

[54] **PROCESS FOR ELECTROFORMING NICKEL CONTAINING DISPERSED THORIUM OXIDE PARTICLES THEREIN**

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[57] **ABSTRACT**

Nickel electroforming is effected by passing a direct current through a bath containing a dissolved nickel salt or a mixture of such salts, such as those present in sulfamate or Watts baths, and finely divided sol-derived thorium oxide particles of 75 to 300 Angstroms, preferably 100 to 200 Angstroms diameters therein, at a pH in the range of 0.4 to 1.9, preferably 0.8 to 1.3. The nickel so deposited, as on a pre-shaped stainless steel cathode, may be produced in desired shape and may be removed from the cathode and upon removal, without additional working, possesses desirable engineering properties at elevated temperatures, e.g., 1,500° to 2,200°F. Although the material produced is of improved high temperature stability, hardness and ductility, compared to nickel alone, it is still ductile at room temperature and has properties equivalent or superior to nickel at room temperatures up to 1,500°F. Further improvements in mechanical properties thereof may be obtained by working. Also disclosed are electrodeposition baths, methods for their manufacture and products resulting from the electrodeposition process.

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19 Claims, No Drawings

**PROCESS FOR ELECTROFORMING NICKEL
CONTAINING DISPERSED THORIUM OXIDE
PARTICLES THEREIN**

This application is a continuation-in-part of my application Ser. No. 177,501, filed Sept. 2, 1971, now abandoned.

This invention relates to the production of nickel having improved properties at high temperatures. More particularly, it relates to the making by electroforming means of such nickels, which sometimes may be utilized directly, with no additional working or processing. The invention also relates to electroforming baths used in carrying out the process.

Electrodeposition of metals and alloys onto formed cathodes to produce metal items is known. The combining or alloying with nickel and other metals of finely divided refractories, such as metal oxides, e.g., thorium oxide, to improve the high temperature properties of the metals, has been successfully practiced, especially in recent years, because of the demands for high temperature-resistant structural materials for the making of rocket engines, gun barrels and other parts of apparatuses subjected to the extraordinarily high temperatures utilized in modern technology. Dispersion strengthened nickel alloys have been produced in which zirconium oxide or thorium oxide, in monoclinic form, was mixed with nickel as a very finely divided powder, hydrogen reduced to remove nickel oxide, pressed and again hydrogen reduced. The described sintering operation has been effected at an elevated temperature, about 800°C., and the alloys resulting are extruded or otherwise worked at elevated temperatures to improve their uniformity and physical properties. Also, metal oxides have been electrodeposited with nickel to improve the strength of the nickel and to obtain better engineering properties for high temperature applications.

Although from the work summarized above it might appear that the production of improved high temperature nickel dispersion alloys by electrolytic means could previously have been effected, the work of the present inventor has shown that this is not the case when especially advantageous properties are desired in the nickel alloy without the need for employing a combination of sintering and working operations. Thus, when the electroplating bath pH is in the range usual for electrodeposition or electroforming solutions, or in the electroplating range usually employed, such as that of a Watts bath, defects appear in the alloy upon heating and the improved properties of the alloy designed to be built in by use of the refractory oxide are lost. However, by following the method of the present invention, with special attention being given to keeping the pH in the very low range described and of using ultrafine thorium oxide particles, which are obtained from a thoria sol or gel, stability of the alloy produced is improved and superior high temperature properties are obtained.

In accordance with the present invention a method of electroforming nickel containing thorium oxide particles comprises passing a direct current between an anode and a cathode in a bath containing a dissolved nickel salt and thorium oxide particles of particle sizes in the 75 to 300 Angstrom diameter range at a pH in the range of 0.4 to 1.9 so as to form on the cathode a

deposit of nickel containing dispersed thorium oxide therein.

The electrolytic baths may contain any suitable source of nickel in ionic form, obtainable from nickel chloride, nickel sulfate, mixtures of nickel chloride and nickel sulfate, known as Watts baths, nickel sulfamate and other soluble nickel salts, preferably of strong acids. The concentrations of such salts in the aqueous medium of the bath, preferably water, is usually within the range of 1 to 60 oz. per gallon (0.7 to 40%, by weight), and is preferably of 3 to 36 oz. per gallon (2 to 25%). When Watts baths are used they will usually contain from 3 to 8 ounces per gallon of nickel chloride and 10 to 40 oz. per gallon of nickel sulfate. Normally it will not be necessary to utilize additives for improving surface properties of the electrodeposited nickel alloy but if they are desired to be present they can be added without interfering with the production of the nickel of improved high temperature characteristics. Thus, minor proportions, generally from 0.01 to 2 oz. per gal. of organic primary or secondary brighteners or other additives, such as quaternary pyridine salts, allyl sulfonic acids, lauryl sulfuric acids, the corresponding water soluble salts, e.g., sodium salts or chlorides, gelatin, gums or other surface active agents or colloids and others of the large number of very well known additives of these types may be present.

