July 14, 1942. C. ADAMOLI 2,289,566

NICKEL-BERYLLIUM ALLOY

Filed Dec. 21, 1939 3 Sheets-Sheet 1

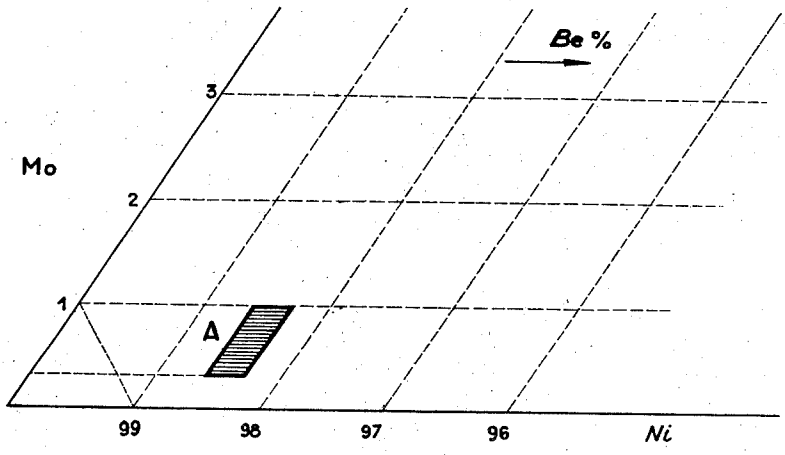


Fig. 1

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NICKEL-BERYLLIUM ALLOY

Filed Dec. 21, 1939 3 Sheets-Sheet 2

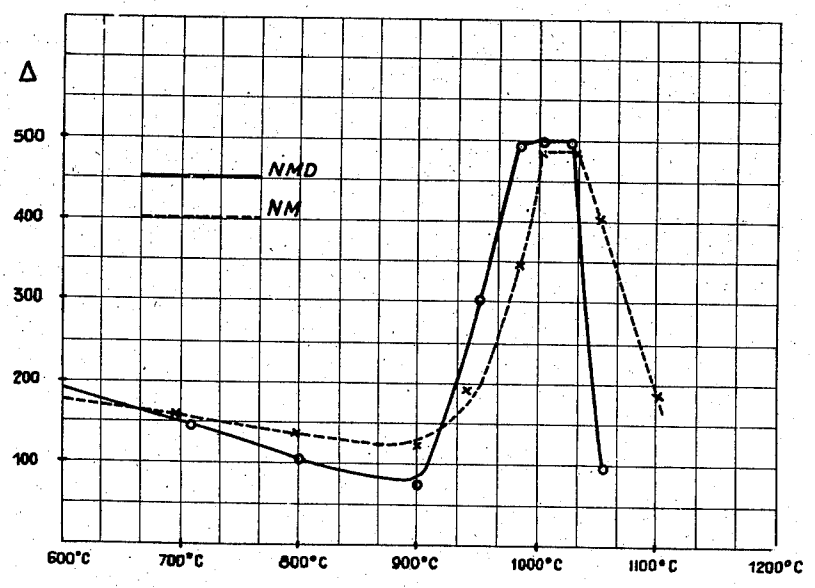


Fig. 2

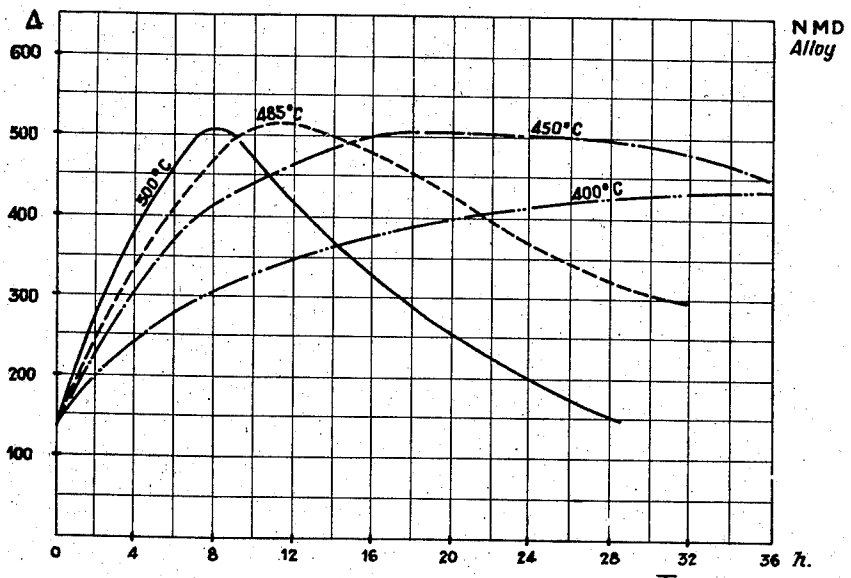


Fig. 3

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NICKEL-BERYLLIUM ALLOY

Filed Dec. 21, 1939 3 Sheets-Sheet 3

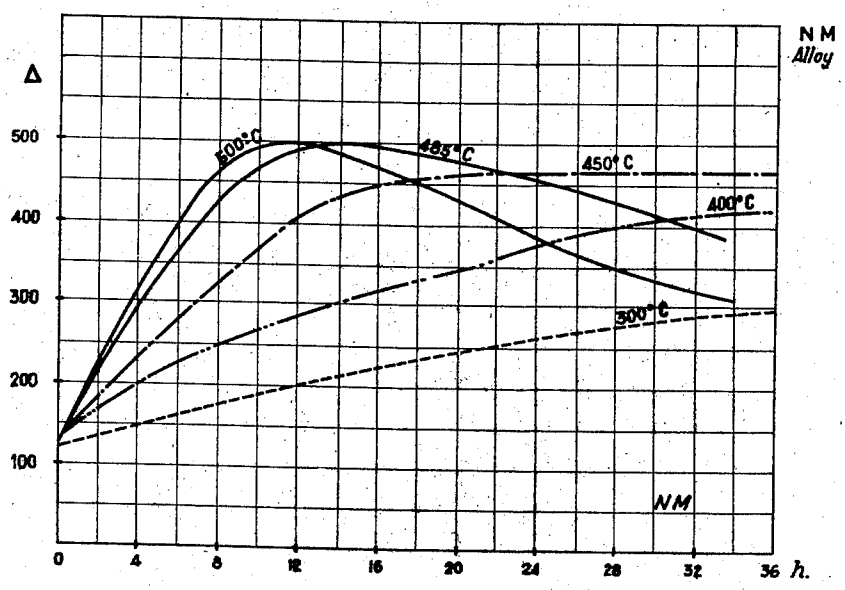


Fig. 4

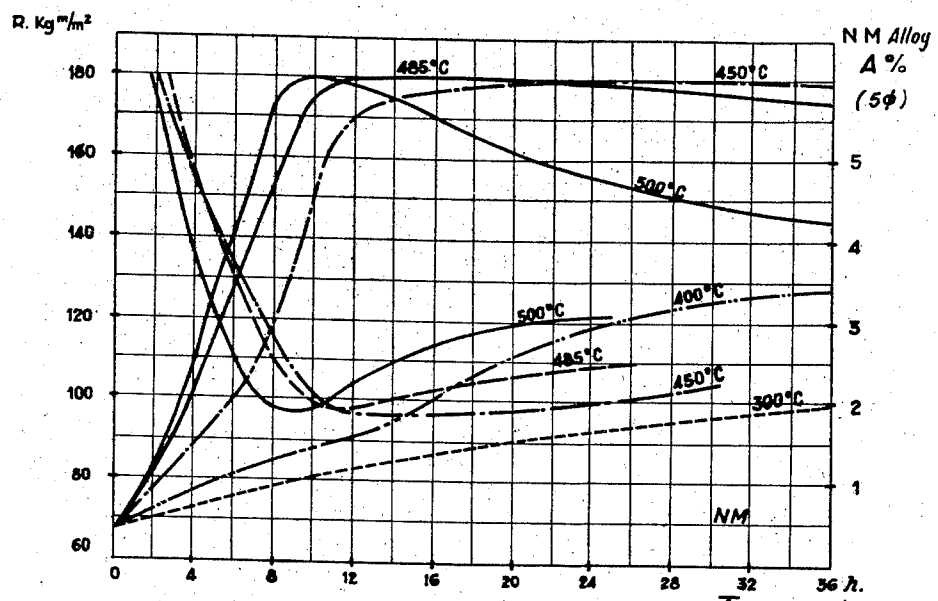


Fig. 5

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UNITED STATES PATENT OFFICE

2,289,566

NICKEL-BERYLLIUM ALLOY

Carlo Adamoli, Milan, Italy, assignor to Perosa Corporation, Wilmington, Del., a corporation of Delaware

Application December 21, 1939, Serial No. 310,367
In Italy June 30, 1937

4 Claims. (Cl. 148—13)

The present application relates to a method for improving nickel-beryllium alloys and is a continuation-in-part of my prior applications Serial No. 172,871 filed on November 5, 1937, and Serial No. 226,290 filed on August 23, 1938.

