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SELECTIVE GRAIN GROWTH OF SILICON STEEL

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This invention relates to a process of effecting selective grain growth in silicon steel and to the products of such process.

It is an object of this invention to provide a method for the selective control of grain growth in silicon steel.

It is another object of this invention to provide a method of selectively controlling the grain growth of silicon steel to produce any desired pattern or design therein.

It has been found that the above objects may be accomplished by the formation of impurities in certain parts of the material which inhibit normal grain growth.

More particularly it has been found that grain growth in silicon steel may be selectively controlled by masking that part of the material in which normal growth of grains is desired with a protective coating such as an electroplated coating of copper, subjecting the material to a carburizing or nitriding treatment which forms normal grain growth inhibiting impurities in that part of the material not protected by the coating, removing the protective coating or mask, and heat treating the article at a temperature of about 950° C. to 1150° C., such heat treatment or anneal effecting the growth of large grains in the formerly protected or uninhibited portion of the article. This process may be used to produce visual differences in a single piece of material, such differences or contrasts being in the metal itself and brought about by the presence of clearly defined areas comprising large grains and other areas containing only small grains. Such a contrast may be used in creating new and pleasing decorative effects in jewelry, signs, nameplates and similar articles. The process also makes possible the production of material for technical uses in which advantage is taken of its controlled heterogeneous character. For example, an air gap effect may be realized in a single, integral, structurally strong piece of material by developing therein two regions of large grains having excellent magnetic characteristics separated by a finite and precise region of small grains having very poor magnetic qualities.

While any steel which lends itself to grain growth may be employed, the preferred starting material is 3%–4% silicon steel which has been cold rolled with or without intermediate heat treatment to the final thickness. Since the difference in size of grains in selected areas depends upon the introduction of certain impurities or inhibitors before final heat treatment into all parts of the material except those areas in which large grains are desired, the latter areas must be pro-

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tected or masked during such inhibiting treatment. This protective coating or mask may take the form of metal electroplate, cement, paint or any other material which will withstand the inhibiting treatment.

For the purpose of this invention a copper electroplate at least 0.5 mil thick has been found to be very satisfactory and easily applied. For example, a copper coating may first be applied to the entire piece employing a suitable plating bath after which the design or pattern desired is laid out on the plated surface. The copper is then removed from all areas except the design by any suitable method. For example the copper to be removed can be converted to copper sulfide and the sulfide removed in a cyanide bath, the design areas being protected from copper removal by paint or other resistant material. A solution of 4 ounces of liver of sulfur to each liter of water can be used to convert a 0.5 mil thick copper plate to the sulfide in about 5 minutes at room temperature. A further treatment at room temperature in a solution containing about 4 ounces of sodium cyanide per liter of water removes the copper sulfide in about 5 minutes. It will be understood, of course, that the concentrations of the above solutions may be varied if different times of reaction are desired. After the copper plate has been removed from the desired areas, the protective or masking coating is removed by mechanical or solvent means.

If desired the copper plate may initially be applied only to certain areas of the steel by covering the remaining areas with a wax or other suitable material which will prevent deposition of copper during the plating process. The protective material may then be removed as by use of a solvent before subjecting the steel to the inhibiting treatment.

The inhibiting treatment or process, which forms grain-growth retarding impurities in all areas except those covered by the copper plate, may be accomplished by carburizing, or nitriding the unprotected areas at temperatures below that at which large grains start to grow. The inhibiting material in the case of the carburizing process probably is essentially iron carbide formed by the introduction of carbon which combines chemically with the iron. In the nitriding process the steel should contain small quantities of aluminum or chromium, for example, about 0.05% as impurities in which case the inhibitor is either aluminum nitride or chromium nitride or both formed by combination of these metals with the added nitrogen.

Any method of carburizing may be used, for example, the pack, gas, or salt bath processes. If desired, carburizing stop-off paints or other masking material known in the carburizing art may be employed in lieu of the copper plate used herein. A combination of carburizing and nitriding may also be employed, such as is accomplished by the known salt bath cyaniding or gas carbo-nitriding treatments.

While the final anneal or grain growth heat treatment may be carried out in air, it is preferably carried out in a non-oxidizing atmosphere such as pure dry hydrogen, a neutral atmosphere such as argon, or in a vacuum, in order to obviate any possible oxidation or other undesired chemical reaction in or on the surface of the steel. A temperature from about 950° C. to about 1150° C. affords the desired grain growth in the uninhibited areas, the higher temperatures giving a more rapid development. The process may be stopped at any point after the desired grain growth has been obtained, and the strip etched with a suitable macroetching solution to bring out a visible contrast in grain size if such is desired.

The following is given as a specific example of the application of the preferred process of the present invention in depicting on a piece of silicon steel strip .01 inch thick the figure "0." The piece is first plated with copper to a thickness of at least 0.5 mil. This is accomplished in about 30 minutes at room temperature with a current density of 0.1 ampere per square inch using a plating bath of the following composition:

Copper cyanide ....pounds..	0.25
Sodium cyanide ....do....	3.7
Sodium carbonate ....do....	1.7
Sodium thiosulfate ....grains..	5
Water ....liters..	5

The figure "0" is next painted in the desired position on the strip with an acid resistant paint. When the paint is dry, the copper plate is removed from all parts of the piece except the painted-over design by immersing the piece in a solution of four ounces of liver of sulfur per liter of water for about 10 minutes at room temperature which converts the copper to the sulfide. This is followed by an immersion for about 5 minutes in a water solution of about 4 ounces of sodium cyanide at room temperature which removes the copper sulfide. The acid resistant paint which protects the copper plate design during the copper removal process is removed with any suitable solvent.