In some cases, in addition to the nickel ions in the electrolyte, other soluble ions may be present, such as aluminum, iron, copper, cobalt and silver ions. Generally, the concentration of such ions in the bath will be no greater than the content of nickel and preferably will be from 10 to 40% thereof, if present at all. Thus, the alloys electrodeposited may include ultrafine thoria dispersoids in nickel or ultrafine thoria dispersoids in a nickel alloy with another metal.

The very small thoria particles dispersed in the electrolytic baths and deposited with the nickel on the cathode by electrophoretic action may be applied with another suitable hard and inert metal oxide which, by its presence, can improve the high temperature stability and properties of the resulting dispersion alloy, by interrupting fault lines in the alloy and preventing recrystallizations to weaker forms. Among the useful oxides preferable are those of zirconium, aluminum, copper, iron, titanium, zinc and silicon, but preferably thorium oxide is employed alone. In the past, the oxides which were useable to produce dispersoids in metals were limited by the availabilities of finely divided powders for the sintering of mechanically mixed powders, with subsequent working to produce the dispersion alloy. Now, however, with the present process, wherein electroforming or electrodeposition from a liquid medium (highly preferably aqueous) is employed, it is possible to utilize sols or gels of thoria which are very finely divided oxides or hydrates thereof, convertible to the oxides in the electrolytic bath. Also, in addition to such gels based on thorium, aluminum, zirconium and silicon gels are also obtainable and it is expected that others will be available in the future, capable of converting to oxides which are depositable from electrolytic baths. Also, the gels may be dehydrated to produce very small particles of the oxides, as sols, in which the particles contain little or no water.

An exemplification of the thorium oxide gels or sols which are used is found in the *Journal of Applied Chemistry*, Volume 17, May 1967, at pages 147 to 150. De-

composition curves for the gel as a function of water removal with increasing temperature are given, showing that the gel retains some water at temperatures even as high as 900°C. This makes the gel an unlikely source of thorium oxide for electrophoretic deposition in an alloy wherein it is important that no water be present, since water in the oxide particle usually causes severe weakening of the alloy as it seeks to escape when the temperature is raised. Similar considerations make the use of the other gels and sols appear unlikely for successful production of dispersion hardened nickel or other metals or alloys. Yet, by the method of the present invention they have been successfully used and help to make superior nickel electroforms.

With agitation in the electrolytic bath, as by ordinary mixing or blending means, the gel or other comparable form in which the refractory thorium oxide (with or without other metal oxide gel) is added to the bath is broken down so that the particle sizes thereof, as electrophoretically or otherwise deposited with the nickel or nickel alloy on the cathode, are small and are evenly spaced, of sizes in the 75 to 300 Angstroms range, preferably from 100 to 200 Angstroms and averaging about 150 Angstroms. The figures given are preferred sizes for thorium dioxide (thoria) but also are often applicable when others of the mentioned oxides are co-deposited. It is possible to use the refractory oxides as fine powders too but in gel, sol or other hydrous form they give best results. It is considered that superior results are obtained when the gel form is used and is converted to a sol during the making of the electroforming bath. The products made are thought to be superior to those made from finely mechanically divided (ball milled) particles of thoria because of the high surface areas of the sol crystallites, which have ten or more times the area of a sphere of the same diameter, e.g., 10 to 1,000 times, preferably about 100 times.

The proportion of thorium oxide, utilized in the electrolytic or electrodeposition bath will usually be from 0.1 to 10% of the nickel in the bath, preferably from 0.5 to 5% and most preferably from 0.5 to 3% thereof. There is a relationship between the percentage of the oxide and its particle size and the proportion thereof deposited in the dispersion type alloy. Generally, it is found that the weight percent of the oxide in the final alloy is less than the proportion in the electrolytic bath, usually from 10 to 50% thereof and similar volume percentages also apply. Normally, the finest particles available will be employed, within the ranges mentioned and in some cases, when possible, even smaller crystallites of thoria can be used. The smaller the crystallites the more crystallite embodiments or termination points there will be in the final alloy to prevent failures along fault lines and to interfere with undesirable recrystallizations. If other oxides are used with thoria the total metal oxide content should be in the previously mentioned 0.1 to 10% range, by weight.

A very surprising feature of the present invention is the importance of maintaining the pH of the electrolyte, containing dispersoid material, at a highly acid value. This is so because it would be expected that use of acidic electrolyte would decrease the nickels' strength and therefore would be avoided. If the pH is in the range of about 0.4 to 1.9, good dispersion of the crystallite oxide is obtained and surprisingly, the content of moisture, either free or chemically sorbed or attached to the crystallites, is low. At higher pH's al-

though good dispersions are made and dispersion alloys are produced, it has been found that at the high temperatures to which they may be subjected in use, e.g., from 1,500° to 2,200°F. and even higher, the alloys are weakened, apparently due to the fact that moisture is still contained in the crystallite and passes through the crystal structure, resulting in a brittle material of low ultimate strength. Preferred pH's for best results and strongest high temperature nickel are within the range of 0.8 to 1.3 and it is more preferable to operate at a pH of 0.8 to 1.1, most preferably about 1.

