Nov. 13, 1956 E. M. HERZOG 2,770,563

LOW ALLOY STEEL TUBING

Filed June 10, 1953 3 Sheets-Sheet 1

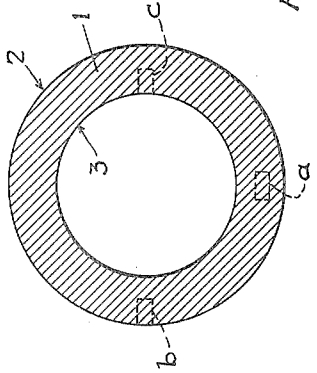


Fig. 1.

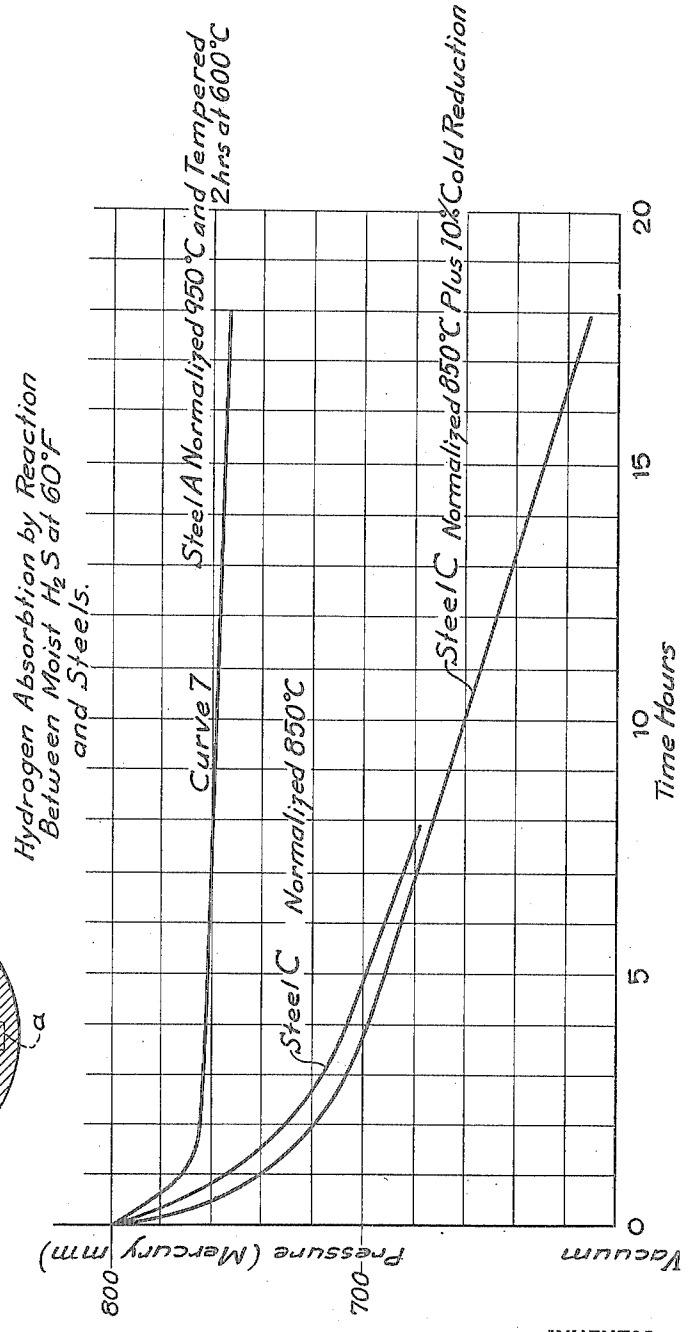


Fig. 6.

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LOW ALLOY STEEL TUBING

Filed June 10, 1953 3 Sheets-Sheet 2

Fig. 2.

Steel A Normalized 950°C-Tempered 600°C X 500 Mag.

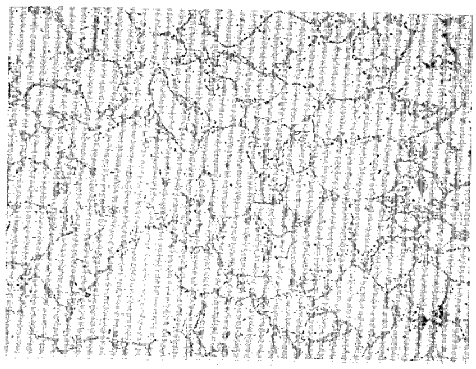


Fig. 3.