It is well known that from the technological point of view a metallic alloy is the more appreciated the more its structure is homogeneous and the higher its physico-chemical characteristics such as hardness, mechanical tensile strength, elasticity, resistance to corrosion and the like are.

In the course of the last years various beryllium-nickel alloys have been proposed, but for none of them the necessity of insuring a practically homogeneous structure with the maximum of the above-mentioned physico-chemical characteristics on a commercial scale has been taken into account. Nor in the methods of thermal treatment which have also been proposed for these Ni-Be alloys has the great importance of a perfectly homogeneous structure been taken into account. It results therefrom that with the present alloys inconveniences are frequently encountered which are due to the unavoidable separations or to the heterogeneousnesses which are not absorbed in a perfect manner at the moment of the solidification of the alloy. The resulting solid solution shows interpositions between a grain and the other, namely small layers or small grains of a distinct constituent, and whatever may be made, either when the heating before quenching is protracted or when one attempts to increase the temperature of the said heating (a thing which is extremely dangerous), one does not succeed in causing the said heterogeneous interpositions between a grain and the other to disappear. The scission of the supersaturated solid solution will take place, according to the known principle of Le Châtelier, certainly preferably in the places where such localized heterogeneousnesses exist and the hardening constituent will form in excessive dimensions in these intergranular spaces. Thus, one will have a hardened alloy, but an alloy in which the individual grains are not well bound together; accordingly, the alloy even then when it shows some mechanical characteristic of interest will not meet the optimum characteristic conditions, nor will it show a practically homogeneous structure. Such a structure may be compared with a masonry structure containing blocks having a resistance attaining 1,000 kilogs. per square decimetre, but bound together by a mortar the resistance of which does not exceed 200 kilogs. per square decimeter. The individual blocks have a good resistance, but the whole is structurally weak.

Now, after long studies which have been made with respect to the better conditions of formation and scission of the fundamental solid solution of the Be-Ni alloys, I have succeeded not only in precising the phenomenon under a novel point of view, but also in discovering a novel and rational method for improving the physico-chemico-mechanical properties of the Be-Ni alloys.

It may be said first, in order to avoid any misunderstanding, that the exposed idea of homogeneous structure must not be considered in an absolute but in a practical manner. The homogeneity which is admitted as being the practical one is that which can be deducted from the largest microscopical enlargements for the time being (500 to 1000 diameters). It is said that an alloy is practically homogeneous when, seen under such enlargements, it does not show any structural heterogeneousness.

I have found that the phenomenon of melioration of the nickel-beryllium alloys must not be considered exclusively as being due to the re-precipitation of the hardening constituent but, already from the beginning, to a diffusion of the beryllium atoms into the elemental cell of the nickel and to the subsequent formation of elemental particles of the hardening constituent Ni-Be. The dimensions of these groups increase in such a manner that greater and greater stresses are exerted upon the reticle of the solid solution of nickel up to a limit which can not be exceeded without the expulsion of the said crystalline groups out of the rectile of the solid solution taking place, and it is in this manner that the re-precipitation takes place. In correspondence with the reality of the phenomena one has in the first phase an increase of the resistance to deformation and, parallelly to this, an increase of the electric resistance and in the second phase a concomitant diminution of the electric resistance and of the mechanical strength. I do not intend to give more details which would not be in their place here, but I shall add that, always guided by this analogy, I have admitted that the phenomenon of the badly bound hardening constituents is due to the fact that the reticular surface arrangement is much more altered than the internal arrangement, what amounts to admitting the presence of fine heterogeneous interpositions between the hardening constituents.

It is thus absolutely necessary, in order to obtain an efficient improvement of the alloy, to find a method which reduces the primary heterogeneousnesses between the hardening grains to minimum proportions and according to the present invention I have found for the first time that certain substances introduced into the nickel-beryllium alloys in comparatively small proportions, which should be never higher than predetermined maxima, have the property to of reducing the heterogeneousness of the interpositions between the hardening constituents by promoting at the moment of the solidification of the alloy their distribution and their solubilization in the granular mass in a perfect manner. It is well known, indeed, that the cohesion force between metals and their saturated solution is the higher the smaller the breaks of continuity between the crystals are, as results from the following equation:

$$\delta = \frac{RT\Delta r}{2N} \log \frac{Sw}{S}$$

where δ is the cohesion force, Δ the density and N the molecular weight of the solid body, S the normal solubility and Sw the solubility of the particles the radius of which is r.