Although it is not important how the pH is obtained (except acidification should be effected after addition of the crystallite oxide) and various acidifying agents may be employed, it is preferred for such agents to be acids which have a common anion with the salts employed in the electrolyte. Thus, hydrochloric acid or sulfuric acid may be used to lower the pH of a Watts bath. Sulfamic acid and sulfuric acid may be employed together, sometimes with sulfonic acids, to lower the pH of sulfamate baths. Sometimes a commonality of anions will not be maintained and then the usual acidifying agents may be used. Ordinarily, one will avoid employing strongly oxidizing acids, although they are operative in various embodiments of the invention. It is preferred to use the strongest acids, such as hydrochloric acid, sulfuric acid, hydrobromic acid, phosphoric acid, and others of this well known class which are essentially 100% ionizable in aqueous solution. Generally, these will be inorganic acids although there is no prohibition against using organic compounds. In Watts baths H_3BO_3 is preferred with HCl.

The electrolytic baths may be made by simple mixing techniques, as previously mentioned with respect to the addition of a sol, gel, or other suitable colloidal form of the crystallite oxide, followed by acidification. Preferably a gel or sol-gel system will be employed. The amount of acid will be such as to obtain the desired pH and generally this will be in the range of from 1 to 20 oz. of 100% acid per gallon. The acid may be added after the dispersion of the crystallite or before, depending on the technique which is found to yield the best dispersion and electroforming in a particular case but generally it is highly preferable (to produce a high temperature strength product) to add it after the dispersion of the crystallite or gel material in the electrolyte.

The electrolytic bath may be of any useful operating temperature but usually will be at a temperature in the range of 30° or 40° to 70°C. preferably 40° to 60°C. The anodes and cathodes may be of any suitable material known in the nickel electroforming art but it is preferred to employ rolled depolarized or sulfur depolarized nickel as the anode and stainless steel or similar material, to which nickel does not adhere strongly as the cathode. By use of a stainless steel cathode, previously shaped so as to produce a nickel electrodeposit of desired form, after plating is completed the nickel may be removed from the cathode without damage. It has been found that the electrodeposited nickel items of this invention even if electroformed to final shapes, have very good high temperature properties, including stability, resistance to erosion and corrosion, and strengths, including yield strength, and elasticity, which are far superior to those of conventionally electroformed nickel at such elevated temperatures. In cases where the final shapes are not capable of being manufactured readily from worked and sintered or otherwise

worked and formed alloys containing the present crystallites, and when the nickel alloy, as formed, is not as good as desired, the nickel alloys may be electroformed by the present methods on flat cathodes or on those with simple curves and may subsequently be worked, as by rolling, hammering, extruding or bending, for from 5 seconds to 1 hour, to increase the degree of dislocation entanglement present in the alloy structure and further to improve the high temperature properties of the product.

The speed of electrodeposition of the alloy is regulated by the passage of current through the electrolyte. Although various current densities may be utilized, one should usually operate at current densities in the range of about 5 to 100 amperes per square foot, preferably about 10 to 50 amps./sq. ft.

The time of plating and the thickness of the electrodeposited alloy are interrelated with the current flow. Generally, plating will be effected in a period of 4 hours to 100 hours, usually from 6 hours to 24 hours. The thickness of alloy deposited will range from about 0.02 centimeter to 1 cm., with preferable ranges being from 0.1 to 0.6 cm., and often, most preferably from 0.2 to 0.4 cm. Electrodepositions may be effected on cathodes from which the forms are removable or the nickel of described improved high temperature strength properties is formed onto final support materials, serving as cathodes. In the latter case such supporting material will normally be chosen so as to be capable of resisting the high temperature to which it may be intended to subject the present nickel alloys.

After production of the "dispersion alloy" of desired thickness by the method of this invention if there should be any water present in the thoria crystallites of the dispersed phase this may be removed to some extent and the product may be strengthened by a heat treatment at a temperature of about 500° to 1,000°C. for a period of from 2 minutes to 24 hours, usually from 1 to 5 hours, in which time some of the water will be caused to escape from electrodeposited nickel. Preferably, if such treatment is effected, the alloy is worked for a period long enough after heating to allow rearrangement of the crystallites and the nickel to fill any voids which may be left due to driving off the water. Usually, the subsequent heat treatment is advantageously employed when the electrodeposition occurs at a pH of 2 to 5, preferably 2 to 4. Of course, it is highly preferred not to have heat treat the formed dispersion alloys to remove water and it has been found that this is unnecessary when the processes of this invention are followed, especially when the electrodeposition takes place in the low pH ranges given. This is so despite the fact that the electrolyte may often comprise a major proportion of water and a gel or other material in which the thorium oxide is added or from which it is obtainable may contain a similar high percentage of water. Preferably however, such gels contain only minor proportions of water, usually from 1 to 40%, preferably from 15 to 25%.