Steel A Normalized 950°C X 500 Mag

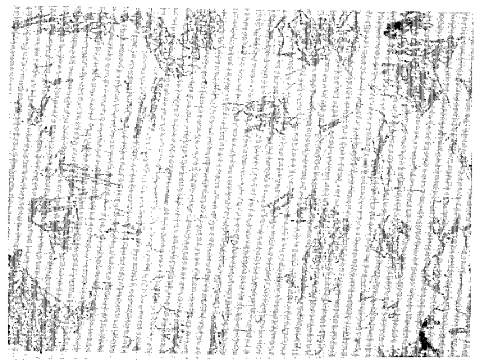
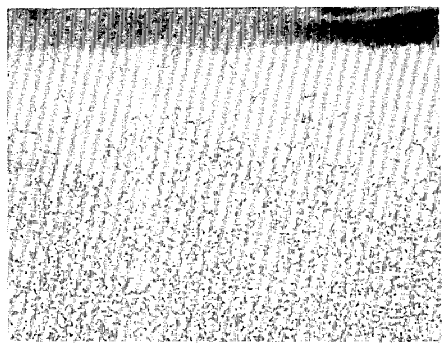


Fig. 4.

Steel A Heat Treat Same as Fig. 2 Surface Decarburized X 100 Mag.



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Filed June 10, 1953 3 Sheets-Sheet 3

Fig. 5.

Steel C	Cr	Mo	Ae	Va	Mn	Si
A—0.095	2.10	0.30	0.40	0.09	0.40	0.25
B—0.12	1.08	—	0.30	—	1.05	0.28
C—0.35	—	0.20	—	—	1.40	0.20

Steel A—Normalized 950°C
Tempered 600°C
Y. P. — 71,000 Psi
U. S. — 89,500
Elong. — 21%

Steel B—Quenched 925°C in water
Tempered 1hr. at 600°C
Y. P. — 90,000 Psi
U. S. — 102,000 Psi, Elongation 12%

Steel C—Normalized 850°C
Y. P. — 81,000 Psi
U. S. — 118,000 Psi Elongation 18%

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LOW ALLOY STEEL TUBING

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Application June 10, 1953, Serial No. 360,677

Claims priority, application France March 7, 1953

7 Claims. (Cl. 148—31)

This invention pertains to improvements in steels particularly adapted for tubing employed in deep oil wells and also in oil refineries, and provides a low alloy steel and tubing thereof of novel analysis and microstructure and superior properties for such applications.

Steel tubings for the above applications are usually rolled from steels having a high tensile strength in order to withstand the high stresses encountered in columns of tubing built up in oil wells, whose depth may range as high as 2000 feet or more.

Under certain corrosive and stress conditions, such tubing is liable to fail suddenly by cracking, for example, when the escaping gases are high in hydrogen sulfide, the proportions of which may range up ot 10%, 20%, or 30% H_2S in the well gases. As is known from recent research investigations, quenched and tempered steels for such applications, having a fully or partially tempered martensitic structure, are prone to stress-cracking corrosion, since the amount of stress to which the tubing is subjected in such applications, often equals or approaches the yield point of the steel. In a number of instances, sudden ruptures of such tubing have occurred when atomic hydrogen was absorbed by the steel, this atomic hydrogen being generated by contact between the iron and moist hydrogen sulfide of the well gases, according to the reaction:

$$Fe+H_2S \rightarrow FeS+2H$$

This atomic hydrogen transforms into molecular hydrogen H_2 preferentially along the grain boundaries of the steel and on internal porosities or segregations thereof. This process is accelerated by straining and stressing of the steel, as a result of which the molecular hydrogen accumulates under high pressure in the regions aforesaid. High tensile stresses in such hydrogen-saturated steel, open up microcracks along the grain boundaries, which thereupon spread out at a slower rate ultimately into large trans- or inter-granular cracks or fissures, according to the conditions and quantities of the escaping gases.

