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METHOD OF PRODUCING DISPERSION STRENGTHENED NICKLE-CHROMIUM ALLOYS

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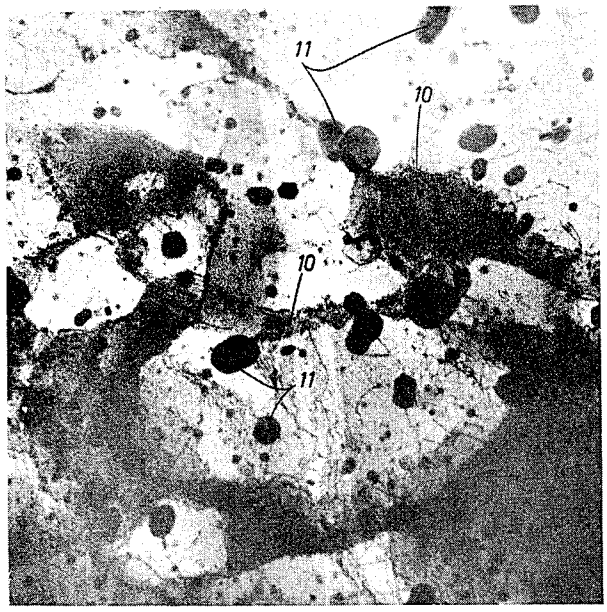
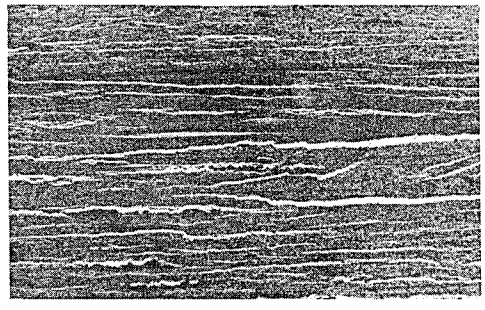



FIG. 1

FIG. 2



Inventors
ROBERT W. FRASER
BUD W. KUSHNIR
BAUKE WEIZENBACH

by: Frank J. Pipp Agent.

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# METHOD OF PRODUCING DISPERSION STRENGTHENED NICKEL-CHROMIUM ALLOYS

Robert William Fraser, Fort Saskatchewan, Alberta, Bud William Kushnir, Edmonton, Alberta, and Bauke Weizenbach, Fort Saskatchewan, Alberta, Canada, assignors to Sherritt Gordon Mines Limited, Toronto, Ontario, Canada, a company of Canada

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This invention relates to a process for producing dispersion strengthened nickel base alloys containing between 10 and 35% by weight chormium and to the novel wrought dispersion strengthened alloy products obtained in accordance with the process.

It is well known that the high temperature oxidation resistance and strength of nickel base alloys can be greatly improved by alloying with chromium. Improvement in high temperature strength characteristics is generally obtained with the addition of more than 10% by weight chromium and high temperature oxidation resistance is improved by the presence of at least 15% by weight chromium. The upper limit of useful chromium content in nickel alloys is about 35% by weight, at which point the solubility limit of chromium and nickel is reached. It has long been conventional in the art to alloy nickel with about 20% by weight chromium to obtain optimum improvement in oxidation resistance and strength.

It is also known that the high temperature service characteristics of metals and particularly of nickel and nickel base alloys can be substantially improved by dispersion strengthening. Dispersion strengthening involves the provision within a matrix metal of a large number of fixed, uniformly disseminated, sub-micron sized refractory particles. These dispersed particles, which are normally refractory oxide particles such as thoria, function to stabilize the matrix metal at elevated temperatures thereby increasing its tensile strength and stress-to-rupture life.

In addition, it is known that the micro-structure of a metal or metal alloy strongly influence its strength characteristics and, further, that such structure is determined to a large extent by the manner in which a material is fabricated and worked. For example, co-pending United States application Ser. No. 465,291, filed June 21, 1965, now Patent No. 3,366,515 describes one method whereby a novel, strength enhancing grain and sub-grain structure can be developed in dispersion strengthened nickel and nickel base alloys. According to this method, a substantially fully dense billet comprised of matrix metal and highly disseminated sub-micron refractory oxide particles is subjected to a series of controlled work cycles in which the billet is cold worked to take reductions in cross-sectional area of less than 20%, preferably less than 10%, followed by a controlled anneal after each such reduction to relieve residual stresses within the workpiece. This working method produces a matrix microstructure comprised of small, elongated fibrous or lamellar grains having a polygonized substructure. A polygonized substructure is characterized by little evidence of recrystallization and relatively small, equi-axed sub-grains bounded by low angled grain boundaries. This particular micro-structure substantially enhances the strength properties of the wrought, dispersion strengthened material in which it is developed.