Other changes in the electroforming process may be desired to effect best forming. For example, in some cases it may be desirable to interrupt the current flow or even to reverse it or impose an alternating current for a short period of time. If desired, the cathode may be enclosed in a diaphragm to prevent any possible adverse effects on the forming from sludge or particulate impurities in the electrolyte or electroforming bath. In

addition to agitating the bath, in some instances it may also be preferred to maintain the cathodes in motion or to direct electrolyte in particular flow patterns with respect to the cathodes. Temperatures of the composition may be varied during the electroforming operation, as may be the pH's, within the ranges given. Bath concentrations may be altered and current densities can be changed to obtain best forming effects, which are usually arrived at empirically. However, by following the methods described herein, improved electrodeposited dispersion alloys will be obtained, having better high temperature properties, e.g., strengths and stabilities.

The improved stabilities and strengths of the products of the invention will be such that the nickel alloys resulting, with about 0.2 to 3.5% (anhydrous basis) of refractory oxide crystallite content, by weight, distributed fairly evenly throughout the alloys, will be capable of being employed at high temperatures, from 1,500° to 2,200°F., and even in many cases as high as 2,600°F. for short time periods. Tensile strengths are not decreased to the same degree as for pure nickel at temperatures up to 2,300°F. Tensile strengths at a temperature of 2,000°F. may be as high as 5,000 lbs./sq. in. and will usually be no lower than 1,000 lbs./sq. in., even without subsequent treatments. With mechanical workings, the tensile strengths increase to as much as twice these figures. Nevertheless, it is often preferred to utilize the lower strength, unworked material because it does not require any additional processing and is still of a sufficiently high strength to be employed.

The present invention seems to contravene some of the laws which had previously been thought to apply to electrodepositions of dispersion alloys. In the acid baths, normally used at comparatively high acid pH's, water would be hydrolyzed to oxonium ions and such ions would charge the refractory oxide crystallites in the electrolyte. When hydrochloric acid was employed as the acidifying means, the chloride ions would be absorbed on the small crystallite primary adsorption sites and the oxonium ions would serve to screen the crystallites, giving them positive charges. They would also mutually repel each other and aid in deflocculating the crystallites, which otherwise would be mutually attracted, in neutral solution, due to Van der Waals forces. With a much more acidic solution it would be expected that the screening effect of the oxonium ions would be insignificant compared to the charges on ions in the electrolyte and consequently, poor electrolytic deposition of the crystallites would be anticipated, as well as some flocculation. Neither of these disadvantageous results has been observed and the additional unexpected advantage of lower moisture content of the crystallite in the alloy has been obtained, causing a great improvement of high temperature stability of the dispersion alloys made.

Although use of the present invention greatly improves the properties of thoria dispersion alloys at high temperatures and makes them easily manufactured, it has been observed microscopically that even with fairly small thicknesses of the alloy being deposited, there is still some columnar growth which is not broken up as well as the crystallites as is desirable. Work is being done to improve the deposition of the strengthened nickel so as to increase even further the strengths and other useful properties of these products at high temperatures and it has been found that best results are ob-

tained using the gel-derived crystallites in the 100 to 200 Angstrom particle diameter range at a pH about 1, e.g., 0.8 to 1.3. Theoretically, according to this invention lower pH's and lower particle sizes would be better but in practice the lower pH's are hard to maintain and lower particle size materials may tend to lump or aggregate.

The following examples will describe several preferred embodiments of the invention. All parts are by weight and all temperatures are in °F. unless otherwise specified.

EXAMPLE 1

A Watts-type nickel electroforming bath is made by dissolving 400 lbs. of nickel sulfate and 50 lbs. of nickel chloride in 100 gallons of water in an electroforming tank. Then, after the salts are in solution, there are added to them 2½ lbs. of a dehydrated thoria gel containing about 21% of chemically sorbed water. This is mixed well into the electrolyte and forms a sol of thoria crystallites of about 100 to 200 Angstroms in diameter, averaging about 150 Angstroms. Next, the pH is adjusted by the addition of about 10 gallons of a 35% solution of hydrogen chloride in water to produce a pH of about 1 in the electrolyte. In the resulting electroforming bath the crystallites of the sol remain separated due to their positive surface charges. Uncharged particles tend to aggregate, which is objectionable and leads to poor dispersion strengthening.

A plurality of nickel anodes and stainless steel cathodes, both having total effective surface areas of about 10 sq. feet, is suspended in the electrolyte. The cathodes are shaped as half cylinders, open sides facing the anodes so as to produce an electrodeposited dispersion alloy in the same shape. A direct current is imposed between the anodes and cathodes so that the current density is about 50 amps./sq. ft. The potential is maintained at 5 volts, the current flowing is about 500 amperes and the bath temperature is 50°C.