The resultant product having a copper "0" on the surface thereof is immersed in a salt bath containing the following ingredients, which, when operating at from 1500° F. to 1600° F., will carburize .01" thick strip sufficiently in 10 minutes:

	Per cent
NaCN	42.0
NaCNO	0.3
$BaCO_3$	30.0
$BaCl_2$	8.7
NaCl	19.0

After the introduction of normal grain growth inhibiting iron carbide into all parts of the strip except that covered by the copper mask design, the copper mask plate is removed as above described, to expose the uninhibited pattern, and the piece subjected to a heat treatment in a non-oxidizing atmosphere and preferably in pure dry hydrogen at from 950° C. to 1150° C. As the grains in the design areas grow normally under such heat treatment while the inhibited grains do not, there results a differential in size of grains as between the figure "0" design area with its large grains and other areas, the growth process being stopped at any stage simply by removing the piece from the high temperature. The piece is then macro-etched with a nitric acid solution to make the contrast grain size visible. The process may also be reversed, causing the figure "0" to be fine-grained in a large grain matrix.

It has been found that thin strip, about 0.01 inch and under, need have the design masked on one side only provided the other side is fully masked since the inhibiting process will penetrate thru to the opposite side. With thicker sheets of metal it is advisable to mask the design area on both faces to insure penetration of the inhibiting effect. However, if the design is to be superficial and on one side only it need usually be masked on only one side.

Material of any convenient thickness may be treated by the present process although with thicker sheets the inhibiting process may tend to undercut the masked area and render an indistinct or less sharp border line between inhibited and uninhibited areas. Using a carburizing salt bath of the above composition the following approximate case depths may be obtained either on one or both sides of the plate.

	1500° F.	1550° F.	1600° F.
	Inches	*Inches*	*Inches*
¼ hour	0.003	0.005	0.006
1 hour	0.010	0.014	0.016
4 hours	0.025	0.030	0.034

If thicker case depths are desired resort may be had to gas or pack carburizing.

A typical nitriding salt bath which may be used in the present process has the following composition:

	Per cent
KCN	64.0
NaCN	34.0
K_2CO_3	1.4
NaCNO	0.2
KCNO	0.3
Na_2O	0.1

Inasmuch as nitriding generally has a less effective depth than carburizing, the latter method is recommended when it is desired to have the grain growth inhibition penetrate to a depth of more than 0.01 inch.

As pointed out above, silicon steel treated as set forth herein is susceptible of both decorative and technical uses. The contrast in grain size which is made visible thru macroetching may be used to give a pleasing and novel effect in jewelry, signs, nameplates and the like by growing the desired design in a single piece of material instead of having to make up the design by using separate contrasting parts. From the technical aspect, since the large grains may be developed to have a preferred crystal orientation, and therefore, magnetic characteristics superior to those of the small grains whose growth was inhibited, there may be obtained in an integral single piece of material regions of varying magnetic qualities. Thus an effect equivalent to an air gap can be realized by separating two areas of large selectively grown grains with extremely good magnetic characteristics by a region of controlled size consisting of small grains with very poor magnetic characteristics. The product is an integral article, is stronger than one fabricated from separate pieces.

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

1. The process of producing large grains in any desired area of a cold rolled steel sheet containing about 3%–4% silicon which comprises inhibiting all other areas against normal grain growth by carburizing followed by a heat treatment at about 950° to 1150° C. to produce the growth of large grains in the uninhibited area.

2. The process of producing large grains in any desired area of a cold rolled steel sheet containing about 3% to 4% silicon and about .05% aluminum which comprises inhibiting all other areas by nitriding followed by a heat treatment at about 950° C. to 1150° C. to produce the growth of large grains in the uninhibited area.

3. The process of producing large grains in any desired area of a cold rolled steel sheet containing about 3% to 4% silicon and about .05% chromium which comprises inhibiting all other areas by nitriding followed by a heat treatment at about 950° C. to 1150° C. to produce the growth of large grains in the uninhibited area.

4. The process of producing large grains in any desired area of a cold rolled steel sheet containing about 3% to 4% silicon and about .05% aluminum and chromium which comprises inhibiting all other areas by nitriding followed by a heat treatment at about 950° C. to 1150° C. to produce the growth of large grains in the uninhibited area.

5. The process of producing large grain growth in any desired area of a cold rolled silicon steel sheet which comprises inhibiting all other areas against normal grain growth by the introduction of an element selected from the class consisting of carbon and nitrogen followed by a heat treatment to produce large grains in the uninhibited areas.

6. The process of producing large grain growth in any desired area of cold rolled silicon steel which comprises copper plating the area of desired large grain growth, carburizing the material to inhibit normal grain growth in all areas except that protected by the copper followed by removal of the copper and heat treatment to produce large grains in the uninhibited area.

7. The process of producing large grain growth in any desired area of cold rolled silicon steel which comprises copper plating the area of desired large grain growth, nitriding the material to inhibit normal grain growth in all areas except that protected by the copper followed by removal of the copper and heat treatment to produce large grains in the uninhibited area.

8. The process of producing large grains in any desired area of cold rolled silicon steel strip which comprises masking the area of desired large grain growth, carburizing the material to inhibit normal grain growth in all areas except that masked followed by removal of the masking and heat treatment to produce large grains in the uninhibited area.

9. The process of producing large grains in any desired area of cold rolled silicon steel sheet which comprises masking the area of desired large grain growth, nitriding the material to inhibit normal grain growth in all areas except that masked followed by removal of the masking and heat treatment to produce large grains in the uninhibited area.

10. A cold rolled and heat treated silicon steel sheet containing 3 to 4% silicon characterized by a surface comprising selected areas of grains which are generally smaller than the grains of the remaining areas of said sheet, the said selected areas having a higher content of an element selected from the class consisting of carbon and nitrogen than the remaining areas of said sheet.

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