Efforts to produce nickel base alloys which combine the desirable high temperature service characteristics separately obtainable from alloying nickel and chromium, dispersion strengthening and specific grain and sub-grain structure control encounter many difficulties. These result



largely from problems inherent in the powder metallurgy techniques conventionally employed in the production of dispersion strengthened alloys. For one thing, metal powders as used for this purpose are particularly susceptible, because of their large surface area, to contamination when exposed to air. In air, thin coatings of oxides and nitrides are formed on the particle surfaces. Such coatings on nickel particles may be removed or cleaned up satisfactorily by heating the particles in a reducing atmosphere such as in hydrogen gas. The contaminant coatings associated with chromium particles, on the other hand, are notoriously difficult to clean up; heating in the presence of hydrogen has little or no affect.

Such contaminant coatings on the chromium particles hinder the inter-diffusion of chromium and nickel when conventional powder metallurgy methods involving powder compaction and sintering are employed to fabricate dispersion strengthened nickel-chromium alloys. As a result, only incomplete homogenization of the nickel-chromium matrix is obtained and the benefit which can normally be derived from alloying 10% to 35% by weight chromium with nickel is not fully realized. In addition, contaminant coatings are apparently a factor in causing undesirable agglomeration of the refractory particles during processing which further adversely affects the high temperature service characteristics of the alloy product.

Another problem is that fully dense dispersion strengthened nickel-chromium alloys produced by conventional powder metallurgy procedures do not normally have a grain or sub-grain structure which contributes appreciably to their strength properties and known methods for developing a desirable micro-structure have been found ineffective or impractical when applied to nickel-chromium alloys containing a dispersed phase. A fibrous grain structure with polygonized sub-grain structure can be developed in the matrix of such alloys by utilization of the working method of United States application Ser. No. 465,291 noted above, but it has been found that while this method is particularly suitable for fabrication of dispersion strengthened nickel products, it is generally uneconomic for fabricating dispersion strengthened nickel-chromium alloys on a commercial basis.

The present invention provides a practical and effective method for producing wrought dispersion strengthened alloys with a well homogenized nickel-chromium matrix with uniformly dispersed refractory particles and any predetermined characteristic matrix micro-structure which can be developed in dispersion strengthened nickel. Alloys obtained by the method of the invention possess the superior high temperature strength properties and oxidation resistance normally attributable to nickel-chromium alloys and have further enhanced high temperature strength characteristics attributable to the homogeneity of the matrix, the uniformity of distribution of refractory particles in the matrix and a specifically controlled microstructure.

The process of the invention derives from the discovery that under certain conditions substantially fully dense wrought dispersion strengthened nickel having any characteristic micro-structure can be alloyed with chromium by high temperature solid state infusion of the chromium into the nickel matrix without causing agglomeration of the dispersed particles or recrystallization of the matrix and while retaining in the nickel-chromium matrix of the final product the characteristic micro-structure of the original nickel matrix. Thus, the invention enables the production of homogeneous, dispersion strengthened nickel-chromium alloys having the uniform dispersoid distribution and preferred micro-structure which can be readily developed in straight nickel-dispersoid wrought products but which heretofore could

not be practically and economically achieved in nickel-chromium-dispersoid wrought products.