After 50 hours the current flow is interrupted and the electrodeposited specimen is examined. It is found to be almost 0.3 cm. thick and evenly deposited on the cathode. The electrodeposited half cylinder is removed from the cathode by known means and portions of it are cut for testing and for ultimate use as interior sections of a high temperature processing vessel. One portion (A) is heated for 10 hours at about 1,900°F. and is then tested for tensile strength at 1,500°F. Another portion (B) is tested at 1,500°F. without previous heating. Still another part, the same size as the other two, is mechanically worked by a combination of hammering, extrusion and rolling, for a period of about 2 hours, after which it is rolled to its original half cylinder form. The samples, designated A and B, respectively, compared to a control, C, of nickel formed without the refractory dispersed crystallite, are superior to the control in ultimate strengths at elevated temperatures. The yield strengths, ultimate strengths and ductilities at room temperature and the yield and ultimate strengths at 1,500°F. are shown in the following table.

	A	Specimen B	C
Yield strength, lbs./sq. in (room temperature)	24,000	30,000	41,500
Ultimate strength, lbs./sq.	53,000	55,000	57,600

-Continued

	A	Specimen B	C
in. (room temperature)			
Ductility, % elongation of 2 in. piece (room temperature)	35	30	25
Yield strength (1,500°F.)	9,500	11,500	2,900
Ultimate strength (1,500°F.)	10,200	12,900	7,500

The mechanically worked part has properties at least as good as specimens A and B and is generally superior in room and high temperature strengths.

When employed in high temperature processing equipment which is subjected to shocks and strains during use, the electrodeposited nickel parts made according to this invention, whether heat treated or not and whether worked or not, are of satisfactory strengths, operating very successfully at temperatures of 1,500°F. Of special importance are improved resistances to oxidation and increased yield and ultimate strengths at the elevated temperatures mentioned. In the same application at such temperature ordinary nickel units fail and electrodeposited half cylinders made in the same manner but at a pH of 4.0, without subsequent controlled driving off of water present in the electroform also fail, apparently due to water escaping from them.

When the above experiment is repeated with nickel sulfamate or nickel chloride baths, similar results are obtained. In both cases, the nickel concentration in the electrolyte is kept the same. Also, when minor proportions of other of the previously mentioned refractory metal oxides, e.g., copper, zirconium, aluminum, titanium, magnesium and iron in gel or dehydrated gel form or otherwise similarly finely divided positively charged particles, are employed with the thoria at concentrations of 10 to 20% of the thoria concentration, improved properties of the electrodeposited nickel also result.

When allyl sulfonic acid or quaternary pyridinium compounds are added as brighteners or surface characteristic modifiers in the proportions previously described, they do not interfere with the electrodeposition of the dispersion alloy nor do they diminish the desirable properties obtained, and they help to improve lustre and appearance.

Following the procedure of this example, variations are made in current density, electrolyte concentration, percentage of dispersed phase, time of operation and shape of cathodes, with the results obtained being useful and superior to those for an ordinary electroformed nickel product. In some such cases, the deposited nickel alloy is not removed from the cathode but is utilized bound to it. In other applications, additional materials are coated onto the surface of the deposited alloy, e.g., dispersion alloys of chromium. In other cases, the electrodeposited materials are ground and subsequently are sintered by conventional dispersion alloy manufacturing method. In such instances, the product obtained is superior to a control nickel alloy in its resistance to high temperature oxidation and in its maintenance of good yield and ultimate strength properties at elevated temperatures.

EXAMPLE 2

Panel specimens like those of Example 1 are produced by electrolysis of a Watts bath but the deposits

obtained, due to the shape of the cathode, are flat. Electrolysis is discontinued after about 24 hours, with the thickness of the nickel alloy produced being about 0.06 cm. The bath used contains no boric acid but in another run, boric acid is employed, to the extent of 30 lbs. in the 100 gallons of water. The pH is not affected much, being about 0.9 in such case. The products obtained, using boric acid in the Watts bath, are of essentially the same properties as those from the bath containing only nickel chloride and nickel sulfate, with or without acidifying acid (HCl or H₂SO₄) in amount to yield the desired pH.

After removal of the electroformed nickel alloy from the cathode it is tested by comparison to a control in the manner described in Example 1, but at 2,000°F. The ultimate strengths of the experimental material and the control (electroformed under the same conditions but without the thoria gel and resulting dispersed crystallites) are about the same but there is a significant improvement in yield strength, the control having a yield strength of 1,900 lbs./sq. in. but the experimental specimen having a yield strength approximately 50% better, 2,800 lbs./sq. in. Furthermore, the dispersion strengthened specimen has the yield strength and ultimate strength thereof improved by cold working, as by flexing, hammering, extruding, elongating and compressing for periods up to two hours at about room temperature. Similar treatments do not improve the pure or control electroformed nickel so as to increase its yield and ultimate strengths at the high temperatures of use and testing described.