A primary object of the present invention is to provide a steel and tubing thereof, for oil wells and the oil refinery industry, which is resistant to attack by humid hydrogen sulfide gases and also to aqueous solutions thereof.

The steel of the invention comprises, as stated, a low alloy steel containing, as essential constituents, in addition to carbon, small amounts of manganese, chromium, silicon, and aluminum, and preferably contains small amounts of molybdenum, and which may also contain small amounts of one or more of vanadium, nickel and titanium.

The broad range of analysis of steel according to the invention is:

	Percent by weight
Carbon	0.08–0.20.
Manganese	0.3–1.20.
Chromium	0.6–5.0.
Silicon	0.1–0.5.
Aluminum	0.15–0.6.
Molybdenum	0–0.5.
Vanadium	0–0.5, preferably 0.05–0.15.
Nickel	0–1.0, preferably 0–0.4.
Titanium	0–0.2, preferably 0.02–0.05.

The balance of the steel is iron except for residual elements and metalloids within usual commercial tolerances. For example, copper should be under 0.25%, sulfur under 0.04%, phosphorus under 0.04%, nitrogen under 0.025% and oxygen under 0.015%.

Within the aforesaid broad range of analysis of steel according to the invention, two types or grades having the properties set forth below are obtained within the following ranges of analyses, respectively, these grades being designated herein as steels "A" and "B."

Steel A

	Percent by weight
Carbon	0.08–0.15, preferred 0.10.
Manganese	0.30–0.80, preferred 0.40.
Chromium	1.00–5.00, preferred 2.50.
Silicon	0.10–0.50, preferred 0.20.
Aluminum	0.15–0.60, preferred 0.3–0.4.
Molybdenum	0.10–0.50, preferred 0.30.
Vanadium	0–0.25, preferred 0.09.
Balance	Iron.

Steel B

Carbon	0.08–0.20, preferred 0.12.
Manganese	0.60–1.20, preferred 1.00.
Chromium	0.60–1.20, preferred 1.00.
Silicon	0.10–0.50, preferred 0.30.
Aluminum	0.15–0.60, preferred 0.3–0.4.
With or without molybdenum.	0.10–0.40, preferred 0.20.
Vanadium	0–0.15, preferred 0.09.
Balance	Iron.

Additions of one or more of vanadium, nickel and titanium to the steel of the invention, increase the tensile strength thereof. Vanadium is moreover additionally beneficial in improving forging or rolling properties, inasmuch as vanadium reduces hot brittleness at high temperatures. The vanadium can be substituted for molybdenum, in the ratio of one part by weight of vanadium to two parts of molybdenum.

The presence of aluminum in the steel is required in order to assure the desired microstructure, as described below, whereas the other alloying metals, i. e., chromium, manganese and molybdenum, strengthen the matrix of ferrite by formation of complex carbides with iron carbide.

The steel of the invention may be hot rolled from bars and thereafter cold rolled, but the cold rolling reduction should not exceed about 10% reduction in thickness. Seamless tubing of the steel is obtained by hot piercing and drawing as conventionally practiced. The finished seamless tubes are then heat treated as follows. The first heat treatment comprising a normalizing operation consisting of a soak at about 950° C. for about one-half hour followed by air cooling. The second treatment comprises a tempering operation for about two hours at about 600° C. to 700° C. followed by air cooling. This same heat treatment is preferably applied to the steel for other applications in which it is first hot rolled and thereupon cold rolled as aforesaid.

The steel has in the "as annealed" condition, a 0.2% offset yield strength of at least 64,000 p. s. i. and an ultimate strength of at least 78,000 p. s. i. When normalized and tempered as aforesaid, the microstructure comprises a low alloyed ferrite, non-saturated with carbon at room temperature, and containing complex carbides in a fine state of subdivision, i. e., having a particle size of about 1 micron, highly dispersed both along the grain boundaries and in the ferritic matrix. These carbides are practically insoluble in the ferrite, and dissolve but slowly, or not at all, on heat treating up to the lower transformation temperature of about 780–820° C. of the steel.

I have discovered that tubing made of steel having this microstructure is not sensitive to hydrogen embrittlement nor to inter-granular stress and corrosion cracking when subjected to stress straining and corrosive conditions as above described.

