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PROCESS OF TREATING MAGNETIZABLE MATERIAL.

1,358,810. Specification of Letters Patent. Patented Nov. 16, 1920.

No Drawing. Application filed April 4, 1919. Serial No. 287,593.

To all whom it may concern:

Be it known that I, TRYGVE D. YENSEN, a citizen of the United States, and a resident of Swissvale, in the county of Allegheny and State of Pennsylvania, have invented a new and useful Improvement in Processes of Treating Magnetizable Material, of which the following is a specification.

My invention relates to magnetizable materials in general and more particularly to iron and to magnetizable alloys of iron with silicon or aluminum, and of iron with silicon and aluminum, and it has, for its object, a method of improving the magnetic qualities, or properties, of alloys of such character.

As disclosed in my Patent No. 1,277,523, dated Sept. 3, 1918, I have found that the magnetic properties of iron and iron alloys are very much improved by reducing their contained impurities, especially carbon, below the amounts ordinarily found in the best grades of present commercial products. The process there set forth consists essentially in melting and treating the iron, or iron alloys, *in vacuo*, to substantially remove or eliminate, the impurities, originally present, particularly carbon. By practising the above-referred-to invention, I have obtained magnetizable materials that have magnetic permeabilities even five times higher and hysteresis losses only one fifth as high as those of the best materials previously known.

On account of the expense involved in practising the process just referred to, it became very desirable to find some other and cheaper method whereby the same results could be obtained.

I have now found that it is possible to purify alloys, such as I have referred to, in their solid state and to thus improve their magnetic qualities very materially. My present invention comprehends the treatment of magnetizable alloys, in solid state, in the form of sheets, rods, bars and the like, and essentially comprises subjecting the alloys to oxidizing conditions, at relatively high temperatures, followed by slow cooling, the process being performed at atmospheric or reduced pressures, as preferred.

For example, in practice, I have re-annealed such materials as 4% iron-silicon alloys, containing only small amounts of impurities, at 950° C. for one hour, in a current of air, with the pressure in the furnace reduced to about 2 millimeters of mercury and have then cooled them, to room temperature, at the rate of about 30° C. per hour, resulting in a doubling or tripling of the maximum permeability. The reduced pressure is not essential, as similar results have been obtained by annealing at atmospheric pressure.

Of course the higher the percentage of impurities present and the greater the cross-section of the pieces being treated, the longer the heat treatment must be continued. On the other hand, the higher the temperature employed, the more rapidly the diffusion of the impurities to the surface will take place and the shorter will be the time necessary for the treatment.

By practising my present invention on commercial 4% silicon steel, containing up to 0.1% carbon I have, for example, been able to obtain a product having a maximum permeability of over 40,000 and a hysteresis loss of less than 250 ergs per cubic centimeter per cycle for B=10,000. In comparison, test pieces from the same steel annealed at the same temperature under other conditions, such as in a vacuum, in a current of hydrogen, or a current of nitrogen, under a pressure of 2 millimeters of mercury, gave a maximum permeability of less than 10,000 and a hysteresis loss of more than 1,000 ergs. It is therefore, evident that the improvement is due to removal of some oxidizable impurity or impurities, the oxids of which are removable as a gas.

The carbon removed from the steel by practising my invention in the above instance corresponded to about 0.10% of the weight of the test pieces calculated from the amount of CO and CO_2 gases given off during the treatment. As this amount corresponded very closely to the original carbon content of the alloy, as determined by chemical analysis, it is believed that the improvements noted are chiefly occasioned by the removal of carbon.

As has been pointed out in my previously-referred-to patent, the carbon content of iron can be reduced to 0.01%, or lower, by subjecting the molten iron to the action of a vacuum in the presence of a small amount

of iron oxid. The reaction, in its simplest form

(1) $C+FeO=CO+Fe$.

takes place from left to right until equilibrium is established. The results obtained in iron-silicon alloys show that this reaction also takes place in the presence of silicon, in preference to the reaction

(2) $Si+2FeO=SiO_2+Fe$.

In the case of solid materials, at temperature above 900° C., both the carbon and silicon are in solid solution in the iron and, in the presence of oxids or oxygen, reaction (1) evidently takes place until the carbon content is very low, perhaps less than 0.01%, while the reaction (2) does not commence until the carbon is eliminated, or very nearly so. If the oxidization is carried beyond the point at which the carbon is eliminated, a decrease in permeability and an increase in hysteresis loss takes place.