EXAMPLE 3

Baths containing about 1,500 lbs. of nickel per 1,000 gallons of electrolyte are made in which there are present 20 lbs. of hydrated thoria gel (about 20% H₂O) of particle sizes in the 75 to 300 Angstrom range. The dispersed oxide material is kept suspended by means of a pump and circulator, which operate at low liquid velocities. The nickel in the bath is obtained from nickel chloride, nickel sulfate and nickel chloride, or nickel sulfamate, but other nickel salts may also be employed and the nickel may be added to the bath as the hydroxide, oxide, or in other suitable form, so long as it is then dissolved in the electrolyte.

Electroformings are effected at various current densities, ranging from 10 to 50 amperes/sq. in. with plating times being from 1 hour to 100 hours at room temperature so that the deposits range from 0.02 to 0.6 cm. in thickness. Voltages are preferably held at about 5 volts, although voltage changes of $\pm 50\%$ are also effected during the platings. Current densities are preferably held about 5 to 30 amperes/sq. in. Conventional brightening and surface active agents are usually employed but in some cases are omitted. In some control experiments pH's are allowed to be as high as 3.5-5.

When the baths are at the higher pH's, e.g., 3.8, 4.5, the strengths (at 1,500°F. and higher) of the alloys produced are not as high as when the lower pH's of this invention are employed. It is considered this is due to the entrapment of water in the alloy matrix or in the crystallite particles.

The electroforms obtained, with the dispersed oxide crystallite therein, are readily removable from the cathodes and, when tested at high temperature, show improved yield strengths, compared to pure electroplated nickel. Furthermore, cold working improves the yield

strength even further, which improvements are not obtained with ordinary nickel. This is also the case when the plating bath concentration of nickel is changed $\pm 50\%$ and when concentrations of the dispersed thoria are changed similarly, but not necessarily concurrently with the change in the concentration of nickel ion. Instead of thoria-containing dispersion strengthened nickel, other analogous products based on copper oxide, zirconia and alumina may be made by the same methods but the thoria-nickel products are considered superior due largely to their significantly improved high temperature properties previously mentioned.

EXAMPLE 4

The following experiment describes the electroforming of nickel with thoria particles of different sizes co-deposited with the nickel being plated, in an effort to strengthen it for use in high temperature applications. Such dispersion strengthening is different from dispersion alloying wherein hard particles are deposited with a softer metal matrix so as to increase its hardness and wear resistance. It has been found that particle size is not as critical in such type of alloying as it is in dispersion strengthening applications. Thoria can be electro-deposited with nickel or other metal and result in no improvement in mechanical strength at elevated temperature. To be dispersion strengthened, the nickel or other metal should have recrystallization inhibited at temperatures approaching the melting point of the metal. Thus, the inert dispersoid particles should act to block the movements of dislocations within the crystal lattice structure, increasing resistances to stress rupture and imparting increased strength to the material when it is subjected to slip (stress in loading) or climb (recrystallization and grain growth in annealing). The characteristics of electrodeposits can be evaluated by comparing microstructures and measuring mechanical properties against controls. Thus, the importances of the size of the dispersoid particles and electrolyte pH can be assessed.

To prove the effect of particle size of thorium oxide particles there are tested three different sizes of thoria, (a) 5 microns diameter and larger; (b) 0.6 to 0.8 microns (Fisher Sieve size), the finest ball milled product available for these experiments; and (c) 0.01 to 0.02 micron (in sols produced from gels). The electroforming conditions are as follows:

50 Bath type	Sulfamate
Voltage	4-5
Current density	30 a.s.f.
Percent thorium oxide in bath	0.5
Bath temperature	120°F.
pH	1.2 - 1.5
55 Anode	Rolled, depolarized nickel
Cathode	Stainless steel
Anode-cathode distance	8 inches, average
Forming rate	0.001 in./hr.

The electroform utilizing the 5 micron thoria particles in the bath is codeposited to a thickness of about 0.020 inch and is removed from the cathode. The material is found to be completely unsatisfactory, being exceptionally brittle, so that no useful tensile data can be obtained, even at a temperature as low as 1,000°F. In a similar run, utilizing the 0.6 to 0.8 micron diameter thoria, a hard but brittle deposit results. After removal from the stainless steel cathode this material can be fractured at room temperature simply by bending it to

an angle less than 90°. Photomicrographs at 100 times magnification show the structure of this product to be of a fine columnar nickel grain typical of sulfamate and Watts type electrolytes, with surface irregularities apparently due to agglomeration of uncharged particles. The deposit is rough and a similar rough deposit results when 5 micron particles were used. After heat treating for 1 hour at 1,800°F., in vacuum, the material recrystallizes and the thoria particles outgas severely, leaving voids and a porous structure. Such voids are non-uniform, showing that the uncharged thoria particles do not deposit uniformly in the electroform. All these characteristics are objectionable and it is evident that this material is unsatisfactory for use at 1,500°F. or any similar elevated temperature.