As regards the substance which is introduced into the alloy as solubilizing and homogenizing substance, it is advisable not to lose sight of the fact that its specific action consists in annihilating or reducing in every way the surface deformations of the hardening constituents; the possibility for this action to appear is limited by the quantity of additional substance which is introduced into the alloy and which is always in small proportions. If the said quantity of introduced substance were increased above a certain maximum, the action would be altered in an essential manner; then hardening bodies are formed which are distinct from the Ni-Be constituents and which, on their side, show the same inconveniences which are due to fine heterogeneous interpositions. The method of improvement does not attain to its purpose and alloys are obtained which are always inferior to the ternary alloy which is described later on and which contains the third element in the reduced proportions.

For instance, if, according to the present invention, molybdenum is introduced as solubilizing and homogenizing substance into nickel-beryllium alloys, the ternary alloys Ni-Be-Mo for which the maximum physico-mechanical characteristics are obtained are those which are indicated by the hachured part A of the diagram shown in Figure 1 of the accompanying drawings and which relates to the Ni-Be-Mo system. It may be seen that the said alloys are those which for a beryllium content varying approximately from 1.4 to 1.7% contain molybdenum in a quantity varying from 0.3 to about 1%, the remainder being substantially all nickel.

This action indicated for molybdenum for beryllium alloys with a nickel basis has also been verified for the following substances which are diffusing, solubilizing and homogenizing substances, i. e. tungsten, tantalum, chromium and zirconium. The following are, only by way of example, the limit proportions between which it is advisable to introduce those different substances into the nickel-beryllium alloys generally containing from 1.4 to 1.7% of beryllium (the remainder being substantially all nickel), in order to obtain the characteristic results of the present invention.

Molybdenum	From 0.3 up to 1%
Tungsten	From traces up to 3%
Tantalum	From traces up to 2%
Chromium	From traces up to 5%
Zirconium	From 0.3 up to 1%

The so obtained alloys are subjected to a thermal treatment which preferably comprises heating to a temperature of 1000 to 1020° C. during 30 to 45 minutes followed by a rapid cooling, for instance in water, and then annealing at a temperature of about 485° C. to 500° C. during 6 to 15 hours to produce the re-precipitation of the hardening constituent diffused in the basic metal, i. e. the nickel, this complete treatment being repeated if desired.

The alloys according to the present invention afford a considerable technical progress in the manufacture of springs, needles and all other objects or articles which especially necessitate a maximum of elasticity even under very high mechanical stresses with a great hardness and also a greatly reduced oxidisability and a considerable facility for manufacture without any appreciable oxidation.

Alloys are especially obtained which possess a very high mechanical strength either as castings or as machined pieces. These alloys possess a very great hardness and a very low consumption through wear and can thus be used, among other things for ball or roller bearings, supports, springs as, for instance, laminated springs, and the like.

The alloys according to the present invention, for instance the Ni-Be-Mo, possess extremely high mechanical and electrical properties and take a good temper after heating at a temperature considerably lower than that required for the usual beryllium alloys, which has the advantage of lessening and practically removing the risk of approaching the fusion or disintegration temperature of the alloy. The solubilizing and homogenizing metal has the effect in this respect of lowering the temperature which is necessary for the intersolubilisation of the constituents of the alloy.

Berryllium alloys—as for instance nickel-beryllium alloys—have already been manufactured and used for the manufacture of springs, needles or other very fine objects, but it has not been possible, on account of the delicacy of these articles, to avoid the risk of causing "burning" of the alloy during the heating before quenching. In the same way nickel-beryllium alloys have been manufactured with the addition, in a high proportion, of another metal such as titanium, but the beryllium and titanium contents were very considerable and on account of this fact these alloys were very costly and very oxidisable and also brittle. Titanium, being in fact, in all the known alloys, used as a partial replacement of beryllium, is always in excess of the quantity which is necessary for the use here under consideration, and the excess of titanium has a prejudicial effect which is entirely different from the effect of the solubilizing metal used according to the invention.

One the contrary, the present invention allows of obtaining alloys which, while containing only comparatively very small proportions of beryllium and additional metal, display a hardness which is very superior to that shown by known alloys. Thus for example the alloys Ni-Be-Mo

have been shown to possess a Brinell hardness of nearly 500 with an annealing about 500° C. while the known alloys of Ni-Be show at most a Brinell hardness of about 400 with an annealing at 550° C.

Apart from the basis metal, beryllium and the solubilizing metal, these alloys may contain, in addition, various elements in a very small proportion; it is more particularly possible to add iron in a proportion which, in every case, is smaller than 4% in order to give the alloy a very high fluidity in casting. It is only in the case of conducting alloys that it is preferable to refrain from adding iron.