While iron and iron alloys may be materially improved, as regards their magnetic qualities, by annealing them under oxidizing conditions, it is possible, as previously pointed out, to carry the oxidization to such extent as to, in part, counteract the advantages obtained. As it is difficult to regulate the duration of the treatment, the temperature to which the metal is annealed and the rate of flow of the oxidizing gas, if an oxidizing gas is used, so accurately as to obtain the best results, I prefer, in many cases, to carry the annealing, under oxidizing conditions, slightly to excess and to then subject the metal to reducing conditions to restore it to its desired state.

For example, in practising my invention, I may first treat the alloy of iron and silicon, or an equivalent alloy, under oxidizing conditions, in the manner previously described, to such extent that the impurities, especially carbon, the oxids of which are carried off as gases, are definitely known to have been decreased to the desired amount. This may be done even at the risk of oxidizing the material itself to some extent.

Following this step, the material may be subjected to a reducing condition in order to reduce the oxid or oxids that may have been formed on or in the material. For this purpose, any suitable reducing agent may be employed that will not re-introduce impurities into the material. For example, in practice, a current of hydrogen has been used to good effect.

In one instance, a sample of 4% iron-silicon alloy was annealed at 1100° C., under slightly oxidizing conditions, with the result that its maximum permeability was raised to 37,500. The sample was then re-annealed at 1100° C. under a more intense oxidizing condition that resulted, after slow cooling, in a decrease of the maximum permeability to 27,000. The same sample was then annealed at 1100° C., in a current of hydrogen, with the result that the permeability was increased to 32,000. A second treatment of hydrogen not only did not increase the permeability but actually decreased it to 23,300 showing that the hydrogen treatment should not be carried on indiscriminately.

It will, therefore, be seen that, by practising my invention, it is possible, if the annealing under oxidizing conditions and the subsequent annealing under reducing conditions are, neither of them, conducted too far, to obtain iron and iron alloys, such as iron-silicon alloys, having unusually high permeabilities and exceptionally low hysteresis losses.

The process embodied in my present invention is applicable to the material in all forms, such as rods, bars, sheets and the like, by regulating the elements of time, temperature and rate of flow of the oxidizing gas. This regulation is, however, very difficult if the material comprises large stacks of very thin sheets of the iron, or iron alloy, and, consequently, non-uniformity of the product is apt to result.

I have found that this difficulty may be overcome by treating the material, in the form of bars, to remove the impurities, particularly carbon, rolling the treated bars down into sheets of the desired thickness and then annealing the sheets to eliminate the effects of the mechanical treatment.

For example, I may take material in the form of sheet-bars, say six inches by twenty-four inches by one-half inch thickness, and treat it under oxidizing conditions to such extent that the impurities are reduced to a sufficiently low amount to give the material the improved magnetic qualities desired. If the time, temperature and the like required for the treatment have been determined by test runs, the usual slow cooling of the treated material may be omitted, at this point, and the sheet-bars may be removed from the furnace, freed from scale in any convenient manner, and rolled down to sheets of the desired thickness. The refined silicon steel, or other material, is much more ductile than before the treatment and may be more easily rolled at lower temperatures than would otherwise be required.

After the material has been rolled into sheets, the sheets must be annealed at a sufficiently high temperature—800 to 1100° C.—to eliminate the effect of the mechanical treatment, after which they are slowly cooled to ordinary temperature. This re-annealing must be carried on under such conditions that the material shall not be contaminated by either carbon or oxygen. This may be done by any suitable means, as the

provision of a neutral or slightly reducing atmosphere, or the initial annealing under oxidizing conditions may be discontinued shortly before all of the removable impurities have been eliminated, under which condition, the remaining impurities will be removed during the re-annealing and will thus keep the material from absorbing oxygen or carbon.

In place of the foregoing operations, I may initially anneal or heat the material, under oxidizing conditions, until it is slightly oxidized, roll it into sheets, re-anneal it, under reducing conditions, as in an atmosphere of hydrogen, and then cool it.