I have further discovered that all microstructures of steel which are not in equilibrium, are sensitive to hydrogen embrittlement and to inter-granular stress corrosion cracking. Not only is this so with respect to martensite, but also as regards superior or inferior bainite, residual austenite enriched in carbon, and carbon super-saturated ferrite.

I have further observed that low carbon steels, either rimmed or killed, are not liable to stress corrosion cracking in H_2S while in the annealed, normalized or otherwise softened conditions. Such steels, however, do not have the required tensile properties as compared to steel according to the present invention, which, heat treated as aforesaid, has a ferritic matrix strengthened by finely dispersed complex carbides, thus to provide the requisite tensile strength.

If necessary, the surface portions of tubing made of steel according to the invention, can be decarburized to a depth of about 0.1–0.4 mm., or about 0.004–0.016", the remaining or internal portions of the tubing having the normal content of the steel, as given above. With the low carbon content of the decarburized surface portions, i. e., under about 0.02%, local corrosion cells between carbides and the iron do not occur, so that the corrosion takes place over the entire surface and not in localized areas, which latter attack results in weakened portions susceptible to pitting or to irregular distribution of the attack.

In the absence of the aluminum in the steel of the foregoing analysis, the resulting microstructure is not in equilibrium, so that such steel, when aluminum-free, is subject to stress corrosion cracking, and even when improved by tempering at about 700° C., i. e., is heat treated to provide stable structures, the steel is still prone to cracking when slightly strained, as by cold working.

As above noted, carbon can be substantially eliminated from the surface portions of the steel by heating in a slightly oxidizing atmosphere. The presence of the aluminum in the steel accelerates the rate of such decarburization, i. e., diffusion of the carbides toward the surface portions which are poor in carbon.

Referring now to the accompanying drawings for further elucidation of the superior properties of steel according to the invention in relation to a known type heretofore commonly employed for oil well tubing:

Fig. 1 is a transverse section through tubing made of steel A according to the invention.

Fig. 2 shows, at a magnification of 500, the microstructure of the steel in the region *a* of Fig. 1, after normalizing and tempering as aforesaid to give the desired microstructure; while

Fig. 3 shows, at the same magnification, the microstructure of the same steel in the "as rolled" condition, which latter microstructure is less stable than that of Fig. 1 and hence not so desirable.

Fig. 4 shows, at a magnification of 100, the microstructure of the steel in the heat treated condition of Fig. 2, and in the region of the superficial layers *b*—*c*, Fig. 1, of the tubing, the tubing having been subjected to surface decarburization.

Fig. 5 illustrates graphically, the stress-strain diagrams resulting from tensile tests, on steels A and B according to the invention, as compared to that of steel C, the latter of a conventional type heretofore employed for oil well tubing. The analyses of these various steels are given on the diagram as are their heat treatments and resulting tensile properties.

Fig. 6 illustrates graphically the relative rates of absorption of hydrogen, from moisture saturated hydrogen sulfide, of steel A according to the invention as compared

to that of the prior art steel C, having the analyses and heat treatments, respectively, given in Fig. 5. In Fig. 6, the rate of absorption is plotted as ordinates against time of exposure to the saturated H_2S, plotted as abscissae. The upper graph for steel C represents the steel in the heat treated condition resulting from normalizing at 850° C. followed by tempering for two hours at 600° C., while the lower graph shows the same steel after a subsequent cold reduction of about 10%.

Figure 2 shows the desired microstructure of the steel for oil well or refinery tubing, obtained as stated, by normalizing at about 950° C., followed by tempering for about two hours at about 600–700° C. Figure 3, on the other hand, shows the microstructure to be avoided, as not so reliable, and even dangerous when stresses above the yield strength are encountered, this microstructure resulting from simply normalizing the steel at about 950° C. followed by air cooling. This represents substantially the "as rolled" condition.

The microstructure of the steel in the Figure 2 condition is shown to comprise only ferrite grains and finely dispersed carbides of about 1–5 microns particle size, dispersed more or less uniformly throughout and about the ferrite grains. By way of contrast, the microstructure of the steel in the Figure 3 condition is shown to comprise the more conventional pearlitic structure consisting of pearlitic aggregates situated between grain boundaries and residual non-decomposed austenite, enriched with carbon resulting from ferrite ejection on cooling from the AC3 point. This microsstructure is that ordinarily obtained as a result of seamless tube rolling.