The alloys according to the invention, for instance the alloys Ni-Be-Mo, likewise display very greatly improved qualities and even more particularly for the conducting alloys a greatly improved electrical conductivity when they have been subjected to physical treatments such as those mentioned above, for example thermal treatments of quenching and annealing, which secure their perfect homogeneity.

In the accompanying drawings various diagrams corresponding to characteristics of alloys made according to the invention are given.

In these drawings:

Figure 2 is a diagram of the hardness curve of two Ni-Be-Mo alloys as a function of the temperature to which the alloys are heated before quenching.

Figures 3 and 4 are diagrams of hardness curves for each of the two alloys respectively, after quenching and annealing at the temperatures indicated on the curves, they illustrate thus the variation of the hardness with varying duration of annealing at specified temperatures.

Figure 5 is a diagram of curves showing the tensile strength (R) and elongation (A%) of an alloy according to the invention after quenching and annealing, at the temperatures specified on the curves, illustrating the variations of the tensile strength and elongation with varying duration of annealing at specified temperatures.

The mean curves for Brinell hardness shown in Figure 2 correspond to the two following allows:

Normal nickel-beryllium-molybdenum alloy (referred to in the diagram by the abbreviation "N. M.")

Be: between 1.4 and 1.6%.
Mo: between 0.3 and 0.5%.
Ni: the remainder.

Hard nickel-beryllium-molybdenum alloy (referred to in the diagram by the abbreviation "N. M. D.")

Be: between 1.4 and 1.7%.
Mo: between 0.3 and 0.5%.
Ni: the remainder.

The variations in Brinell hardness (ordinates) are presented as a function of the temperature of heating before quenching (abcissae). These alloys should be preferably heated to 1000° C.–1020° C. for 45 minutes, quenched with water, then annealed at 485° C. for about 10 hours, in order to obtain harder alloys, or for 15 hours in order likewise to obtain greater tenacity.

The mean curves of hardness in Figures 2 and 3 apply respectively to the two alloys above with nickel as base, referred to by the abbreviations "N. M. D." and "N. M.". These curves give the variations in the hardness after annealing for different temperatures, as a function of the duration of annealing shown in hours H (abscissae).

Figure 4 relates solely to the alloy "N. M.". The three curves in thin lines marked "A" illustrate the variations in percentage elongation A% for varying periods of annealing at the annealing temperatures marked on the curves. The five curves in heavy lines marked "R" show the variations in tensile strength R in hgs. per mm.^{2} with varying periods of annealing at the temperatures shown on the curves.

What I claim is:

1. A process for improving the physico-mechanical properties of alloys of beryllium with nickel consisting in introducing into nickel-beryllium alloys containing beryllium in the proportion of about 1.4 to 1.7%, as a metallic substance acting as a diffusing, solubilizing and homogenizing agent for beryllium, molybdenum in a proportion from 0.3 up to 1%, the balance being substantially all nickel, heating the alloys so constituted at a temperature of about 1000 to 1020° C., for 30 to 45 minutes, then cooling the same rapidly and subjecting them to an annealing treatment producing the reprecipitation of the hardening constituent diffused in the alloys.

2. A process for improving the physico-mechanical properties of alloys of beryllium with nickel consisting in introducing into nickel-beryllium alloys containing beryllium in the proportion of about 1.4 to 1.7%, as a metallic substance acting as a diffusing, solubilizing and homogenizing agent for beryllium, molybdenum in a proportion from 0.3 up to 1%, the balance being substantially all nickel, heating the alloys so constituted at a temperature of about 1000 to 1020° C., for 30 to 45 minutes, then cooling the same rapidly and subjecting them to an annealing treatment at a temperature of about 485 to 500° C. for six to fifteen hours.

3. A nickel-beryllium alloy containing beryllium in the proportion of about 1.4 to 1.7% and as a metallic substance acting as a diffusing, solubilizing and homogenizing agent for beryllium, molybdenum in a proportion from 0.3 up to 1%, the balance being substantially all nickel.

4. A nickel-beryllium alloy containing beryllium in the proportion of about 1.4 to 1.7% and as a metallic substance acting as a diffusing, solubilizing and homogenizing agent for beryllium, molybdenum in a proportion from about 0.3 up to 1%, the balance being substantially all nickel, the said alloy having been hardened by heating the alloy to a temperature of about 1000 to 1020° C., for 30 to 45 minutes, then cooling the same rapidly and subjecting it to an annealing treatment at a temperature of about 485 to 500° C. for six to fifteen hours.

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