said mixture to an elevated temperature and for a time whereby said ammonium halide and said aluminum interact to produce an aluminum halide compound in the vapor state, said aluminum halide compound reacting with said nickel to produce nickel aluminide, said thoria dispersion being unaffected by said reaction and being present in said nickel aluminide as a uniform dispersion of submicron size particles.

2. A method of making thoria dispersion strengthened nickel aluminide comprising the steps of heating nickel which contains 1–10% by volume of submicron size particles of thorium dioxide uniformly dispersed therein to a temperature of about 1950° F.–2050° F. and reacting said nickel with an aluminum halide compound in the vapor state whereby said nickel is converted to the intermetallic compound nickel aluminide, said nickel aluminide comprising substantially equal atomic proportions of nickel and aluminum and said nickel aluminide containing about 0.5%–5% by volume of submicron size thoria particles uniformly dispersed therein.

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