In a preferred embodiment of the invention, about 10% to about 35% by weight chromium is deposited on a wrought dispersion strengthened nickel shape which has been specifically fabricated by procedures which produce a uniform distribution of dispersoid in the matrix and which develop a fibrous or lamellar matrix grain structure with a polygonized sub-structure. The dispersion strengthened nickel shaped with deposited chromium is then heated in a protective atmosphere at a temperature within the range of 2000° F. to 2400° F. to substantially completely homogenize the deposited chromium and the nickel matrix. Surprisingly, despite the extensive heating and the massive infusion of chromium into the nickel matrix with corresponding increase in the volume thereof, the homogenized nickel-chromium matrix is substantially free of recrystallization and exhibits a grain structure and sub-grain structure having the same characteristics as the original nickel matrix. That is, the grains of the matrix are elongated, fibrous or lamellar and have a polygonized sub-structure. The product has high temperature tensile strength and stress-to-rupture life equal to or better than that of the starting material and also possesses excellent high temperature oxidation resistance.

The invention is described in detail hereinbelow in conjunction with the drawings in which:

FIGURE 1 is a photomicrograph of a section of 77.2% nickel, 3% thoria, 19.8% chromium dispersion strengthened material produced in accordance with the invention, magnification 300×; and

FIGURE 2 is an electron micrograph of a small area of material shown in FIGURE 1, magnification 32000×.

The starting material for the process of the present invention can be any fully dense or substantially fully dense wrought dispersion strengthened nickel shape produced by any conventional or unconventional methods. However, since the high temperature strength characteristics of the starting material reflect directly in the high temperature strength characteristics of the final product, the preferred starting material is dispersion strengthened wrought nickel which itself has optimum high temperature properties.

Co-pending United States application Ser. No. 543,495, filed Apr. 18, 1966 describes a composite nickel-thoria powder which is particularly suitable for powder metallurgical fabrication of dispersion strengthened nickel, and co-pending United States application Ser. No. 465,291 describes a preferred fabrication method whereby a microstructure which substantially improves strength properties can be developed in fully dense dispersion strengthened nickel. The invention is described hereinbelow as applied to starting material produced from composite nickel-dispersoid powder and by fabrication techniques described in the aforementioned pending applications. However, it is to be understood that the inventive process is applicable to any wrought shapes comprising a nickel matrix containing dispersed refractory particles and having any characteristic micro-structure.

Referring more specifically to the preferred embodiment, the composite nickel-refractory oxide powder of co-pending United States application Ser. No. 543,495 from which the preferred starting material is formed consists of irregular-shaped particles of nickel comprised of clusters of sub-particles of nickel between about 0.2 and about 0.5 micron in size. The sub-particles have ultra-fine thoria fixed in the surfaces thereof and may occur singly or be agglomerated in clusters up to 10 microns or more in size. The thoria particles preferably are between 10 and 30 millimicrons in size and are uniformly dispersed in the surfaces of the nickel sub-particles. Typical powders have an apparent density between 0.5 and 0.9 gram per cubic centimetre and Fisher sub-sieve number of less than 1.3 and preferably contains from about 2.0 to 4.0 percent by volume of one or more refractory oxides. The refractory oxide particles must have a melting point higher than the matrix metal, good thermal stability, low solubility in the matrix metal and should be non-reactive with the matrix metal at elevated temperatures of the order of 2400° F. There are a number of refractory oxides known to the art which satisfy the conditions necessary for use as the dispersed phase in dispersion strengthened nickel. For example, yttria, ceria and thoria have all been shown to be particularly suitable. Because of its ready commercial availability and high free energy of formation value, thoria is a preferred dispersoid.

The above-described nickel-dispersoid powders or any other powders of a similar nature can be processed into completely dense wrought dispersion strengthened shapes using any one of several techniques known to the art. One such technique involves a two-stage procedure whereby the powder is first compacted into a partially densified, self-supporting, green compact, such as by isostatic compaction to about 60% of absolute theoretical density, and the green compact is then hot worked to take a reduction in cross-sectional area of approximately 50% to produce a completely dense article. Alternatively, the powder or a preformed green compact or billet can be formed directly into dense finished or semi-finished shapes by extrusion.