For example, a sample of commercial 4% silicon steel in the form of a three-eighths inch sheet-bar was annealed at 900° C., *in vacuo*, and slowly cooled. It then had a maximum permeability of about 5,000 and a hysteresis loss of about 1,950 ergs per cubic centimeter, per cycle. After annealing the sample in accordance with my present invention under oxidizing conditions, at 900° C. and at reduced pressure, until the carbon was substantially eliminated, and slowly cooling it, its maximum permeability was over 30,000 and its hysteresis loss was less than 600 ergs. The sheet-bar was then forged and rolled into thin sheets, varying from 14 to 125 mils, which were annealed *in vacuo*, at 900 to 1100° C., to counteract the effect of the rolling. The maximum permeability of these sheets was then found to be between 17,000 and 30,000 and the hysteresis loss was from 450 to 650 ergs. The same sheet-bar, if rolled directly down to sheets of the above thicknesses would, after annealing *in vacuo*, have a maximum permeability of only 5000 to 6000 and a hysteresis loss as great as 1,400 to 1,600 ergs.

From the foregoing description, it will be understood that my present invention essentially comprises heating the iron, or iron alloy, for a suitable length of time, at a temperature of 800 to 1100° C., under oxidizing conditions, either with or without reducing the pressure, and then slowly cooling it.

While the two steps of annealing and cooling are the essential features of my process, certain other operations may be performed before the final step of cooling, if desired. For example, if the annealing under oxidizing conditions has been carried so far as to slightly oxidize the alloy, the latter may be re-annealed, under reducing conditions, and then slowly cooled. Also, after the annealing under oxidizing conditions, or after the annealing under reducing conditions, if such annealing is employed, the material may be forged, rolled or the like, into sheets or other preferred form, again annealed to eliminate the effect of the mechanical treatment, and then slowly cooled. Furthermore, the annealing, under oxidizing conditions, may be shortened slightly so that slight impurities will remain to be removed by the final annealing, after the mechanical treatment, to keep the material from absorbing oxygen or carbon during such final annealing or the final annealing may be done in a neutral or slightly reducing atmosphere.

While I have described my process as comprising subjecting the material to oxidizing conditions, I wish it understood that the term includes the treatment of the material with some oxid, as iron oxid, such as annealing it surrounded by, and in contact with, the oxid, as well as in a current of some oxidizing gas.

The time required, at the various temperatures which may be employed in practising my invention, may be illustrated by the following examples. Samples, in the form of bars three-eighths of an inch thick, each weighing 1600 grams and formed of 4% silicon steel containing 0.1% carbon were employed. The several samples were annealed at 900°, 950°, 1000° and 1050° C., respectively, in a current of air of 120 cubic centimeters per minute and at a pressure of 2 millimeters of mercury. Under these conditions, to bring the maximum permeability of the samples above 30,000, it was necessary to anneal the sample at 1050° for thirteen hours, the sample at 1000° for twenty hours, that at 950° for one hundred hours and that at 900° for two hundred hours. It is, therefore, distinctly advantageous to employ the higher temperatures, even if doing so involves more furnace difficulties than arise with the lower temperatures. The amounts of carbon eliminated from the several samples were substantially the same.

As a matter of fact, the relationship between the maximum permeability—or hysteresis loss—and the carbon remaining is so constant that the amount of carbon removed may be utilized as an indicator of the progress made in the treatment of the material. Knowing the total carbon content of the steel to be treated, from previous chemical analysis, the curve between the time required and the carbon to be eliminated may be determined and the treatment may be continued accordingly until the carbon content has been reduced to the desired amount. For the best results this should be less than 0.01%.

Although I believe that the elimination of carbon during the annealing process is the chief factor in improving the magnetic qualities of the alloys, it is very probable that other impurities are also eliminated to a greater or less degree. However, as yet, I have no definite evidence to this effect but I do know that annealing iron, or iron alloys, under oxidizing conditions, for certain lengths of time and at the temperatures

specified, reduces the carbon content to perhaps less than 0.01% and remarkably improves the magnetic permeability and hysteresis loss.

The presence of even a few hundredths of a per cent. of carbon in silicon steel may produce 100% increase in the hysteresis loss over that of carbon-free alloy and I have found that even up to 0.05% carbon will remain even if the alloy is melted and kept under a pressure of 2 millimeters of mercury unless there is enough oxid present to oxidize the carbon, which is rarely the case with silicon steel.