Referring to Figure 4, it will be seen that the surface of the tubing which has been decarburized to a depth of 0.1–0.4 mm., shows at 100 magnification, an outer layer of substantially pure ferrite.

Referring now to the stress-strain graphs of Figure 5, it will be seen that for the steel A according to the invention, there occurs at the yield point E a "jog" or sharp break at the terminus of the straight line or reversible part of the curve, following which plastic flow occurs as indicated by the second part of the curve. The slopes between these two portions of the stress-strain diagram are quite different, which is to be considered as proof that the steel has been properly heat treated and also as establishing a criterion of high resistance to stress corrosion cracking for this type A steel.

On the other hand, in the graph for steel B, the first or elastic part is, as usual, a straight line, of substantially the same slope as that for steel A, following which there occurs a yielding area, parallel to the strain or axis, constituting a wide "jog," amounting up to about 2% of permanent strain, such as ordinarily occurs in softened mild steels. This is a criterion of the correct heat treatment for steels of type B, which are poorer in chromium and molybdenum as compared to steel A. Plastic flow is recorded for the third or remaining part of the stress-strain diagram for the steel B.

By way of comparison with the diagrams for steels A and B according to the invention, the dotted graph for steel C is that of a conventional type of steel heretofore employed for such tubing, namely, N80 grade steel in current use for tubes for deep wells, but prone to stress corrosion cracking in the presence of hydrogen sulfide. This steel, having an analysis of 0.35% C, 1.4% Mn, and 0.2% Mo, shows, after a normalizing treatment at 850° C., no sharp break at the end of the elastic portion of the stress-strain curve, nor two different slopes between the linear or elastic and the more curved or plastic flow portions of the graph. To the contrary, the graph merges gradually and continuously from the elastic portion into the definitely plastic flow portion. After tempering, a break or "jog" can be shown to exist in the stress-strain diagram for this steel, but the steel is not resistant to stress corrosion in hydrogen sulfide, and is ordinarily inferior to the steels A and B of the invention.

Steels A and B when fully quenched or air hardened, and without subsequent tempering, have stress-strain diagrams like that of steel C, and are thus prone to cracking, but even in this condition, their life is considerably longer than that of the conventional N80 grade. Such tensile tests are useful in checking the tubes in order to ascertain whether or not the heat treatments are correct, and as a criterion for the necessity of further checking by microstructure examination.

A third criterion of the improved properties of steel according to the invention as compared to steels conventionally employed for oil well tubing, such as N80, is the rate of hydrogen absorption by the steel when exposed to a moist atmosphere of hydrogen sulfide. This is illustrated by the graphs in Figure 6. In the graphs therein depicted, the relative hydrogen absorption is plotted as ordinates against time of exposure to the saturated H_2S, plotted in hours as abscissae. The steel A graph was for such exposure to a steel according to the invention of the analysis given in Figure 5, after normalizing at 950° C. and tempering two hours at 600° C. The graphs for steel C are for the N80 grade aforesaid, the upper graph being for the steel as normalized at 850° C. and tempered for two hours at 600° C., and the lower graph for the same steel after cold reducing about 10%.

In carrying out the tests plotted in this figure, a specimen of the steel was placed in a closed container, which was first evacuated and then connected to a supply of moist hydrogen sulfide gas at constant pressure of 800 mm. mercury. During the test the H_2S supply was shut off and the container connected through an appropriate valve directly to a monometer, thus to record any change in pressure resulting from the absorption by the steel of the hydrogen sulfide.

As shown by Figure 6, for all of the steels there was a relatively rapid initial reduction in pressure indicative of H_2S absorption, following which the graph for steel A flattens out almost to the horizontal, showing no further appreciable absorption. For steel C, however, whether in the quenched and tempered or in the quenched, tempered and cold rolled condition, the absorption increases progressively with time until at the end of about eighteen hours, the absorption of steel C was approximately five times that of steel A.

After cold working, steels A and B, have in common with other steels, continuous stress-strain diagrams.