In the run utilizing the 0.01 to 0.02 micron thoria, charged to the electroforming baths as a hydrated gel (containing about 21% water) and converted therein to a sol, plating can be effected to a greater thickness, and an electroform 0.050 inch thick is made and tested. As is shown by a photomicrograph thereof at 100 times magnification, the nickel-thoria electroform exhibits a typical columnar grain structure which, even after a thermal treatment at 2,300°F. for 1 hour, does not undergo recrystallization. It is concluded that the presence of the very fine particles, within the 75 to 300 Angstrom diameter range, inhibits recrystallization and results in dispersion strengthening of the nickel. Similar resistance to recrystallization is obtained at 1,500°F. In another experiment, utilizing essentially the same conditions, but with increased thoria content in the bath a 0.048 inch thick electroform is made containing about 1.8% by weight of thorium oxide, the particles thereof being those obtained from a 0.01 to 0.02 micron diameter thoria sol. The electroform is reduced by cold working from about 0.048 inch to about 0.024 inch in thickness, approximately equally in four working passes through cold working rolls, followed by stress relieving each time. Normally, under such conditions any cold worked metal will undergo high angle grain growth and there will be a severe loss of strength when it is subjected to thermal treatment in the annealing temperature range (the stress relieving treatment). However, the described electroform undergoes almost no recrystallization and the stronger cold work structure thereof is retained. The annealing is to a temperature of about 1,800 to 2,000°F. after each cold working. The small grain size resulting is unexpected and is attributed to the small particle sizes of the dispersoid and the exceptionally good dispersion thereof in the nickel matrix. Mechanical tests at 1,500°F. on this material show that it has a yield strength in excess of 16,000 p.s.i., more than double the ultimate strength of pure nickel at this test temperature.

When the above-described experiments are run using other particle sizes within the 75 to 300 Angstrom diameter range, at pH's of 1.1, 1.0 and 0.9, at temperatures of 30° to 70°C., with thoria concentrations of 0.5 to 5%, preferably 0.5 to 3%, of the nickel present, to plate out electroforms of thicknesses from 0.03 to 1 cm. thick, preferably 0.1 to 0.5 cm., similar increases in high temperature strengths are obtained, with even greater increases resulting at these lower pH's.

When similar experiments are run in which the electroforming bath pH is varied to be inside and outside the 0.4 to 1.9 range a significant change in ultimate

strength of the electroform resulting is noted, which is illustrated in the following table.

TABLE

Effects of Nickel Electrolyte pH on Dispersion Content and Product Strength at 1,500°F.				
pH	Thorium Oxide in Electrolyte (g./liter)	Thorium Oxide in Deposit (% by weight)	Ultimate Strength (p.s.i.)	Elongation (% 2 inches)
3.2	4.03	1.77	1,300	Under 1
2.3	4.78	1.75	6,300	4
1.6	4.58	0.96	11,000	2

As is seen from the table, decreasing the pH results in improved ultimate strength at elevated temperature, despite the fact that the lower pH also results in a decrease in the thorium oxide deposited. When the pH is held at 4.0 the electroform fails in a brittle fracture mode at an ultimate strength below that of pure electrodeposited nickel but when the pH is maintained lower than the values given in the above table, e.g., 1.2, 1.1, 1.0 and 0.9, the ultimate strength is greater than that of pure nickel (which is about 7,000 p.s.i.) and in the 0.8 to 1.3 pH range can be greater than 11,000 p.s.i. Because greater deposits of the thoria are obtained at higher pH's it would have been expected that, in the absence of the desorption phenomenon or other reason for the observed results, one would use higher pH's to improve product strength. Therefore, the present results are unexpected.

From the above description and the specific examples given it is seen that this invention represents a significant advance in the art of manufacturing dispersion strengthened nickel. Accordingly, the invention is to be construed as covering the described subject matter and those modifications thereof wherein equivalents or substitutes are employed, without going beyond the inventive concept.

What is claimed is:

1. A method of electroforming dispersion strengthened nickel containing dispersed ultrafine thorium oxide particles, which electroformed nickel is of improved high temperature properties, which comprises passing a direct current between an anode and a cathode in an electroforming bath containing a dissolved nickel salt and 0.1 to 10%, on the basis of the dissolved nickel present, of thorium oxide particles of diameters in the range of 75 to 300 Angstroms, and at a pH in the range of 0.4 to 1.9, which electroforming bath contains ultrafine thorium oxide particles obtained by admixing a thorium oxide sol or a hydrated thorium oxide gel with an aqueous medium to produce a sol, so as to form on the cathode a deposit of nickel containing the dispersed ultrafine thorium oxide particles therein, which nickel deposit is mechanically deformable at room temperature and of improved high temperature strength compared to ordinary electroformed nickel.