In any case, the fully densified shape must normally be subjected to further working operations to reduce it to final dimensions and/or to produce a desirable microstructure in the matrix. As described in co-pending United States application Ser. No. 465,291, a preferred working procedure comprises subjecting the densified material to a series of working cycle in which cold reductions in cross-sectional area of less than 20% are taken followed by a controlled anneal after each such reduction to relieve residual strains. The reductions in cross-sectional area may be effected using any of the several known methods such as rolling, swaging or drawing. The intervening and final anneals are carried out at a temperature which is below the melting point of the matrix. The annealing time and temperature is adjusted, having regard to the size and composition of the wrought shape to minimize recrystallization. For example, a 0.02 inch thick nickel-thoria strip containing 2.5% by weight thoria may satisfactorily be annealed by heating at 2200° F. for about 30 minutes. Annealing at excessively high temperatures for extended periods of time will result in recyrstallization which is evidenced by the growth of large grains without a characteristic sub-grain structure. Recrystallization and loss of the grain and sub-grain structure results in a substantial reduction in high temperature strength properties.

By subjecting the wrought shape to repeated cold working cycles with cross-sectional area reductions of less than 20% and preferably less than 10% and controlled intervening anneals, a preferred grain structure is developed. Such a grain structure is described in co-pending United States application Ser. No. 465,291. The grains are fibrous or lamellar and have a well developed sub-structure which is characterized by low angle sub-grain boundaries and an absence of recrystallization.

In carrying out the present invention, the wrought dispersion strengthened nickel shape is alloyed with chromium by solid state diffusion of the chromium into the nickel matrix. The first step of the process is the deposition of the desired amount of chromium on the dispersion strengthened nickel shape. Two procedures which are particularly suitable for this purpose are chromizing and electroplating. Chromizing is a surface treatment at elevated temperature generally carried out in pack, vapour or salt-bath in which an alloy is formed by the inward diffusion of chromium into the surface of the base metal. The known pack vapour deposition technique has been found particularly suitable for the chromium deposition step of this invention. This technique involves placing the article to be chromized in a container together with a mixture of chromium and alumina powders and heating

the container contents. The powder mixture is composed of about 55% by weight chromium and 45% by weight alumina, with the alumina powder being provided to facilitate recovery of the article from the container at the termination of the heating period. The amount of chromium provided should be a substantial excess over the amount which it is desired to deposit onto the wrought dispersion strengthened nickel shape. An excess of chromium is helpful in ensuring a sufficient supply of chromium vapour at the surface of the wrought shape. Generally, it is desirable to deposit at least 10% by weight chromium which is the minimum amount required to give some improvement in the oxidation resistance of the nickel. Preferably about 20% by weight chromium should be deposited to ensure optimum high temperature oxidation resistance. The maximum amount of chromium deposition is about 35% by weight which is close to the solubility limit of chromium in nickel. The powder mixture containing the appropriate amount of chromium and alumina is placed within a steel container and the wrought shape is completely immersed within the powder mixture. The container is then sealed and heated together with its contents to a high temperature, for example, to about 2350° F. Heating is continued at the elevated temperature for a period of time sufficient to enable the amount of chromium desired in the final product to deposit on the wrought dispersion strengthened nickel shape. In order that the chromium content will be uniform through the final product, care must be taken to maintain a constant temperature throughout the article during the heating to avoid preferential deposition of the chromium at hot spots. Care should also be taken to protect the system from air contamination.

The temperature of the chromizing step is very important. The rate of chromizing depends upon the temperature used. The higher the temperature, the faster the vaporization and deposition of chromium. However, the chromizing temperature must be below the melting point of the matrix or the desired microstructure will be lost and also agglomeration of the dispersed particles may occur. The normal temperature range from chromizing is from about 2000° F. to about 2400° F., preferably 2200° F. to 2400° F.

The length of time used for chromizing a particular wrought shape is determined by routine experiment. The temperature used, the thickness of the wrought shape, the amount of chromium available to vaporize and deposit and the amount of chromium desired in the final product will all influence the length of time which must be used.

Following chromium deposition, the wrought shape is heated at an elevated temperature in a protective atmosphere such as hydrogen to homogenize the deposited chromium with the nickel matrix. During heating, the chromium which initially is concentrated at the surface of the wrought shape, gradually becomes uniformly distributed throughout the matrix.

The homogenizing temperature is important in that the rate of diffusion of chromium in the nickel matrix is temperature dependent. However, the homogenizing temperature must be less than the melting point of the matrix in order to avoid loss of the desired micro-structure and to avoid agglomeration of the dispersed phase. Generally, homogenization is carried out at a temperature within the range of about 2000° F. to about 2400° F., preferably 2200° F. to 2400° F.