Tensile tests on steel A gave the following results: The 0.2% offset yield strength ranged from 68,000 to 98,000 p. s. i., as normalized or quenched at 950° C., and thereafter tempered for two hours at 650° C. The corresponding ultimate strength ranged from 98,000 to 110,000 p. s. i. For steel B, the 0.2% offset yield strength was from 79,500 to 85,000 p. s. i., as quenched in water from 925° C. and thereafter tempered for two hours at 600° C. The corresponding ultimate strength was from 99,000 to 106,500, respectively.

Tubes rolled from bars of steel A, heat treated as above and cold reduced up to 10% in thickness, showed no cracking when stressed to the yield point in atmosphere of moist H_2S for a period of 2800 hours, this test being carried out at 15°–20° C. In oil wells high pressures are usual, so that an effort was made to reproduce actual oil well conditions, favorable for absorption of hydrogen, as the concentration C for dissolution of a gas in a metal obeys Seivert's law, $C=\sqrt{PH_2}$, where P is the pressure of the hydrogen sulfide gas. Hydrogen absorption is expected to be higher at higher pressures than at atmospheric pressures.

Other tests run in mixtures of 50% H_2S, 30% CO_2 and 20% H_2O at 80° C. and 120 atmospheres pressure, likewise showed no cracking of steels A and B heat treated as above specified. In the as quenched or air hardened condition, ruptures occurred, however, after 15 to 500 hours of testing. On the other hand, the normalized N80 grade steel, broke within several hours of such testing.

High pressure tests were also performed in a sealed bomb, machined from steel A, heat treated and hot enameled in order that the corrosive gases from the vessel could attack only the specimens placed therein, and not the interior surfaces of the vessel. For producing the high pressure in the bomb there was introduced therein a mixture comprising ice, solid carbonic acid, and liquified hydrogen sulfide, the latter at —100° C. The vessel was then sealed and closed and slowly reheated first to room temperature and then in an oil bath to 80° C. A pressure gauge tapped to the vessel measured the pressure. The pressure thus obtained increased to 1700 lbs. per square inch without injury to the specimen.

Specimens tests in this way for a period of four months, were not broken nor cracks detected therein by microscopical examination after exposure as above described. During testing the specimens were periodically cleaned of corrosion products by brushing, for tests run at atmospheric pressure, twice a week, and for high pressure tests, once a week.

Tubing made of steel according to the invention can be produced either by piercing and hot rolling or by hot extrusion. In the appended claims where reference is made to "rolled tubing," this expression is intended also to embrace extruded tubing.

What is claimed is:

1. Rolled steel steel tubing made of an alloy steel having substantially the following composition 0.08–0.2% carbon, 0.3–1.2% manganese, 0.6–5% chromium, 0.1–0.5% silicon, 0.15–0.6% aluminum, up to 0.5% molybdenum and the balance iron, said tubing being subjected to a heat treatment comprising a normalizing heating and cooling or quenching following by an annealing conferring to it a microstructure consisting of ferrite grains and uniformly dispersed carbides.

2. Rolled steel tubing made of an alloy steel having substantially the following composition 0.08–0.2% carbon, 0.3–1.2% manganese, 0.6–5% chromium, 0.1–0.5% silicon, 0.15–0.6% aluminum, up to 0.5% molybdenum and the balance iron, said tubing being subjected to a heat treatment comprising a normalizing heating and cooling or quenching followed by an annealing conferring to it a microstructure consisting of ferrite grains and uniformly dispersed carbides, the inner surface of said tubing being decarburized.

3. Rolled steel tubing according to claim 2 wherein the outer surface is also decarburized.

4. Rolled steel tubing according to claim 1 wherein the steel also contains up to .50 vanadium.

5. Rolled steel tubing according to claim 1 wherein the steel contains up to .20 titanium.

6. Rolled steel tubing according to claim 1 wherein the steel contains up to .50 vanadium and up to .20 titanium.

7. A process of manufacturing low alloy steel using as essential constituents in addition to iron, 0.08–0.2% of carbon, 0.3–1.2% of manganese, 0.6–5.0% of chromium, up to 1.0% of molybdenum and 0.15–0.6% of aluminum, and subjecting said steel to a heat treatment comprising two parts, the first including an austenite forming step consisting in a heating at about 950° C. followed by a cooling at a speed at least equal to a cooling in a calm atmosphere, whereas the second part comprises a relatively long tempering or annealing at a temperature comprised between 500 and 700° C.

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