I am aware that silicon steel has been annealed at temperatures between 1100 and 1325° C., preferably the latter, under a requisite low pressure, not to exceed 2.5 millimeters of mercury, or in a reducing atmosphere, to remove some of its impurities, particularly the oxygen, and to thus reduce its hysteresis loss as much as 30%. A patent to William E. Ruder, No. 1,110,010, dated Sept. 8, 1914, covers such a method and attributes its effectiveness to the reduction of oxids and to the fact that by it the normal grains of silicon steel are coalesced into a lesser number of larger grains.

I have taken the product resulting from the Ruder process with its 30% decreased hysteresis loss, treated it in accordance with my present invention, and thereby reduced its previously reduced hysteresis loss by 50% and even 75%.

This clearly indicates the distinction between the Ruder process, which is essentially one of reduction, and my process which is primarily one of oxidization. As even melting a silicon steel *in vacuo* will leave in it a residue of as much as 0.05% carbon, it appears that the Ruder process would leave at least that much carbon present and I ascribe the marked decrease in hysteresis loss, achieved by my process, as occasioned by the elimination of all, or nearly all, of this carbon.

In other words, by my process, which is essentially one of oxidization, I remove a remarkable proportion of the carbon. Because of the difficulty of accurate analysis, the ultimate limit of carbon removal by my process is not definitely known but I believe that, by prolonged treatment, it may be reduced to as low as 0.001%. However, analysis of the CO_2 gas given off from the furnace during the treatment would indicate that the marked improvement in the magnetic qualities of 4% silicon steel takes place over the decrease from 0.03% to 0.01% of carbon.

As I have not only described the essential features of my invention but have also set forth a number of added operations, which may be performed at the will of any one practising my invention, or to suit various conditions and requirements, no restrictions are to be imposed upon my invention other than such as may be necessitated by the prior art or as are specified in the appended claims.

I claim as my invention:

1. The method of improving the magnetic qualities of a magnetizable metallic material which comprises heating the material at a relatively high temperature, but short of fusion, under oxidizing conditions and then slowly cooling it.

2. The method of improving the magnetic qualities of a magnetizable metallic material which comprises heating the material at relatively high temperature, but short of fusion, to remove certain impurities, particularly carbon and then cooling it.

3. The method of improving the magnetic qualities of a magnetizable metallic material which comprises heating the material at a temperature between 800 and 1100° C. to remove substantially all of the carbon and then cooling it.

4. The method of improving the magnetic qualities of a magnetizable metallic material which comprises heating the material under slightly oxidizing conditions until substantially all the carbon has been removed and then cooling it at the rate of substantially 30° C. per hour.

5. The method of improving the magnetic qualities of magnetizable alloys such as alloys of iron with silicon, or aluminum, or both which comprises heating the alloy at relatively high temperature, but short of fusion, under oxidizing conditions until substantially all carbon present has been eliminated and then slowly cooling it.

6. The method of improving magnetic qualities of a magnetizable iron alloy which comprises heating the alloy at a relatively high temperature, but short of fusion, under oxidizing conditions, further heating the alloy at a relatively high temperature, but short of fusion, under slightly reducing conditions and then slowly cooling it.

7. The method of improving the magnetic qualities of a magnetizable alloy which comprises heating the alloy at a temperature between 800 and 1100° C. and under slightly oxidizing conditions until all or substantially all of the carbon has been eliminated, further heating the alloy under slightly reducing conditions and then slowly cooling the alloy.

8. The method of treating magnetizable alloys which comprises heating the alloy under oxidizing conditions until all or substantially all of the carbon has been eliminated, forging the alloy to the desired form, annealing the alloy and then slowly cooling the alloy.

9. The method of treating a magnetizable iron alloy which comprises heating the alloy

under oxidizing conditions to remove substantially all of its contained carbon, heating the alloy under slightly reducing conditions, to remove any oxids formed by the previous heating, mechanically treating the alloy to suitably form it, annealing the formed alloy to counteract the effects of the mechanical treatment and slowly cooling the annealed alloy.

10. The method of treating a magnetic alloy which comprises heating the alloy under oxidizing conditions to remove substantially all of its carbon content, forging and rolling the alloy to sheet form, annealing the alloy to eliminate the effect of the mechanical treatment, the annealing being done under conditions preventing absorption of carbon and oxygen and slowly cooling the annealed alloy.

In testimony whereof, I have hereunto subscribed my name this 25th day of March, 1919.

TRYGVE D. YENSEN.