2. A method according to claim 1 wherein the bath is aqueous and contains a source of nickel selected from the group consisting of nickel sulfamate, nickel chloride, nickel sulfate and a mixture of nickel chloride and nickel sulfate, the content of thorium oxide particles therein is from 0.5 to 5% of the dissolved nickel present, the bath is at a temperature in the range of 30° to 70°C. and the forming is continued for a period of time long enough to form a thickness of dispersion

strengthened nickel from 0.02 to 1 cm., with thorium oxide particles distributed therein.

3. A method according to claim 2 wherein the bath contains from 3 to 36 oz. per gallon of a mixture of nickel chloride and nickel sulfate, nickel chloride or nickel sulfamate at a pH of from 0.8 to 1.3 and is at a temperature in the range of 40° to 60°C., electroforming is continued for a time long enough to form a thickness of nickel from 0.02 to 0.6 cm. thick with thorium oxide particles distributed therein, and the electroforming is effected on a cathode from which the nickel containing dispersed thorium oxide particles is readily removable.

4. A method according to claim 3 wherein electroforming is effected on a stainless steel cathode of a shape corresponding to that of a desired finished piece so that additional shaping of the nickel is minimized.

5. A method according to claim 3 wherein after forming of the nickel containing dispersed thorium oxide particles the electroform is worked mechanically to increase its high temperature strength.

6. A method according to claim 3 wherein the electroforming bath is an aqueous bath of the Watts or sulfamate type.

7. A method according to claim 3 wherein the thorium oxide particles are charged to an electroforming bath as a sol or hydrated gel containing from 1 to 40% of chemically sorbed water.

8. A method according to claim 7 wherein the electroforming bath is acidified to a pH of 0.8 to 1.3 after charging of the thorium oxide.

9. A method according to claim 8 wherein the nickel containing dispersed thorium oxide crystallite particles is electroformed onto a cathode of a shape corresponding to that of the desired finished piece and the electroformed nickel is removed therefrom.

10. A method according to claim 8 wherein the electroforming is effected on a stainless steel cathode and the electroformed nickel containing dispersed thorium oxide crystallite particles is removed from the cathode and is mechanically worked to increase its high temperature strength.

11. An electroforming bath comprising a dissolved nickel salt and undissolved thorium oxide particles therein, at a pH in the range of 0.4 to 1.9, with the thorium oxide particles being of particle sizes of diameters in the 75 to 300 Angstrom range and being sufficiently suspended in the bath so as to form on a cathode a deposit of nickel containing dispersed thorium oxide when a direct current is passed through the bath, which deposit is of improved high temperature strength.

12. An electroforming bath according to claim 11 wherein the nickel salt is nickel sulfamate, nickel chloride, nickel sulfate or a mixture of nickel chloride and nickel sulfate, the thorium oxide particles are those obtained by admixing a hydrated thorium oxide gel with an aqueous medium and are present to the extent of from 0.5 to 5% of the dissolved nickel present and the bath is at a temperature in the range of about 30° to 70°C.

13. An electroforming bath according to claim 12 wherein the nickel salt concentration is from 3 to 36 oz. per gallon of a mixture of nickel chloride and nickel sulfate, nickel chloride or nickel sulfamate, the bath is aqueous, at a pH of from 0.8 to 1.3, at a temperature in the range of 40° to 60°C. and the thorium oxide particles are of a size of from about 100 to 200 Angstroms in diameter and are present to the extent of from 0.5 to 3% of the dissolved nickel present, which bath is acidified to a pH of 0.8 to 1.3 after incorporation therein of the thorium oxide particles.

14. An electroforming bath according to claim 13 wherein the thorium oxide particles are crystallites of particle sizes of a diameter of about 150 Angstroms.

15. An electroforming bath according to claim 14, of the Watts or sulfamate type.

16. A method of making a nickel electroforming bath which comprises admixing with an aqueous solution of a nickel salt of the nickel sulfamate, nickel chloride, nickel sulfate, or mixed nickel chloride and nickel sulfate type, 0.1 to 10% on the basis of dissolved nickel present, of particles of thorium oxide, as a sol or a hydrated gel which forms a sol thereof therein and adjusting the pH of the bath to a value in the range of 0.4 to 1.9.

17. A method according to claim 16 wherein the admixing is effected at a temperature of 40° to 60°C., the particles of thorium oxide are of diameters in the range of from 75 to 300 Angstroms and the electroforming bath is an aqueous bath containing from 3 to 36 oz. per gallon of a mixture of nickel chloride and nickel sulfate, nickel chloride or nickel sulfamate at a pH of from 0.8 to 1.3.

18. A method according to claim 17 wherein the thorium oxide particles are crystallites of particle sizes in the range of 100 to 200 Angstroms and are admixed with a sulfamate or Watts-type nickel electroforming bath as a thorium oxide aqueous gel or sol, after which acidification to the desired pH is effected with hydrochloric acid.

19. A product of the process of claim 1.

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