The actual heating time to effect homogenization in each case will depend on the size and shape of the wrought shape, the percentage of chromium to be diffused, the heating temperature and other operating factors. As an example, a 1 in. x 6 in. x 0.20 in. chromized nickel-thoria strip, having a chromium content of 32.7% at the surface and 9.0% at the centre was homogenized by heating at 2200° F. in a hydrogen atmosphere. After 64 hours of heating, the chromium content was 19.8% at the surface and 18.8% at the centre. The chromium distribution gradient may be reduced still further by continued heating, if so desired.

The matrix of the final product contains homogenized nickel and chromium and exhibits essentially the same grain and sub-grain structure as that of the nickel matrix of the starting material. Also, the distribution of the longed heating during chromium disposition and homogenization and the massive infusion of chromium into the nickel with accompanying volume increase of the matrix does not alter the basic characteristics of grain and subgrain structure which was present in the nickel matrix of the starting material. Also, the distribution of the refractory oxide particles in the final nickel-chromium matrix is essentially the same as that in the initial nickel matrix; no agglomeration of the dispersoid occurs when chromium deposition and homogenization are carried out under the controlled conditions described hereinabove. Thus, in the preferred embodiment of the invention where the nickel matrix of the starting material contains highly disseminated refractory particles and has a well developed fibrous micro-structure with a polygonized sub-structure, the final nickel-chromium alloy product exhibits the same characteristics. The product retains the high temperature strength properties attributable to these characteristics and, at the same time, has the superior high temperature oxidation resistance of nickel-chromium alloys.

It is anticipated that other alloy metals, such as iron, cobalt, tungsten, molybdenum, niobium and tantalum may be included within the composition of the final product. Metal powders can be mixed with the nickel and dispersoid prior to processing or they can be introduced later by techniques such as vapour-deposition.

The following example illustrates a practical embodiment of the invention.

## EXAMPLE 1

### (A) Preparation of wrought dispersion strengthened nickel starting material (prior art)

Nickel-thoria powder was compacted in a 1.25 inch by 2.4 inch die under a 100 ton load to make a 60 gram billet 0.20 inch in thickness. The nickel-thoria powder was obtained by the hydrometallurgical process described in co-pending United States application Ser. No. 543,495 and had the following characteristics:

Analysis:

| | | |
|---|---|---|
| Thoria | percent by weight | 3.1 |
| Sulphur | do | 0.002 |
| Carbon | do | 0.007 |
| $H_2$ loss | percent | 0.8 |
| Nickel and incidental impurities | | Balance |
| Apparent density | grams/cc | 0.99 |
| Fisher subsieve No. | | 0.53 |
| Thoria size range | millimicrons | 10 to 30 |

The billet which was about 60% fully dense, was heated in a flowing hydrogen atmosphere to a temperature of 2200° F. to prepare it for hot working and to remove any nickel oxide present. It was then hot rolled to take a 50 percent reduction, resulting in a substantially 100% dense strip product 0.10 inch in thickness. The strip was subsequently annealed in a flowing hydrogen atmosphere at 2200° F. for 30 minutes.

The fully dense strip was cooled and cold rolled to take a 10% reduction. Following cold working, the strip was annealed at 2200° F. for 30 minutes and the cold roll-anneal working cycle was repeated with 10% reductions until the strip had undergone a total of 15 work-anneal cycles resulting in a final strip thickness of 0.02 inch.

The ultimate tensile strength of the worked strip at 2100° F. was 13,800 p.s.i.

(B) Preparation of dispersion strengthened nickel-chromium alloy product in accordance with the invention

55 grams of −200 +325 Tyler mesh screen, pure commercial grade chromium powder was mixed with 45 grams of alumina powder in a cone blender for 30 minutes. The powder mixture was placed in a 5 in. x 6½ in. x 1 in. I.D. stainless steel furnace boat. A piece of nickel-thoria strip 1 in. x 6 in. x 0.02 in. in dimension from part A above was completely immersed within the powder mixture in the boat. A stainless steel plate was welded on the boat and the boat and contents were then placed in a furnace and heated to 2200° F.

The boat and contents were maintained at this temperature for 135 hours. On cooling, it was found that 20% by weight chromium had deposited on the strip. The chromium gradient within the strip varied from 32.7% at its surface to 9.0% at its centre.

Following chromizing, the nickel and chromium were homogenized by heating the strip at 2200° F. in a flowing hydrogen atmosphere for 64 hours. At termination of this homogenization step, the chromium content at the surface of the strip was 19.8% and 18.8% at the centre.

The strength characteristics of the finished strip were:

| | | |
|---|---|---|
| Ultimate strength at 2100° F. | p.s.i. | 15,000 |
| Stress for 100 hours rupture life at 2000° F. | p.s.i. | 6,000 |
| Oxidation factor[1] (based on a factor of 1.0 for the nickel-thoria strip from part A) | | 0.02 |

[1] Normalized weight gain under static air oxidation test at 1900° F. for 100 hours.

FIGURES 1 and 2 show the microstructure of the final product. FIGURE 1 is a micrograph, magnification ×300 of a transverse section taken parallel to the direction of working. The characteristic fibrous grain structure is readily apparent. X-ray diffraction studies across the section show uniform nickel-chromium distribution.

FIGURE 2 is an electron micrograph magnification ×32,000 of a small section of the material of FIGURE 1 showing the sub-grain structure of the material which is characterized by low-angle sub-grain boundaries **10** and an absence of any evidence of recrystallization. Dark spots **11** are thoria particles. It will be noted that these characteristic micro-structural features are essentially the same as those of the dispersion strengthened nickel starting material which is described in detail in co-pending United States application Ser. No. 465,291.

It will be understood, of course, that modifications can be made in the preferred embodiment of the present invention as described hereinabove without departing from the scope and purview of the appended claims.

What we claim as new and desire to protect by Letters Patent of the United States is:

**1.** A process for producing wrought dispersion strengthened nickel-chromium alloys which comprises providing a substantially fully dense wrought shape having a nickel matrix with a characteristic micro-structure and containing a dispersion of refractory particles; depositing from about 10% to about 35% by weight chromium on said wrought shape; thereafter homogenizing the deposited chromium with the nickel matrix by heating the shape at a temperature within the range of about 2000° F. to about 2400° F. in a protective atmosphere for a period of time sufficient to produce a substantially uniform chromium distribution throughout the wrought shape whereby a dispersion strengthened nickel-chromium alloy product having substantially the same characteristic micro-structure as the initial nickel matrix is obtained.

**2.** A process according to claim **1** wherein the wrought shape which is provided has a nickel matrix with a micro-structure characterized by well developed fibrous or lamellar grains having a polygonized substructure.

**3.** A process according to claim **1** wherein about 20% by weight chromium is deposited on the wrought shape.

**4.** A process according to claim **1** wherein the chromium is deposited by chromium electroplating the wrought nickel shape.

**5.** A process according to claim **1** wherein chromium is deposited by vapour deposition carried out at a temperature within the range of about 2200° F. to about 2400° F.

**6.** The process for the production of a dispersion strengthened nickel-base alloy article which comprises processing composite nickel-thoria powder to produce a completely dense article comprised of a nickel matrix containing a uniform dispersion of ultra-fine thoria particles; cold working the said article with a plurality of working cycles, each cycle consisting of taking a reduction in cross-sectional area of less than 20% followed by a residual stress relieving anneal, to produce a wrought article having a matrix micro-structure of elongated fibrous grains having a polygonized substructure; chromizing the wrought article in a protective atmosphere at a temperature below the melting point of the matrix to deposit about 20% by weight chromium thereon; and heating the chromized article within the temperature range of 2200° F. to 2400° F. in a hydrogen atmosphere to homogenize the deposited chromium with the nickel matrix, whereby a homogeneous, dispersion strengthened, nickel-base alloy containing about 20% by weight chromium and having a matrix micro-structure of elongated fibrous grains having a polygonized substructure is produced.

**7.** A process as defined in claim **6** in which the composite nickel-thoria powder comprises irregular-shaped nickel particles formed of nickel sub-particles between 0.2 and 0.5 micron in size agglomerated in clusters and having refractory oxide particles between 10 and 50 millimicrons in size attached to the surfaces thereof.

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L. DEWAYNE RUTLEDGE, *Primary Examiner.*

W. W. STALLARD, *Assistant Examiner.*

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